

- FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412–415.
 GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 778–791.
International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press.
 LINDQVIST, I. (1957). *Acta Cryst.* **10**, 29–32.
 LOUIS, R., METZ, B. & WEISS, R. (1974). *Acta Cryst.* **B30**, 774–780.
 LOUIS, R., PELISSARD, D. & WEISS, R. (1974). *Acta Cryst.* **B30**, 1889–1894.
 MAIER, C. A. & PAUL, I. C. (1971). *Chem. Commun.* pp. 181–182.
 MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
 PELISSARD, D. & LOUIS, R. (1972). *Tetrahedron Lett.* pp. 4589–4592.
 VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303–306.
 VRANKA, R. G. & AMMA, E. L. (1966). *Inorg. Chem.* **5**, 1020–1025.
 WIEST, R. & WEISS, R. (1973). *Chem. Commun.* pp. 678–679.

Acta Cryst. (1976). **B32**, 1485

The Crystal Structure of $\text{La}_4[\text{Re}_2]\text{O}_{10}$, a Fluorite-Related Structure Containing Rhenium Doublets

BY KJELL WALTERSSON

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden

(Received 1 September 1975; accepted 23 October 1975)

The crystal structure of La_2ReO_5 has been determined from three-dimensional X-ray diffractometer data (Mo $K\alpha$ radiation); the constitutional formula was found to be $\text{La}_4[\text{Re}_2]\text{O}_{10}$. The tetragonal unit cell, space group $I4/m$ (No. 87), has the dimensions $a = 8.935$, $c = 6.011$ Å, $V = 479.9$ Å³. The unit cell contains two formula units of $\text{La}_4[\text{Re}_2]\text{O}_{10}$. Least-squares refinement reached $R_w = 0.0438$ for 2223 measured independent reflexions for which $\sigma(F_o)/F_o \leq 0.20$. The structure is closely related to the fluorite type. The O atoms are in the F positions while four of five Ca sites are occupied by La atoms and the fifth accommodates a pair of Re atoms with its axis parallel to the c axis. The Re–Re distance is only 2.259 (1) Å, close to the distance reported for $\text{K}_2\text{Re}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$. The structural relationships between $\text{La}_4[\text{Re}_2]\text{O}_{10}$ and $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$ are discussed.

Introduction

Although the preparation of ternary oxides containing rare-earth elements including Y and La (=Ln) and Re in different oxidation states has been reported by several authors (see below) the structures of only a few of these compounds have been reported, *viz.* $\text{La}_4\text{Re}_6\text{O}_{19}$ (Morrow & Katz, 1968; Longo & Sleight, 1968) and $\text{Nd}_4\text{Re}_2\text{O}_{11}$ (Wilhelmi, Lagervall & Muller, 1970).

Extensive preparative studies of the Ln metal-rich (Ln/Re ~ 2) part of several lanthanoid rhenium–oxide systems were reported by Muller (1968), Muller & Roy (1969), and Baud & Capestan (1968). Five structure types with nearly the same stoichiometry, Ln_2ReO_5 , were reported by Muller & Roy (1969), *viz.*

$\beta\text{-Nd}_2\text{ReO}_{5.25}$ type (Ln = Nd, Sm and Gd), $\alpha\text{-Nd}_2\text{ReO}_5$ type (Ln = La and Nd), $\alpha\text{-Sm}_2\text{ReO}_5$ type (Ln = Sm and Gd), Yb_2ReO_5 type (Ln = Gd, Dy, Y, Er and Yb) and the $\text{Y}_{2+x}\text{ReO}_{5+y}$ type (Ln = Y).

The Nd-compound, belonging to the first structure type, was investigated some years ago by Wilhelmi *et al.* (1970). In view of the structure determination, the compound was reformulated as $\text{Nd}_4\text{Re}_2\text{O}_{11}$ (or $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$). This paper deals with the structure determination of La_2ReO_5 ($\alpha\text{-Nd}_2\text{ReO}_5$ type).

Experimental

A black crystalline sample of the compound was prepared by Dr A. W. Sleight (Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898, U.S.A.). The selection of a suitable crystal and the determination of possible space groups were performed by X-ray photographic methods (oscillation and Weissenberg techniques). The crystal, $0.050 \times 0.050 \times 0.114$ mm, was mounted with the largest dimension parallel to the crystallographic c axis. Cell dimensions were calculated from diffractometer measurements (Table 1a) and were the same as those reported by Muller & Roy (1969), within the limits of error.

