

INORGANIC COMPOUNDS

Acta Cryst. (1995). C51, 787–790

CeMo₈O₁₄, a Third Crystalline Form of the RMo₈O₁₄ Series (R = La, Ce, Pr, Nd, Sm)

G. KERIHUEL AND P. GOUGEON

Université de Rennes I, Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS n° 1495, Avenue du Général Leclerc, 35042 Rennes CEDEX, France

(Received 1 March 1994; accepted 19 September 1994)

Abstract

The crystal structure of cerium octamolybdate, CeMo₈O₁₄, contains a mixture of *cis*-edge-sharing and *trans* bicapped octahedral Mo₈ clusters in equal proportions. The Mo₈ clusters and the O atoms form layers parallel to the *bc* plane of the orthorhombic unit cell. The arrangement of the O atoms derives from a close packing with the layer sequence ABAC... The Mo—Mo distances range from 2.5825 (9) to 2.778 (1) Å and from 2.5958 (8) to 2.886 (2) Å in the *trans* and *cis*-edge-sharing isomeric clusters, respectively. The shortest Mo—Mo distance between Mo₈ clusters within the same layer is 3.0790 (9) Å, and that between clusters of adjacent layers is 3.635 (1) Å. The Mo—O distances are between 2.027 (6) and 2.110 (7) Å in the *trans* isomer and between 1.944 (5) and 2.169 (5) Å in the *cis*-edge-sharing isomer. The environment of each of the two crystallographically independent Ce³⁺ ions is constituted by 12 O atoms forming a distorted cuboctahedron. The Ce—O distances lie between 2.569 (6) and 2.920 (5) Å and between 2.442 (7) and 2.943 (6) Å for the Ce(1) and Ce(2) sites, respectively.

Comment

Compounds of the general formula RMo₈O₁₄ (R = La, Ce, Pr, Nd, Sm) have been obtained recently by solid-state chemistry (Gougeon & McCarley, 1991) and by fused-salt electrolysis in the case of LaMo_{8-x}O₁₄ (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Leligny, Labbe, Ledesert, Hervieu, Raveau & McCarroll, 1993). Single-crystal structures of the La and Nd compounds revealed that their main metallic building block is the bi-face-capped octahedron, Mo₈, which exhibits different configurations and arrangements. The simplest arrangement is observed in LaMo_{7.7}O₁₄ (Leligny *et al.*, 1990) and NdMo₈O₁₄ (Gougeon & McCarley, 1991) where only the *cis*-edge-sharing isomeric form of the Mo₈ cluster is found. They

both crystallize in the space group *Aba2* with the following parameters: $a_{La} = 9.196$ (1), $b_{La} = 9.985$ (1), $c_{La} = 11.171$ (1) Å; $a_{Nd} = 9.209$ (3), $b_{Nd} = 10.008$ (2), $c_{Nd} = 11.143$ (4) Å. The structure of the stoichiometric compound LaMo₈O₁₄ (Leligny *et al.*, 1993) is more complex due to a one-dimensional commensurate modulation of wave vector $\mathbf{q}^* = \mathbf{b}^*/3$ [$a = 11.129$ (1), $b = 10.000$ (1), $c = 9.218$ (1) Å]. The structure, which was solved in superspace group $P\overline{C}2ca_{111}$, consists of *cis*-edge-sharing and *trans* isomers, each form occurring in two distinct configurations. We present here the structure of CeMo₈O₁₄, which constitutes the third stoichiometric form of RMo₈O₁₄. A fourth form, PrMo₈O₁₄, will be reported in a forthcoming paper (Kerihuel & Gougeon, 1995).

