$La_3Os_2O_{10}$, a New Compound Containing Isolated Clusters Os_2O_{10} with Metal–Metal Bonds

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The formula of a new compound isolated in the La–Os–O system has been established by means of crystal structure determination. There are two $La_3Os_2O_{10}$ units in a face-centered monoclinic unit cell (S.G. $C2/m$); $a = 7.911(2)$ Å, $b = 7.963(2)$ Å, $c = 6.966(2)$ Å, $\beta = 115.76(2)°$. For 1082 intensities, collected on an automated single-crystal diffractometer, the final R value was 0.025 after absorption corrections. The structure consists of isolated Os_2O_{10} clusters composed of two edge-shared OsO_6 octahedra. These dimeric units are connected together by two types of La^{3+} ions in eightfold coordination. In view of the Os–Os distance inside the pair (2.462 Å), $La_3Os_2O_{10}$ provides an example of metal–metal bonding involving a transition metal in a half-integral formal oxidation state of 5.5.

Introduction

During an investigation of ternary oxides of the platinum metals, particular attention was paid to the combinations of these oxides with lanthanum oxide. In the case of rhenium, several authors report preparations of different oxides (1–3) and structural studies of two of them, $La_4Re_6O_{19}$ (4, 5) and $La_4Re_2O_{10}$ (6); but for osmium only one compound, $La_4Os_6O_{19}$ (7), has been identified and structurally investigated. The three-dimensional $Os_{12}O_{36}$ network is built up by corner-sharing Os_2O_{10} clusters; the distance between Os atoms across an edge-shared octahedra (2.50 Å) supports a direct metal–metal interaction.

It has been observed that $La_4Os_6O_{19}$ is sometimes accompanied by a crystalline phase. In order to establish unambiguously its composition and to specify the oxidation state of osmium, a structure determination

has been performed on which we report in this paper.

Experimental

Rectangular-plate-shaped crystals were obtained, together with $La_4Os_6O_{19}$, by heating at 900°C during several hours a mixture of composition La_2O_3, 3 Os with excess $KClO_3$, in a gold container inside a vacuum-sealed silica tube. Several single crystals, suitable for X-ray structure analysis, were isolated but the quantity was not large enough for chemical analysis or even density determination.

The selected single crystal is $0.137 \times 0.086 \times 0.021$ mm³. Oscillation and Weissenberg photographs display $2/m$ symmetry. The systematic absences hkl if $h + k = 2n + 1$ are consistent with space group $C2$, Cm, or $C2/m$.

The monoclinic unit-cell dimensions are refined by means of 17 unambiguously

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indexed reflections (Table I), using a Guinier camera and KCl as internal standard: $a = 7.911(2)$ Å, $b = 7.963(2)$ Å, $c = 6.966(2)$ Å, $\beta = 115.76(2)°$. Collection of intensity data is performed on a Philips PW 1100 automated diffractometer using MoK_α radiation and a graphite monochromator. In order to achieve good absorption corrections and to minimize systematic errors, the totality of reciprocal space is explored to $\theta = 40°$. Reflections (4165) with $I > 2\sigma(I)$ are corrected for Lorentz and polarization effects. At this stage, because of the unknown structure of the phase, it is not possible to correct accurately for absorption effects. Atomic scattering factors for Os^{4+} and La^{3+} are taken from Cromer and Waber (8) and those for O^{2-} from Tokonami (9). Anomalous dispersion corrections are made according to the data of Cromer and Liberman (10).

Structure Determination and Refinement

The structure is solved by the heavy-atom method. Since only one major peak is observed on the section 0, y, 0 of the three-dimensional Patterson map for $y = \frac{1}{2}$, it is inferred that the most probable space group is $C2/m$. This choice is later confirmed by the success of the determination. The most prominent peak of the Patterson map occurs at $x \simeq 0.266$, $y = 0$, $z \simeq 0.351$. It implies an interatomic distance of ~2.4 Å, which was already observed in $La_4Os_6O_{19}$ (7) between osmium atoms across edge-shared octahedra. Os is accordingly located at $4i$ (x, 0, z) positions with $x = 0.133$ and $z = 0.180$. The remaining major peaks of the Patterson map are then assigned to metallic atoms located at special positions: $4h$ (0, y, 0) with $y \simeq 0.242$ and $2b$ (0, $\frac{1}{2}$, 0).

