

Trisilver oxoruthenate(V),  $\text{Ag}_3\text{RuO}_4$ 

Wilhelm Klein and Martin Jansen\*

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

Correspondence e-mail: m.jansen@fkf.mpg.de

Received 22 October 2004

Accepted 18 November 2004

Online 11 December 2004

$\text{Ag}_3\text{RuO}_4$  is constituted of anionic helical chains of edge-sharing  $\text{RuO}_6$  octahedra, extending along the  $c$  axis. The metal atoms all lie at sites with imposed twofold symmetry. The oxide anions are arranged in an approximate cubic close packing. The Ag atoms occupy the remaining octahedral voids, so that  $\text{Ag}_3\text{RuO}_4$  may be regarded as a derivative of the NaCl structure type.

## Comment

Ruthenium oxides of various chemical compositions have been investigated intensively, especially for their interesting magnetic and conductive properties. Among the Ru oxides reported to date, only two contain Ag, *viz.*  $\text{Ag}_{0.4}\text{Na}_{2.3}\text{Ca}_{4.3}\text{RuO}_8$  (Müller-Buschbaum & Frenzen, 1996) and  $\text{Ag}_2\text{RuO}_4$  (Hansen, 2003). We have now obtained crystals of  $\text{Ag}_3\text{RuO}_4$  from a reaction of the metal powders under elevated oxygen pressure.

In  $\text{Ag}_3\text{RuO}_4$ , Ru is coordinated by six O atoms, which form a slightly distorted octahedron. These  $\text{RuO}_6$  octahedra are linked by two common edges in a skew position, forming helical strings of octahedra running parallel to  $[001]$  (Fig. 1). The distortion of the octahedra results from the off-centre shift of the  $\text{Ru}^{\text{V}}$  cation towards the two *cis*-positioned terminal O atoms, so that the terminal Ru—O bonds [1.907 (5) Å] are considerably shorter than the bridging Ru—O bonds (average 1.979 Å; Table 1). As another consequence, the shared octahedral edges are shorter, due to a significant decrease of the respective O—Ru—O angles [78.2 (2)°] compared with the remaining angles [between 87.1 (3) and 95.9 (2)°].

Octahedral coordination is rather common for  $\text{Ru}^{\text{V}}$  and has been found, for instance, in  $\text{Na}_3\text{RuO}_4$  (Darriet & Galy, 1974) and in the pyrochlore  $\text{Cd}_2\text{Ru}_2\text{O}_7$  (Wang & Sleight, 1998). While the pyrochlore consists of a three-dimensional network of corner-linked octahedra,  $\text{Na}_3\text{RuO}_4$  contains edge-sharing  $\text{RuO}_6$  octahedra which, unlike in  $\text{Ag}_3\text{RuO}_4$ , form oligomeric  $[\text{Ru}_4\text{O}_{16}]^{12-}$  units. Spirals of octahedra similar to those found in  $\text{Ag}_3\text{RuO}_4$  [designated as  $s_4$  chains in the nomenclature of Müller (1981)] are known in, for example, the tetragonal spinels  $\text{Li}_2\text{TeO}_4$  (Daniel *et al.*, 1977) or  $\text{LiZnNbO}_4$  (Marin *et*

*al.*, 1994), which crystallize in the same tetragonal  $P4_122$  space group.

The three crystallographically independent  $\text{Ag}^{\text{I}}$  cations in  $\text{Ag}_3\text{RuO}_4$  are coordinated in different ways. Cation  $\text{Ag}1$  is in a typical, only slightly bent, dumb-bell-like coordination, with two close O ligands at an  $\text{Ag}1\text{—O}$  distance of 2.149 (5) Å, cation  $\text{Ag}2$  has a 2+2 environment [ $2 \times 2.305$  (5) Å and  $2 \times 2.483$  (5) Å] and cation  $\text{Ag}3$  has six nearly equidistant O-atom neighbours forming a skew octahedron (average 2.505 Å). If