The X-ray intensity data were collected by a Siemens AED diffractometer with graphite-monochromatized Mo $K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The θ – 2θ scan technique was used. Each reflexion was measured according to the five-values technique. The scan range for the individual reflexions was given by the expressions $+\Delta\theta = 0.78 + 0.12^\circ \tan \theta$, and $-\Delta\theta = 0.70 + 0.17^\circ \tan \theta$. The constants were evaluated after scanning a few reflexions manually and recording the widths of the peaks. Each

intensity measurement was taken in steps of 0.01° in θ , with the maximum step time 0.60 s. For strong reflexions the step time was automatically changed in order to accelerate the data collection. In order to keep

counting losses low for strong reflexions, the automatic attenuator mechanism was set to add filters.

Two standard reflexions (004 and 060), automatically monitored throughout the data collection, indicated no deterioration of the crystal.

All the 2337 possible reflexions, systematic extinctions excluded, within one octant of the reciprocal lattice sphere to $\theta = 65^\circ$, were measured. The 2223 reflexions with $\sigma(I_n)/I_n \leq 0.40$ were used in the subsequent calculations. The net intensity I_n , was calculated as $I_t - I_b$, and its estimated standard deviation was obtained from the expression $\sigma(I_n) = (I_t + I_b)^{1/2}$, where I_t and I_b are the number of counts for the total and background intensities respectively.

The net intensities were corrected for Lorentz, polarization and absorption effects. The linear absorption coefficient, $\mu(\text{Mo } K\alpha) = 441 \text{ cm}^{-1}$, was used in calculating a transmission factor for each reflexion (*International Tables for X-ray Crystallography*, 1962). The absorption was estimated by the Gaussian integration method with $6 \times 6 \times 16$ grid-points. The factor (A) in the formula $I = Lp \cdot I_n/A$ ranged from 0.1475 to 0.2279. Preparatory calculations for extinction correction were included.

The calculations were performed by IBM 1800 and IBM 360/75 computers.

Structure determination and refinement

The crystal structure of La_2ReO_5 belongs to the tetragonal system with the reflexions $h+k+l = 2n+1$ systematically absent; the possible space groups were: $I4/m$ (No. 87), $I4$ (No. 79) and $I\bar{4}$ (No. 82).

The structure determination was started with the assumption that the space group $I4/m$ (No. 87) was the correct one. From a three-dimensional Patterson synthesis tentative coordinates of one Re atom were derived in point set 4(e). The discrepancy index $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ was at this stage 0.28.

From a three-dimensional ($F_o - F_{\text{Re}}$) synthesis with approximate signs given by the refined Re position, one La atom was located in point set 8(h). These metal positions explained all the prominent vectors in the

Table 1(a). *The crystal structure of $\text{La}_4[\text{Re}_2]\text{O}_{10}$*

$\text{La}_4[\text{Re}_2]\text{O}_{10}$: M.W. 1088.0. Space group: $I4/m$ (No. 87). Cell dimensions according to Muller & Roy (1969): $a = 8.935$, $c = 6.011 \text{ \AA}$ and $V = 479.9 \text{ \AA}^3$. $D_c = 7.42$, $D_o = 7.53 \text{ g cm}^{-3}$ (Baud & Capestan, 1968). Cell content: $2\text{La}_4[\text{Re}_2]\text{O}_{10}$.

Point set	Numbering of atoms
4(d)	$\frac{1}{2}, 0, \frac{1}{2}$ (n, 1)
	$0, \frac{1}{2}, \frac{1}{2}$ (n, 2)
	$0, \frac{1}{2}, \frac{3}{2}$ (n, 3)
	$\frac{1}{2}, 0, \frac{3}{2}$ (n, 4)
4(e)	$0, 0, z$ (1)
	$0, 0, \bar{z}$ (2)
	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$ (3)
	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$ (4)
8(h)	$x, y, 0$ (1)
	$\bar{x}, \bar{y}, 0$ (2)
	$\bar{y}, x, 0$ (3)
	$y, \bar{x}, 0$ (4)
	$\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2}$ (5)
	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2}$ (6)
	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}$ (7)
	$\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2}$ (8)
16(i)	x, y, z (n, 1)
	\bar{x}, \bar{y}, z (n, 2)
	x, y, \bar{z} (n, 3)
	$\bar{x}, \bar{y}, \bar{z}$ (n, 4)
	\bar{y}, x, z (n, 5)
	y, \bar{x}, z (n, 6)
	\bar{y}, x, \bar{z} (n, 7)
	y, \bar{x}, \bar{z} (n, 8)
	$\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$ (n, 9)
	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ (n, 10)
	$\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$ (n, 11)
	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ (n, 12)
	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} + z$ (n, 13)
	$\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$ (n, 14)
	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$ (n, 15)
	$\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$ (n, 16)