The structure of CeMo₈O₁₄ is characterized by the coexistence of *cis*-edge-sharing and *trans* bi-face-capped octahedral Mo₈ clusters in equal proportions. The ordering of the two isomeric clusters induces a doubling of the *b* parameter of the unit cell of NdMo₈O₁₄ (*c* parameter in CeMo₈O₁₄), while the other parameters are almost identical in the two polymorphic compounds. Both isomeric forms of the Mo₈ cluster are shown in Fig. 1 along with their O-atom environments. The *cis*-edge-sharing isomer was first observed in LaMo_{7.7}O₁₄ and NdMo₈O₁₄, and the *trans* isomer in La₅Mo₃₂O₅₄ (Gall, Toupet & Gougeon, 1993) where it coexists with the original Mo₇–Mo₁₀–Mo₇ tricluster chain fragment. The perspective view of the structure along the *b* axis (Fig. 2a) clearly shows that the Mo₈ clusters, as well as the O atoms, are arranged in layers parallel to the *bc* plane. The O-atom framework is similar to that in LaMo_{7.7}O₁₄ and NdMo₈O₁₄ and derives from a close packing of sequence ABAC, where, in the A layers, some of the O atoms are missing or substituted by Ce ions and the B and C layers are entirely occupied by O atoms. Fig. 2(b) depicts the arrangement of the Mo₈ clusters within the unit cell. The Mo—Mo distances within the *trans* bi-face-capped Mo₈ cluster show no large variations from those reported previously for La₅Mo₃₂O₅₄. They range from 2.5825 (9) to 2.778 (1) Å [2.5728 (9)–2.7777 (8) Å in La₅Mo₃₂O₅₄] and the average value of 2.708 Å is also of the same order as that observed in La₅Mo₃₂O₅₄ (2.705 Å). With the exception of the two capping Mo atoms, each of which is surrounded by six O atoms forming a distorted octahedron, the other Mo atoms are each bonded to five O atoms in an approximately square-pyramidal arrangement. The Mo—O distances are between 2.027 (6) and 2.110 (7) Å, with an average distance of 2.062 Å (2.069 Å for the *trans* isomer in La₅Mo₃₂O₅₄). The Mo—Mo distances in the *cis*-edge-sharing isomer cover a range from 2.5958 (8) to 2.886 (2) Å, slightly wider than in the *trans* isomer and its homologue found in NdMo₈O₁₄ [2.590 (1)–

2.848 (1) Å]. The most important modifications concern the bonds between atoms Mo(7) and Mo(8), which have a 'butterfly' shape and vary by about 0.04 Å with respect to the analogous bonds in NdMo₈O₁₄. The other Mo—Mo distances within the *cis*-edge-sharing cluster are not significantly different from those observed in the Nd compound. The mean Mo—Mo distance is 2.738 Å, which is somewhat longer than the distance of 2.731 Å found in NdMo₈O₁₄. As in the *trans* isomer, each Mo atom is surrounded by five or six O atoms. However, the range of Mo—O distances is broader with distances varying between 1.944 (5) and 2.169 (5) Å. The average Mo—O distance of 2.042 Å is significantly shorter than that calculated for the *trans* isomer and suggests that the number of electrons per Mo₈ cluster is smaller in the *cis*-edge-sharing than in the *trans* isomer. The shortest Mo—Mo intercluster distance, which occurs between atoms Mo(3) and Mo(8) of two Mo₈ isomers within the same layer, is 3.0790 (9) Å and corresponds to the analogous distance observed in both LaMo_{7.7}O₁₄ [3.078 (1) Å] and NdMo₈O₁₄ [3.068 (1) Å].

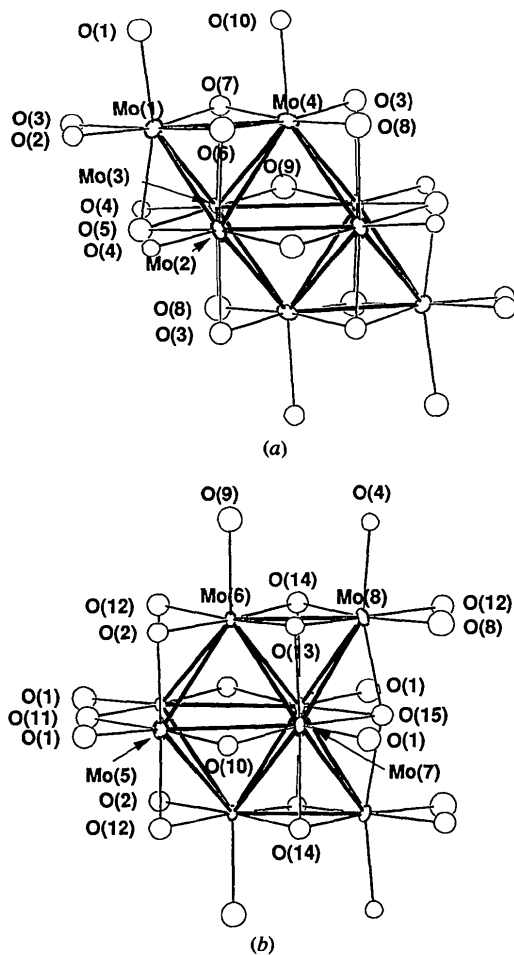


Fig. 1. (a) The *trans* and (b) the *cis*-edge-sharing bi-face-capped Mo₈ clusters with their O-atom environments.