From the nominal composition of the starting mixture of oxides, it is assumed that the formula of the compound is close to $La_4Os_6O_{19}$. Absorption corrections, using the method of De Meulenaer and Tompa (11), are computed. Refining the atomic parameters and isotropic temperature factors with a full-matrix least-squares program yields a conventional R value of 0.105, but the B coefficient of the $2b$ Os atoms (Table II) is obviously too high for a sixfold coordination. The nature of these atoms is accordingly changed to La_1, which brings the final B values closer to those usually obtained, while R reduces to 0.089. Absorption corrections are computed again, in accordance with the new formula $La_6Os_4O_x$ ($x \sim 17$–21). Owing to the platelet form of the crystal, transmission factors range from 0.03 to 0.36 ($\mu MoK\alpha = 502$ cm^{-1}).

A Fourier map based on this model reveals 20 O atoms occupying one $8j$ and three $4i$ positions. Atomic parameters and isotropic temperature factors are then refined to $R =$

TABLE I

POWDER DIAGRAM OF $La_3Os_2O_{10}$

h	k	l	d_{obs}	d_{calc}	h	k	l	d_{obs}	d_{calc}
$\bar{1}$	1	0	5.2974	5.3095	2	0	1	2.6427	2.6434
1	1	1	4.9089	4.9127	0	2	2	2.4639	2.4639
0	2	0	3.9785	3.9813	1	3	1	2.4435	2.4426
2	0	1	3.9103	3.9129	1	1	2	2.3838	2.3835
2	0	0	3.5610	3.5623	$\bar{3}$	1	0	2.2774	2.2758
1	1	1	3.5256	3.5282	0	0	3	2.0913	2.0911
0	2	1	3.3621	3.3615	0	4	0	1.9908	1.9907
2	0	2	3.1205	3.1212	4	0	3	1.7947	1.7946
$\bar{2}$	2	1	2.7912	2.7907					

TABLE II

RESULTS OF THE ISOTROPIC TEMPERATURE
FACTOR REFINEMENT OF METALLIC ATOMS

	La$_4$Os$_6$ hypothesis	La$_6$Os$_4$ hypothesis
R	0.105	0.089
Site 4h	La $B = 0.42$	La $B = 0.54$
Site 4i	Os $B = 0.14$	Os $B = 0.26$
Site 2b	Os $B = 1.41$	La $B = 0.61$

0.04. A new refinement cycle with aniso-tropic temperature coefficients for metallic atoms reduces R to a final value of 0.027. Use of a weighting scheme ($w = 1/\sigma(F_0)^2$ with $\sigma(F_0) = \sigma(I)/2I^{1/2}$) gives no further modification ($R = 0.025$, $R_w = 0.044$). Final atomic coordinates and thermal parameters for 1082 reflections are given in Tables III and IV. Bond lengths and angles in osmium and lanthanum coordination polyhedra are listed in Tables V and VI.[1]

An ultimate three-dimensional Fourier difference synthesis is then computed. The height of the most prominent peak is only one-sixth of the height of an oxygen peak in the preceding synthesis. In accordance with these results, the compound is formulated as La$_3$Os$_2$O$_{10}$, with two formula units per unit cell.

The preparation of the pure phase by reaction of the appropriate amounts of lanthanum oxide and osmium, under oxidiz-ing conditions, has not yet been achieved. Several attempts have been made, between 800 and 900°C, in gold, platinum, or silica tubes, with KClO$_3$ or NaClO$_3$ in stoi-chiometric quantity or in excess. Unknown phases, poorer in Os than La$_3$Os$_2$O$_{10}$, are always found, while osmium tetroxide is present in the tube. Other experiments, using mixtures containing more osmium, lead to the formation of La$_3$Os$_2$O$_{10}$ together with La$_4$Os$_6$O$_{19}$ or another unknown phase, depending on the composition of the starting mixture and on the rate of the cooling. Failures to achieve preparation of a pure compound are attributed to the stability of OsO$_4$ in the temperature range of our experiments.