Atom(n)	Point set	$x + \sigma(x)$	$y + \sigma(y)$	$z + \sigma(z)$
Re	4(e)	0	0	0.18788 (4)
La	8(h)	0.18154 (3)	0.39372 (3)	0
O(1)	4(d)	$\frac{1}{2}$	0	$\frac{1}{2}$
O(2)	16(i)	0.09517 (32)	0.18615 (30)	0.25775 (54)

Table 1(b). *Final anisotropic temperature factors defined as $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ (β_{ij} values are given in $\text{\AA}^2 \times 10^5$, estimated standard deviations in parentheses) with r.m.s. components (R_i) of thermal displacements along the ellipsoid axes and the r.m.s. radial (R) thermal displacements*

Atom (n)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3	R
Re	94 (2)	94 (2)	220 (4)	0	0	0	0.0617	0.0617	0.0635	0.1079
La	107 (2)	142 (2)	338 (4)	6 (1)	0	0	0.0655	0.0759	0.0787	0.1275
O(1)	166 (39)	166 (39)	152 (61)	0	0	0	0.0527	0.0819	0.0819	0.1272
O(2)	170 (17)	133 (16)	546 (46)	-18 (13)	-18 (24)	0 (23)	0.0713	0.0842	0.1003	0.1491

Extinction parameters $\times 10^4$

ϵ_{11}	ϵ_{22}	ϵ_{33}	ϵ_{12}	ϵ_{13}	ϵ_{23}
12.37 (108)	2.63 (24)	3.80 (39)	-1.00 (37)	3.14 (50)	-1.85 (28)

Principal semi-axis of the assumed ellipsoidal particle (microns)

0.202 (10)	0.438 (20)	0.365 (20)
------------	------------	------------

three-dimensional Patterson map. Refinement of these positions yielded a conventional R value of 0.10. Two O atoms were next located, one in point set 4(d) and one in 16(i), from a three-dimensional difference ($F_o - F_{\text{metal}}$) synthesis, calculated from the refined metal coordinates. With the O positions included, least-squares refinement reduced R to 0.08.

Refinement was continued with a full-matrix program including anisotropic temperature factors and anisotropic extinction corrections. The scattering factors were taken for neutral atoms from McMaster, Kerr del Grande & Hubbell (1969), and the anomalous scattering values were taken from *International Tables for X-ray Crystallography* (1962).

The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The conventional R value and the weighted R_w value, defined by $R_w = (\sum w\Delta^2)^{1/2} / (\sum wF_o^2)^{1/2}$, were 0.0351 and 0.0438 respectively for the final cycle of refinement. The weights applied to the structure factors were calculated according to the formula:

$$w = [\sigma^2(F_o) + 10 + F_o/80 + 80/F_o]^{-1}.$$

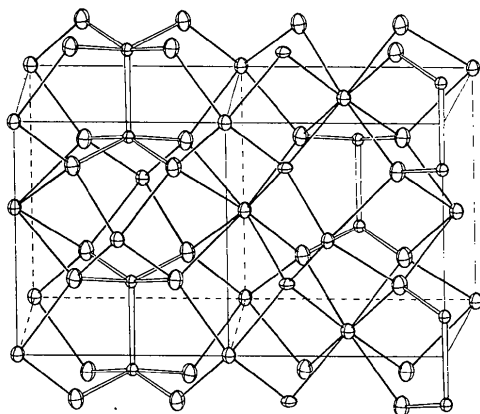


Fig. 1. The two different fluorite subcells. The La atoms or the Re pairs are situated either at the corners or at the faces of the subcells.

There were 27 variables in final least-squares refinement: the six positional parameters, 14 anisotropic temperature-factor coefficients, one scale factor, and six anisotropic-extinction parameters.

Anisotropic-extinction corrections were performed, with extinction assumed to be dominated by particle size (type II) (Coppens & Hamilton, 1970). The assumed ellipsoidal particle shape is described by the tensor ϵ_{ij} .

The principal semi-axis j of the ellipsoid is given by the expression $\lambda/\sqrt{\epsilon_{ij}}$ (in microns) (see Table 1*b*). Corrections with extinction assumed to be dominated by mosaic spread (type I) (Coppens & Hamilton, 1970) were also tested, but both the R and R_w values were significantly higher than for type II, which therefore was considered the more realistic model.

Attempts were also made to refine the structure in the space groups $I4$ (No. 79) and $I\bar{4}$ (No. 82). The coordinates thus obtained did not differ significantly from those found for space group $I\bar{4}/m$ (No. 87), which was therefore considered as the actual symmetry of the compound.