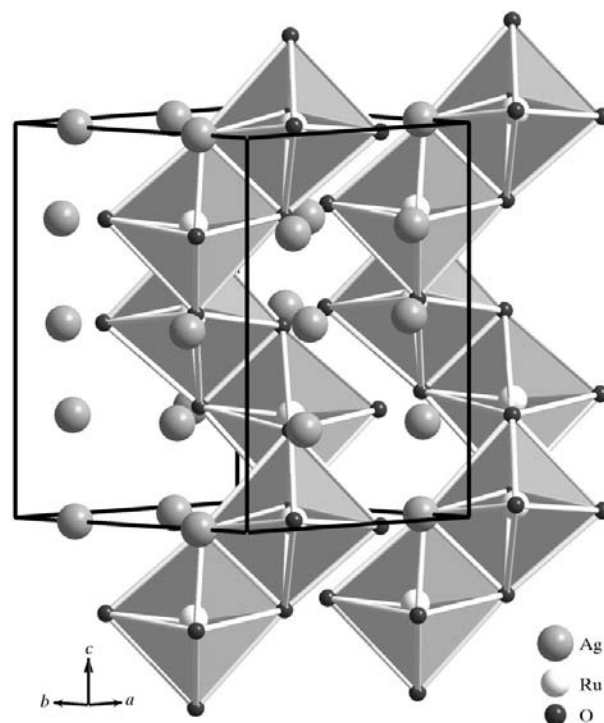


Figure 1  
A perspective view of  $\text{Ag}_3\text{RuO}_4$  along  $[110]$ .

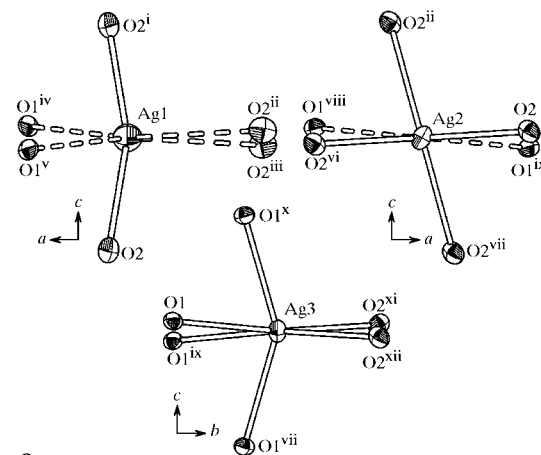


Figure 2  
The surroundings of the three crystallographically independent  $\text{Ag}^{\text{I}}$  cations in  $\text{Ag}_3\text{RuO}_4$ . Bonds longer than 2.55 Å are drawn as dashed and displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i)  $x, -y, \frac{1}{2} - z$ ; (ii)  $-y, x, \frac{1}{4} + z$ ; (iii)  $-y, -x, \frac{1}{4} - z$ ; (iv)  $1 - y, x - 1, \frac{1}{4} + z$ ; (v)  $1 - y, 1 - x, \frac{1}{4} - z$ ; (vi)  $-x, y, -z$ ; (vii)  $y, x, -\frac{1}{4} - z$ ; (viii)  $x - 1, y, z$ ; (ix)  $1 - x, y, -z$ ; (x)  $1 - y, x, \frac{1}{4} + z$ ; (xi)  $x, 1 + y, z$ ; (xii)  $1 - x, 1 + y, -z$ .]

the more remote neighbours are included for all Ag atoms, they all achieve a distorted octahedral coordination by oxygen (see Fig. 2). In this more general view, the crystal structure of  $\text{Ag}_3\text{RuO}_4$  can be traced back to the NaCl structure type, with an approximate cubic close packing of oxygen, where the  $\text{Ag}^+$  and  $\text{Ru}^{5+}$  cations fill all the octahedral voids in an ordered manner.

## Experimental

Single crystals of  $\text{Ag}_3\text{RuO}_4$  were prepared *via* reaction of silver and ruthenium metal powders in stoichiometric amounts under an elevated oxygen pressure, in the presence of 3 M aqueous KOH solution as an accelerator. The mixture was annealed for 120 h in a gold crucible placed in a stainless steel autoclave (Linke & Jansen, 1997). The reaction temperature and oxygen pressure were 573 K and 200 MPa, respectively.