Description of the Structure

The structure of La$_3$Os$_2$O$_{10}$ consists of slightly distorted OsO$_6$ octahedra occurring in pairs. The common edge O(1)–O(1') (Fig. 1) and the mean plane of the dimeric unit Os$_2$O$_{10}$ lie in the mirror planes of the unit cell, and their centers are located at the 0, 0,

TABLE III

ATOMIC COORDINATES ($\times 10^5$) AND (EQUIVALENT) ISOTROPIC THERMAL
PARAMETER ($\times 10^2$ Å)

Atom	Site	x	y	z	B or $\langle B \rangle$ eq
La(1)	2b	0	$\frac{1}{2}$	0	(61)
La(2)	4h	0	24319(7)	$\frac{1}{2}$	(54)
Os	4i	13397(5)	0	17838(5)	(29)
O(1)	4i	86059(105)	0	10590(108)	50(8)
O(2)	8j	13993(80)	23735(75)	21221(88)	81(7)
O(3)	4i	40242(97)	0	28138(105)	37(8)
O(4)	4i	17857(101)	0	47689(112)	53(8)

TABLE IV

ANISOTROPIC TEMPERATURE COEFFICIENTS FOR METALLIC ATOMS $(\times 10^5)$;
THE THERMAL PARAMETER IS
$$\exp\left|-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right|$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La(1)	414(12)	193(9)	491(15)	0	190(7)	0
La(2)	284(8)	150(6)	456(11)	0	334(11)	0
Os	115(5)	94(4)	255(7)	0	80(4)	0
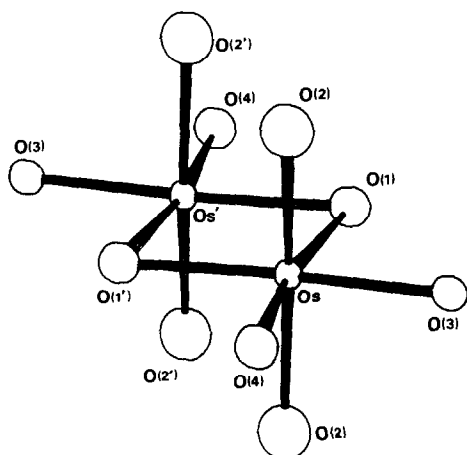
FIG. 1. The dimeric unit Os_2O_{10}.

0 and $\frac{1}{2}$, $\frac{1}{2}$, 0 positions; so, each unit can be deduced from another by means of the unit cell or base-centered translations.

The double octahedra are linked by two kinds of lanthanum atoms, namely, La(1) and La(2). The former connects four Os_2O_{10} clusters, the centers of which are situated at the corners of a practically regular square in the $x0y$ plane: Thus, the structure is best described by means of sheets of composition $La(Os_2O_{10})$ (Fig. 2). These sheets are then linked by La(2) atoms (Fig. 3), which connect four clusters situated at the vertices of a distorted tetrahedron. So, from a structural point of view, the compound may be formulated as $La_2|La(Os_2O_{10})|$.

TABLE V

BOND LENGTHS (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS IN Os COORDINATION POLYHEDRON (see Fig. 1)

Os–Os'	2.468(1)	O(1')–Os–O(3)	82.8(4)
Os–O(1')	1.996(8)	O(1)–Os–O(1')	103.7(10)
Os–O(1)	1.999(8)	O(1)–Os–O(4)	86.8(5)
Os–O(2)	1.903(6)	O(3)–Os–O(5)	86.8(6)
Os–O(3)	1.924(7)	O(1)–Os–O(2)	96.5(5)
Os–O(4)	1.952(8)	O(1)–Os'–O(2')	89.9(5)
O(1)–O(1')	3.142(19)	O(3)–Os–O(2)	89.4(4)
O(1)–O(2')	2.754(8)	O(2)–Os–O(4)	83.4(4)
O(1)–O(2)	2.911(9)	O(2)–Os–O(2)	166.8(22)
O(1)–O(3)	2.594(8)		
O(1)–O(4)	2.712(8)		
O(2)–O(3)	2.692(8)		
O(2)–O(4)	2.564(8)		
O(3)–O(4)	2.662(13)		
O(2)–O(2')	2.820(10)		

TABLE VI

BOND LENGTHS (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS IN La COORDINATION POLYHEDRA