The final positional, thermal, and extinction parameters together with their estimated standard deviations as well as the numerical values of the root mean square thermal displacements are given in Table 1(*b*). The weight

Table 2. Weight analysis obtained after the final cycle of the least-squares refinement of $\text{La}_4[\text{Re}_2]\text{O}_{10}$

$\Delta = ||F_o| - |F_c||$, w = weighting factor. The $w\Delta^2$ values have been normalized.

Interval in F_o	$w\Delta^2$	Number of reflexions	Interval in $\sin \theta$	$w\Delta^2$	Number of reflexions
0—20	0.76	240	0.0—0.422	2.77	264
—30	1.22	253	—0.532	0.99	246
—40	0.66	220	—0.609	2.74	233
—50	0.96	217	—0.670	0.54	226
—60	0.64	199	—0.722	0.52	225
—75	0.67	251	—0.768	0.35	220
—90	0.89	178	—0.808	0.49	201
—115	0.45	240	—0.845	0.35	225
—150	2.62	199	—0.879	0.32	208
> 150	1.30	225	—0.906	0.30	174

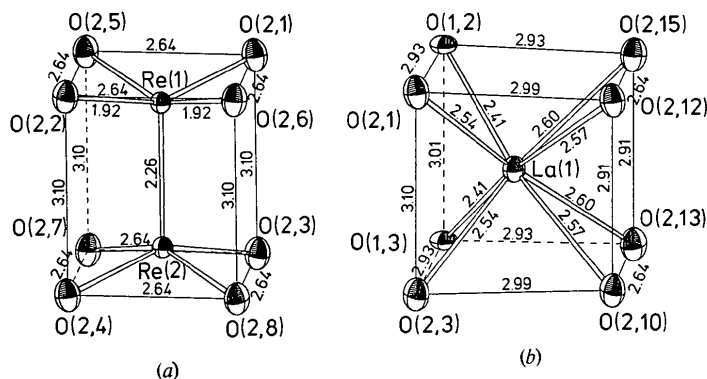


Fig. 2. The two metal coordination polyhedra in the $\text{La}_4[\text{Re}_2]\text{O}_{10}$ structure. The atomic distances are given in Å. The thermal ellipsoids are drawn at 90% probability. (a) The Re_2O_8 unit. (b) The LaO_8 polyhedron.

analysis after the last cycle of least-squares refinement is shown in Table 2.* Figs. 1 and 2 are pictorial repre-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31377 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances* (\AA) *and bond angles* ($^\circ$) *in* $\text{La}_4[\text{Re}_2]\text{O}_{10}$

Estimated standard deviations in the last decimal place are given within parentheses. The atoms are numbered according to Table 1(a).

(a) Re_2O_8 cube

Metal-oxygen distances		Uncorrected	Corrected		
Re(1)-O(2,1)	O(2,2)	1.915 (3)	1.917		
	O(2,5)				
	O(2,6)				
	O(2,3)				
	O(2,4)				
	O(2,7)				
O(2,8)	3.266 (3)	3.267			
Metal-metal separations					
Re(1)-Re(2)	2.259 (1)	2.262			
Re(2)-La(5)	3.752 (1)	3.754			
La(6)	3.538 (1)	3.541			
La(7)					
La(8)					
Bond angles		Distances between the O atoms			
O(2,1)-Re(1)-O(2,5)	O(2,6)	87.2 (1)	2.642 (4)	2.648	
	O(2,2)				
O(2,1)-O(2,2)	O(2,6)	154.7 (2)	3.736 (5)	3.741	
	O(2,5)				
Re(2)-Re(1)-O(2,1)	O(2,2)	102.7 (1)			
	O(2,5)				
	O(2,6)				
Remaining oxygen distances					
O(2,1)-O(2,3)	O(2,3)-O(2,7)	3.099 (7)	3.103	2.642 (4)	2.648
O(2,2)-O(2,4)	O(2,8)				
O(2,5)-O(2,7)	O(2,4)-O(2,7)				
O(2,6)-O(2,8)	O(2,8)				

(b) LaO_8 cube

Metal-oxygen distances		Uncorrected	Corrected
La(1)-O(1,2)	O(1,3)	2.406 (1)	2.406
	O(2,1)		
O(2,3)	O(2,10)	2.537 (3)	2.538
	O(2,12)		
O(2,13)	O(2,15)	2.571 (3)	2.572
O(2,15)		2.600 (3)	2.600
Metal-metal separations			
La(1)-Re(3)		3.538 (1)	3.541
Re(4)			
La(2)			

Table 3 (cont.)