### Crystal data

$\text{Ag}_3\text{RuO}_4$	Mo $K\alpha$ radiation
$M_r = 488.68$	Cell parameters from 4178 reflections
Tetragonal, $P4_122$	$\theta = 2.9\text{--}35.0^\circ$
$a = 7.0082$ (4) Å	$\mu = 16.99 \text{ mm}^{-1}$
$c = 8.6518$ (7) Å	$T = 293$ (2) K
$V = 424.93$ (5) Å <sup>3</sup>	Column, black
$Z = 4$	$0.50 \times 0.10 \times 0.10 \text{ mm}$
$D_x = 7.639 \text{ Mg m}^{-3}$	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	510 independent reflections
$\omega$ scans	505 reflections with $I > 2\sigma(I)$
Absorption correction: semi-empirical (SADABS; Sheldrick, 1998)	$R_{\text{int}} = 0.059$
$T_{\text{min}} = 0.028$ , $T_{\text{max}} = 0.183$	$\theta_{\text{max}} = 27.8^\circ$
4499 measured reflections	$h = -8 \rightarrow 9$
	$k = -9 \rightarrow 9$
	$l = -11 \rightarrow 11$

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{\text{max}} = 2.06 \text{ e \AA}^{-3}$
$wR(F^2) = 0.078$	$\Delta\rho_{\text{min}} = -1.38 \text{ e \AA}^{-3}$
$S = 1.37$	Absolute structure: Flack (1983),
510 reflections	with 173 Friedel pairs
41 parameters	Flack parameter = 0.6 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 3.3199P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

The crystals are systematically twinned and, during the structure refinement, the Flack (1983) parameter tended to be significantly larger than zero. A refinement of the chiral twinning was performed

**Table 1**

Selected interatomic distances (Å).

Ru—O2	1.907 (5)	Ag2—O2 <sup>ii</sup>	2.483 (5)
Ru—O1 <sup>v</sup>	1.959 (5)	Ag3—O1 <sup>x</sup>	2.476 (5)
Ru—O1	1.999 (4)	Ag3—O2 <sup>xi</sup>	2.496 (5)
Ag1—O2	2.149 (5)	Ag3—O1	2.543 (5)
Ag2—O2	2.305 (5)		

Symmetry codes: (ii)  $-y, x, \frac{1}{4} + z$ ; (v)  $1 - y, 1 - x, \frac{1}{4} - z$ ; (x)  $1 - y, x, \frac{1}{4} + z$ ; (xi)  $x, 1 + y, z$ .

where the volume fractions of the two domains are close to 0.5 (slightly larger for the reported twin individual). The maximum and minimum electron-density peaks in the final electron-density difference map are located 0.47 and 0.75 Å from Ru, respectively.

Data collection: SMART32 (Bruker, 2000); cell refinement: SAINT32 (Bruker, 2000); data reduction: SAINT32; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2000); software used to prepare material for publication: SHELXL97.

The authors thank Dr Jürgen Nuss for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1060). Services for accessing these data are described at the back of the journal.

## References

- Brandenburg, K. (2000). *DIAMOND*. Release 2.1d. Crystal Impact GbR, Bonn, Germany.
- Bruker (2000). SMART32 and SAINT32. Bruker AXS Inc., Madison, Wisconsin, USA.
- Daniel, F., Moret, J., Philippot, E. & Maurin, M. (1977). *J. Solid State Chem.* **22**, 113–119.
- Darriet, J. & Galy, J. (1974). *Bull. Soc. Fr. Minéral. Cristallogr.* **97**, 3–5.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hansen, T. (2003). Proceedings of the IXth European Conference on Solid State Chemistry, p. 247, Stuttgart, 2–6 September, 2003.
- Linke, C. & Jansen, M. (1997). *Z. Anorg. Allg. Chem.* **623**, 1441–1446.
- Marin, S. J., O'Keefe, M. & Partin, D. E. (1994). *J. Solid State Chem.* **113**, 413–419.
- Müller, U. (1981). *Acta Cryst.* **B37**, 532–545.
- Müller-Buschbaum, H. & Frenzen, S. (1996). *Z. Naturforsch. Teil B*, **51**, 485–488.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (1998). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Wang, R. & Sleight, A. W. (1998). *Mater. Res. Bull.* **33**, 1005–1007.