On the other hand, the spacing between Mo₈ clusters of adjacent layers can be as great as 3.635 (1) Å. Both crystallographically independent Ce³⁺ ions sit on inversion centers and are surrounded by 12 O atoms forming a distorted cuboctahedron. The Ce—O distances range from 2.569 (6) to 2.920 (5) Å and from 2.442 (7) to 2.943 (6) Å for the Ce(1) and Ce(2) sites, respectively.

Using the bond-length–bond-strength formula (Brown & Wu, 1976) for the Mo—O bond $\{s = [d(\text{Mo—O})/1.882]^{-6.0}\}$, an assignment of Mo oxidation states was made. In the formula, s is the bond strength of an Mo—O bond, d is the crystallographic Mo—O bond length and the values 1.882 (Mo—O bond of unit strength) and -6.0 are fitted parameters. The valence of each independent Mo atom was determined as follows: Mo(1) +3.43, Mo(2) +2.91, Mo(3) +2.87, Mo(4) +2.96, Mo(5) +3.38, Mo(6) +2.90, Mo(7) +2.91 and Mo(8) +3.83. These values lead to average Mo oxidation states of +3.04 and +3.25 for the *trans* and *cis*-edge-sharing isomers, respectively. The average calculated valence of molybdenum in CeMo₈O₁₄ is +3.14, which is close to the value based on the stoichiometry (+3.125) when considering all the Ce³⁺ ions as trivalent. Similar calculations for the Ce³⁺ ions $\{s =$

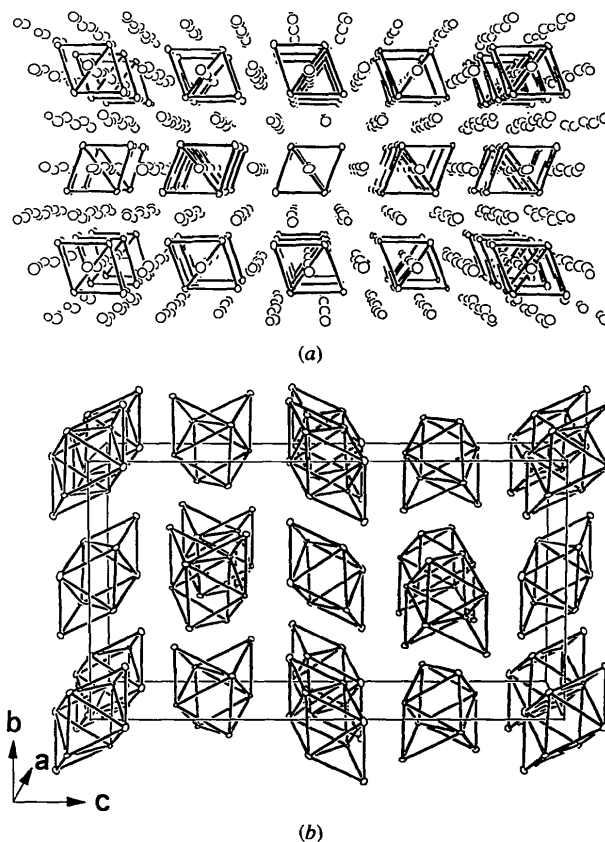


Fig. 2. (a) Perspective view of the structure along the *b* axis with the Mo₈ clusters emphasized by bold lines and (b) the arrangement of the Mo₈ clusters within the unit cell.

$[d(\text{Ce—O})/2.160]^{-6.5}$ led to values of +2.86 and +3.37 for the Ce(1) and Ce(2) sites, respectively. These values are consistent with those observed in other molybdenum oxides containing Ce^{3+} ions such as CeMo_5O_8 (+2.94) (Gall, 1993), $\text{Ce}_{16}\text{Mo}_{21}\text{O}_{56}$ (Gall & Gougeon, 1993), where the eight crystallographically independent Ce atoms have calculated valences ranging between +2.93 and +3.38, and $\text{Ce}_6\text{Mo}_{10}\text{O}_{39}$ (+3.01 to +3.38) (Gatehouse & Same, 1978).