La(1) coordination polyhedron (Fig. 4)			
La(1)–O(1) (2x)	2.618(8)	O(1)–La(1)–O(3)	62.1(3)
La(1)–O(3) (4x)	2.522(6)	O(1)–La(1)–O(2')	71.8(3)
La(1)–O(3) (2x)	2.399(9)	O(1)–La(1)–O(2)	108.2(4)
O(2)–O(2')	2.820(10)	O(3)–La(1)–O(2')	105.3(5)
O(1')–O(2) ⎱		O(3)–La(1)–O(2)	74.7(3)
O(1)–O(2') ⎰	3.016(10)	O(2)–La(1)–O(2')	68.0(3)
O(1)–O(3)	2.594(8)	O(1)–La(1)–O(3')	117.9(7)
O(2)–O(3) ⎱		O(2')–La(1)–O(2'')	112.0(3)
O(2''')–O(3) ⎰	2.987(9)		
La(2) coordination polyhedron (Fig. 5)			
La(2)–O(2) (2x)	2.679(7)	O(2)–La(2)–O(2'')	89.4(4)
La(2)–O(2') (2x)	2.682(5)	O(2)–La(2)–O(4)	59.9(3)
La(2)–O(3) (2x)	2.465(4)	O(2)–La(2)–O(4')	118.3(6)
La(2)–O(4) (2x)	2.443(6)	O(4)–La(2)–O(4')	75.1(5)
O(2)–O(3) ⎱		O(4)–La(2)–O(2'')	68.2(2)
O(2')–O(3') ⎰	2.987(9)	O(4')–La(2)–O(2'')	117.0(5)
O(2)–O(4) ⎱		O(2)–La(2)–O(3') ⎱	
O(2')–O(4') ⎰	2.564(8)	O(2')–La(2)–O(3) ⎰	70.9(3)
O(4)–O(2'') ⎱		O(2')–La(2)–O(3') ⎱	
O(4')–O(2''') ⎰	2.902(7)	O(2)–La(2)–O(3) ⎰	110.9(5)
O(3)–O(2'') ⎱		O(3)–La(2)–O(3')	62.9(2)
O(3')–O(2''') ⎰	2.692(8)	O(2)–La(2)–O(2''')	95.3(2)
O(3)–O(3')	2.752(13)	O(2'')–La–O(3)	62.9(2)
O(4)–O(4')	2.979(18)		

Discussion

Since all osmium atoms are located in the same crystallographic positions, the formal oxidation state of the transition metal is 5.5. The OsO$_6$ octahedron is only slightly distorted: Os–O distances are close to their mean value (1.946 Å). Taking $r(O^=) =$ 1.38 Å, the ionic radius of osmium in La$_3$Os$_2$O$_{10}$ is then 0.566 Å. The variation of r (Os) in sixfold coordination versus oxidation degree using data collected by Shannon (12) or determined by the authors in La$_4$Os$_6$O$_{19}$ (7) shows that the above value is indeed consistent with an oxidation state of 5.5.

The distance between osmium atoms in the double octahedra is only 2.46 Å which is,

as outlined above, close to the corresponding distance observed in La$_4$Os$_6$O$_{19}$. Furthermore, the value of α (1.16), which provides a better estimation of bond order (13), indicates the presence of an Os–Os bond across the common edge.

The coordination of the lanthanum atoms is eightfold: In each case, the polyhedron is a distorted cube. Around La(1) (Fig. 4) are found two sets of O(1) and O(3) atoms belonging to clusters situated at the same x level. A more distorted cube is found around La(2) (Fig. 5), four additional La–O bonds at 3.14 [2 × La(2)–O(1)] and 3.21 Å [2 × La(2)–O(4)] being too large to be counted into the coordination sphere of La atoms; however, La(2)–O mean distances (2.57 Å) are close to La(1)–O (2.52 Å). Both are in fair agreement
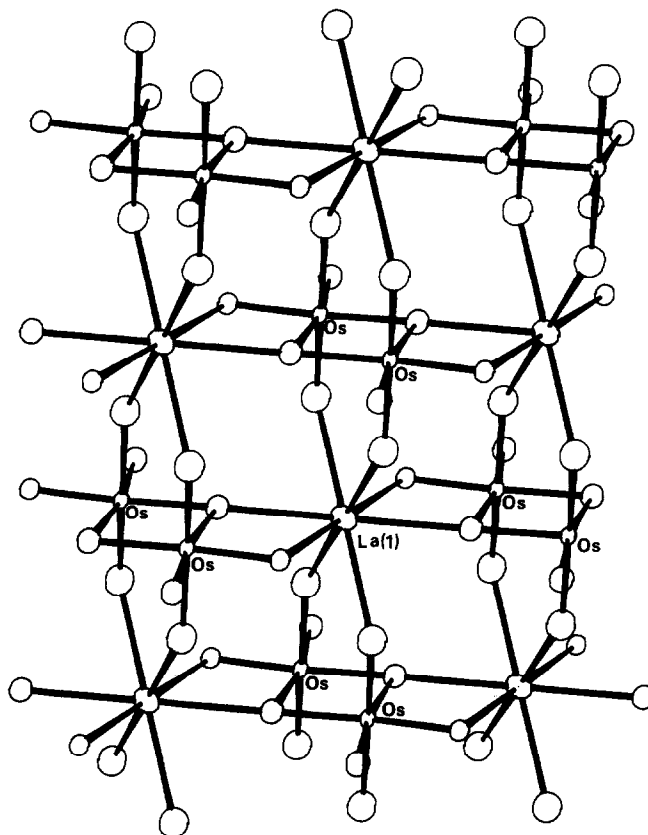
FIG. 2. The sheet $La(Os_2O_{10})$.