Experimental

Single crystals were obtained by heating a stoichiometric mixture of CeO_2 , MoO_3 and Mo in a sealed molybdenum crucible at about 2220 K for 15 min. The crucible was then cooled at a rate of 100 K h^{-1} to 1300 K and finally furnace cooled to room temperature.

Crystal data

$\text{CeMo}_8\text{O}_{14}$
 $M_r = 1131.63$
 Orthorhombic
Pbcn
 $a = 9.1937(7)\text{ \AA}$
 $b = 11.121(1)\text{ \AA}$
 $c = 20.014(1)\text{ \AA}$
 $V = 2046.3(4)\text{ \AA}^3$
 $Z = 8$
 $D_x = 7.346\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073\text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 11\text{--}32^\circ$
 $\mu = 13.77\text{ mm}^{-1}$
 $T = 295\text{ K}$
 Irregular
 $0.14 \times 0.12 \times 0.10\text{ mm}$
 Black

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
 $T_{\min} = 0.19$, $T_{\max} = 0.23$
 6930 measured reflections
 6930 independent reflections

3568 observed reflections
 $[I > 2\sigma(I)]$
 $\theta_{\max} = 40^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 20$
 $l = 0 \rightarrow 36$
 3 standard reflections
 frequency: 90 min
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R = 0.040$
 $wR = 0.042$
 $S = 1.582$
 3568 reflections
 141 parameters
 $w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
 $(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 2.90\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.05\text{ e \AA}^{-3}$
 Extinction correction: Stout & Jensen (1968)
 Extinction coefficient: $9.612(4) \times 10^{-8}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Ce(1)	0	1/2	0	0.553 (8)
Ce(2)	1/2	0.52433 (5)	1/4	0.474 (8)
Mo(1)	0.62127 (8)	0.72582 (5)	0.07950 (3)	0.234 (8)

Mo(2)	0.62114 (8)	0.62338 (5)	0.45640 (3)	0.169 (7)
Mo(3)	0.12332 (8)	0.12486 (5)	0.53670 (3)	0.183 (7)
Mo(4)	0.62070 (8)	0.48808 (5)	0.07921 (3)	0.225 (8)
Mo(5)	0.61987 (8)	0.87129 (5)	0.21275 (3)	0.171 (7)
Mo(6)	0.87862 (7)	0.49638 (5)	0.33014 (3)	0.116 (8)
Mo(7)	0.12454 (8)	0.61638 (5)	0.29386 (3)	0.177 (8)
Mo(8)	1.12024 (7)	0.72976 (5)	0.16762 (3)	0.188 (8)
O(1)	0.2581 (6)	0.2619 (4)	0.8345 (3)	0.45 (7)
O(2)	0.5124 (7)	0.8674 (4)	0.1258 (3)	0.33 (6)
O(3)	0.7616 (7)	0.3679 (4)	0.0377 (3)	0.41 (7)
O(4)	0.2599 (6)	0.7557 (4)	0.5876 (3)	0.26 (6)
O(5)	0.9905 (7)	0.7396 (4)	0.0010 (3)	0.44 (6)
O(6)	0.9918 (7)	0.1053 (4)	0.3680 (3)	0.55 (7)
O(7)	0.2324 (6)	0.6064 (5)	0.4601 (3)	0.38 (7)
O(8)	0.5076 (8)	0.3658 (4)	0.3742 (3)	0.56 (7)
O(9)	0.2350 (7)	0.4963 (5)	0.0796 (3)	0.52 (7)
O(10)	0.2364 (7)	0.0110 (4)	0.8298 (3)	0.34 (7)
O(11)	1/2	0.2561 (6)	3/4	0.44 (9)
O(12)	0.7562 (7)	0.1314 (4)	0.7898 (3)	0.41 (7)
O(13)	0.9870 (6)	0.6095 (4)	0.1180 (3)	0.30 (6)
O(14)	0.7362 (7)	0.6144 (4)	0.2878 (3)	0.40 (7)
O(15)	1/2	0.2620	1/4	0.37 (9)

Table 2. Selected geometric parameters (\AA)

<i>trans</i> -Mo ₈ cluster			
Mo(1)—Mo(3)	2.5825 (9)	Mo(2)—O(5)	2.043 (5)
Mo(1)—Mo(2)	2.604 (1)	Mo(2)—O(4)	2.052 (6)
Mo(1)—Mo(4)	2.6439 (8)	Mo(2)—O(6)	2.061 (6)
Mo(2)—Mo(4)	2.753 (1)	Mo(2)—O(9)	2.065 (7)
Mo(2)—Mo(3)	2.763 (1)	Mo(2)—O(3)	2.079 (6)
Mo(2)—Mo(3)	2.7642 (8)	Mo(3)—O(7)	2.038 (6)
Mo(2)—Mo(4)	2.778 (1)	Mo(3)—O(9)	2.062 (7)
Mo(3)—Mo(4)	2.708 (1)	Mo(3)—O(5)	2.067 (6)
Mo(3)—Mo(4)	2.7742 (9)	Mo(3)—O(4)	2.076 (5)
Mo(3)—Mo(8)†	3.0790 (9)	Mo(3)—O(8)	2.080 (6)
Mo(1)—O(5)	2.047 (6)	Mo(4)—O(8)	2.027 (6)
Mo(1)—O(7)	2.050 (6)	Mo(4)—O(3)	2.038 (6)
Mo(1)—O(1)	2.052 (6)	Mo(4)—O(7)	2.044 (6)
Mo(1)—O(6)	2.078 (6)	Mo(4)—O(6)	2.054 (6)
Mo(1)—O(2)	2.083 (6)	Mo(4)—O(10)	2.110 (7)
Mo(1)—O(3)	2.087 (6)		
<i>cis</i> -Mo ₈ cluster			
Mo(5)—Mo(5)	2.661 (2)	Mo(6)—O(13)	2.046 (6)
Mo(5)—Mo(7)	2.7292 (8)	Mo(6)—O(12)	2.051 (6)
Mo(5)—Mo(6)	2.7304 (9)	Mo(6)—O(2)	2.085 (6)
Mo(5)—Mo(6)	2.755 (1)	Mo(6)—O(9)	2.087 (7)
Mo(6)—Mo(8)	2.5958 (8)	Mo(7)—O(1)	2.000 (6)
Mo(6)—Mo(7)	2.724 (1)	Mo(7)—O(10)	2.039 (7)
Mo(6)—Mo(7)	2.8180 (9)	Mo(7)—O(13)	2.041 (6)
Mo(7)—Mo(8)	2.692 (1)	Mo(7)—O(14)	2.076 (6)
Mo(7)—Mo(8)	2.8239 (9)	Mo(7)—O(15)	2.169 (5)
Mo(7)—Mo(7)	2.886 (2)	Mo(8)—O(4)	1.950 (6)
Mo(5)—O(11)	1.944 (5)	Mo(8)—O(8)	2.015 (6)
Mo(5)—O(12)	1.988 (6)	Mo(8)—O(15)	2.017 (1)
Mo(5)—O(2)	2.002 (6)	Mo(8)—O(14)	2.046 (6)
Mo(5)—O(10)	2.045 (7)	Mo(8)—O(13)	2.067 (6)
Mo(5)—O(1)	2.085 (6)	Mo(8)—O(12)	2.097 (6)
Mo(6)—O(14)	2.039 (6)		
Ce environment			
Ce(1)—O(7)	2.569 (6)	Ce(2)—O(11)	2.442 (7)
Ce(1)—O(13)	2.660 (5)	Ce(2)—O(14)	2.508 (7)
Ce(1)—O(5)	2.666 (5)	Ce(2)—O(6)	2.529 (6)
Ce(1)—O(9)	2.684 (8)	Ce(2)—O(10)	2.725 (7)
Ce(1)—O(3)	2.745 (6)	Ce(2)—O(15)	2.918 (7)
Ce(1)—O(2)	2.920 (5)	Ce(2)—O(12)	2.943 (6)

† Distance between Mo₈ clusters of the same layer.

Data were corrected for Lorentz and polarization effects. The structure was solved with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. Refinement of the

occupancy factors for the Ce and Mo sites confirmed that they are fully occupied. All calculations were performed with the *MolEN* (Fair, 1990) programs on a Digital MicroVAX 3100.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brown, I. D. & Wu, K. K. (1976). *Acta Cryst.* B32, 1957–1959.
 Fair, K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
 Gall, P. (1993). Thesis, Univ. of Rennes, France.
 Gall, P. & Gougeon, P. (1993). *Acta Cryst.* C49, 659–663.
 Gall, P., Toupet, L. & Gougeon, P. (1993). *Acta Cryst.* C49, 1580–1584.
 Gatehouse, B. M. & Same, R. (1978). *J. Solid State Chem.* 25, 115–120.
 Gougeon, P. & McCarley, R. E. (1991). *Acta Cryst.* C47, 241–244.
 Kerihuel, G. & Gougeon, P. (1995). *Acta Cryst.* In the press.
 Leligny, H., Labbe, P., Ledesert, M., Hervieu, M., Raveau, B. & McCarroll, W. H. (1993). *Acta Cryst.* B49, 444–454.
 Leligny, H., Ledesert, M., Labbe, P., Raveau, B. & McCarroll, W. H. (1990). *J. Solid State Chem.* 87, 35–43.
 Main, P., Fiske, S., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 Stout, G. & Jensen, L. H. (1968). In *X-ray Structure Determination*. London: MacMillan.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* A39, 158–166.