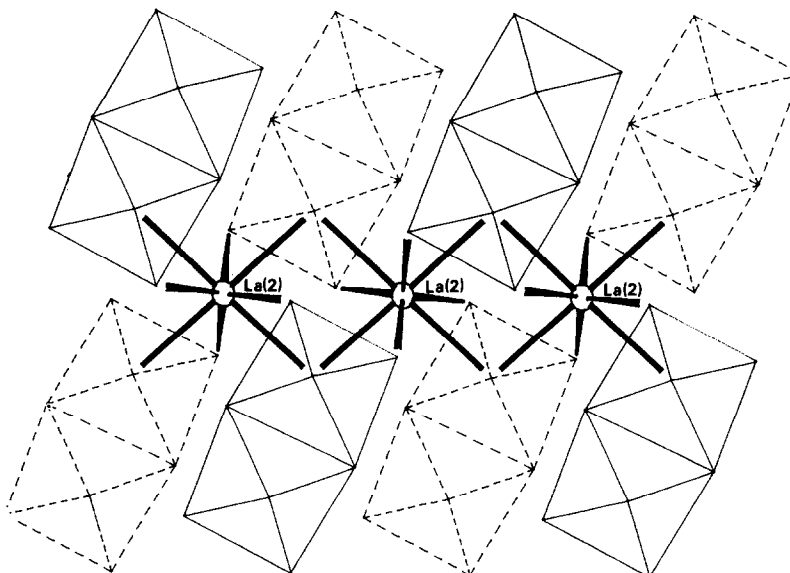FIG. 3. Projection of the structure along Oy showing the linkage between sheets by La(2) atoms. Solid-line clusters are situated at $y = 0$ and broken-line clusters at $y = \frac{1}{2}$.
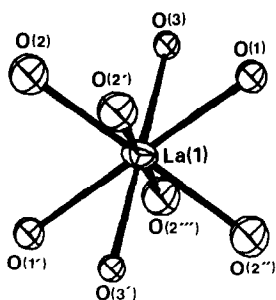
FIG. 4. La(1) polyhedron.

rare earth–transition metal oxides like $La_4Re_2O_{10}$ (6) and $Nd_4Re_2O_{11}$ (15): Both compounds exhibit Re–Re bonds inside isolated clusters (Re_2O_8 units in the former and Re_2O_{10} in the latter). However, $La_3Os_2O_{10}$, with the recently published work on $La_8Ru_4O_{21}$ (16), provide the first examples of ternary oxides containing discrete clusters with a transition metal in a noninteger oxidation state.

with the value of ionic radius of La^{3+} in eightfold coordination proposed by Shannon (12).

Owing to the distance between neighboring clusters, it is possible to describe $La_3Os_2O_{10}$ as composed of isolated clusters: The four nearest neighbors are situated in the same sheet, at a distance of about 5.6 Å, and the next-nearest neighbors belong to adjacent sheets and are ∼7 Å apart. Such a situation was found by Meunier, Frit, and Galy (14) in $Cr_2Te_4O_{11}$; however, there is no evidence, in this latter compound, of a metal–metal interaction between chromium atoms of the dimeric units. From this point of view, $La_3Os_2O_{10}$ is to be compared to other
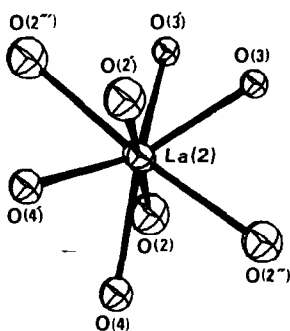

FIG. 5. La(2) polyhedron.

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