Acta Cryst. (1995). C51, 790–792

Structure Refinement of Y₂Ru₂O₇ by Neutron Powder Diffraction

BRENDAN J. KENNEDY

Department of Inorganic Chemistry, The University of Sydney, New South Wales 2006, Australia

(Received 2 March 1994; accepted 14 November 1994)

Abstract

The structure of the pyrochlore yttrium ruthenium oxide, Y₂Ru₂O₇, was determined by Rietveld analysis of time-of-flight neutron powder diffraction data. Each Ru atom has a nearly regular octahedral coordination environment whereas each Y atom has a distorted eightfold-coordination geometry. The JCPDS file number for yttrium ruthenium oxide is 28-1456.

Comment

A number of oxide pyrochlores, especially those incorporating Ru or Ir, exhibit high electrocatalytic activity for several oxygen-transfer reactions, including O₂ reduction or evolution (Egdell, Goodenough, Hamnett & Naish, 1983) and the oxidation of organic molecules (Felthouse, Fraundorf, Friedman & Schosser, 1991). Their activity is believed to be related to their oxygen non-stoichiometry, their general formula being given by A₂B₂O_{7-y}. These materials are also of interest because of the sensitivity of their electronic structure to the A-type cation. This sensitivity is believed to be a consequence of changes in both the RuO₆ geometry and the Ru t_{2g} band width.

As part of a detailed study of structural (Facer, Howard & Kennedy, 1993; Facer, Elcombe & Kennedy, 1993) and electrocatalytic (Gokagac & Kennedy, 1993, 1994) properties of metal pyrochlores, it was decided to investigate the structure of Y₂Ru₂O₇ in order to obtain an accurate description of the YO₈ and RuO₆ polyhedra, and to determine the anisotropy of the displacement parameters. The previously reported powder X-ray measurements were expected to be relatively insensitive to O-atom displacements and thermal vibrations (Kanno, Takeda, Yamamoto, Kawamoto & Yamamoto, 1993). The results of the structure determination of Y₂Ru₂O₇ using powder neutron diffraction data are reported here.

The neutron diffraction refinement of the structure of Y₂Ru₂O₇ confirms that the material adopts a regular pyrochlore structure (Subramanian, Aravamudan & Subba Rao, 1983). No 420 reflection was observed in the neutron and X-ray diffraction data, indicating that there was no vacancy ordering on the O2 site (Beyerlein *et al.*, 1984). Refinement proceeded in space group *Fd* $\bar{3}$ *m*. Refinement of the occupancies of the Y, Ru and O sites indicated no significant deviation from the expected stoichiometry.

The refined positional parameter for the O1 atom, 0.33536(3), is in excellent agreement with that determined by X-ray powder methods (Kanno, Takeda, Yamamoto, Kawamoto & Yamamoto, 1993). The YO₈ scalenohedron is axially compressed with six O atoms at 2.4503(2) Å from Y and two at 2.19601(3) Å. These Y—O bond lengths are similar to those found in Y₂Sn₂O₇ (Facer, Howard & Kennedy, 1993). The Ru—O distance, 1.9911(1) Å, is slightly longer than that found in Bi₂Ru₂O_{6.9} (1.974 Å; Facer, Elcombe & Kennedy, 1993), while the O—Ru—O angle has decreased to 128.45(2)° in Y₂Ru₂O₇ relative to that of 133° in Bi₂Ru₂O_{6.9}, indicating weaker Ru—O—Ru interactions in Y₂Ru₂O₇. This is consistent with the semiconducting properties of Y₂Ru₂O₇ and metallic properties of Bi₂Ru₂O_{6.9}. The displacement parameters for both the Y and O1 atoms are large and highly anisotropic. For the Y atom, movement along the three-fold axis, that is towards the two closest O atoms, is