		Bond angles	Distances between the O atoms	
O(2,10)-La(1)-O(2,13)	O(2,12)	61.5 (1)	2.642 (4)	2.648
	O(2,15)			
O(2,13)	O(2,15)	68.1 (1)	2.912 (7)	2.916
	O(2,12)			
O(2,10)	O(2,12)	69.0 (1)	2.912 (7)	2.916
	O(1,2)			
O(1,2)	O(2,15)	71.6 (1)	2.931 (3)	2.935
	O(2,13)			
O(1,3)	O(2,12)	71.8 (1)	2.994 (6)	3.000
	O(2,10)			
O(2,1)	O(2,1)	72.7 (1)	2.931 (3)	2.935
	O(2,3)			
O(1,3)	O(2,3)	75.3 (1)	3.099 (7)	3.103
	O(2,1)			
O(2,1)	O(2,3)	77.3 (1)	3.005 (1)	3.010
	O(1,3)			
O(1,2)	O(2,15)	99.0 (1)	3.932 (5)	
	O(2,13)			
O(1,2)	O(2,12)	106.2 (1)	3.982 (3)	
	O(1,3)			
O(1,3)	O(2,10)	107.6 (1)	4.145 (4)	
	O(2,15)			
O(2,3)	O(2,13)	112.3 (1)	4.241 (4)	
	O(2,1)			
O(2,1)	O(2,10)	112.5 (1)	4.164 (3)	
	O(2,12)			
O(1,2)	O(2,13)	117.7 (1)	4.231 (3)	
	O(2,15)			
O(1,3)	O(2,3)	170.5 (1)	4.960 (3)	
	O(2,1)			
O(1,2)	O(2,10)	170.6 (1)	5.119 (3)	
	O(2,12)			
O(1,3)	O(2,13)			
	O(2,15)			

sentations of the thermal vibrations of the atoms. Corrections for the thermal motions have been applied to the Re-O and La-O distances, based on the riding-motion model. The metal-metal and oxygen-oxygen distances are corrected under the assumption of independent movements. The most important distances and angles are given in Table 3.

A final three-dimensional difference-Fourier synthesis was computed in sections 0.30 \AA along the c axis. The residual peaks showed a maximum height of less than 14% of the smallest oxygen peak in the corresponding ($F_o - F_{\text{metal}}$) synthesis.

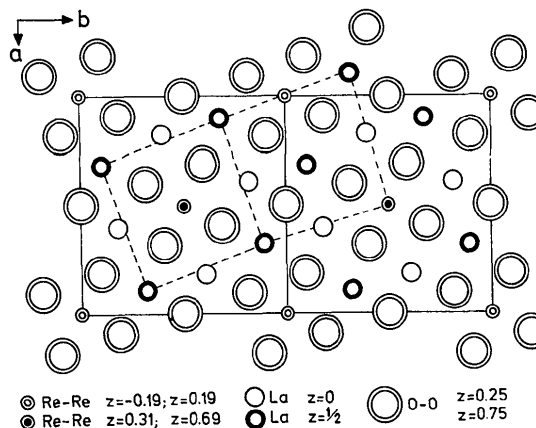


Fig. 3. $\text{La}_4[\text{Re}_2]\text{O}_{10}$ structure projected on (001). The two sorts of fluorite subcells are outlined with dotted lines.

Description of the crystal structure

The structure of La_2ReO_5 , projected on (001) in Fig. 3, is closely related to the fluorite type. The unit cell contains four Re, eight La, and twenty O atoms. The atoms are numbered according to the system set forth in Table 1(a).

All the O atoms, forming a somewhat distorted primitive cubic oxygen arrangement, are in the fluoride positions, while four of the five Ca sites are occupied by La atoms and the fifth accommodates a Re atom pair oriented parallel to the c axis. Because of the Re doublets, it seems advisable to write the formula as $\text{La}_4[\text{Re}_2]\text{O}_{10}$ (cf. Fig. 1).

The rhenium-non-metal coordination (cf. Fig. 2a) consists of two parallel square ReO_4 units, which form square pyramids with the Re atoms at the tops. The two ReO_4 halves are connected by a Re-Re bond in an eclipsed conformation. The Re-O distances are 1.915 Å and the Re atom is 0.42 Å above the plane of the square pyramid. Two ReO_4 square pyramids, regarded as a unit Re_2O_8 , form an elongated cube with two kinds of O-O distances, viz. eight distances of 2.642 and four of 3.099 Å (average 2.794 Å) (see Table 3a). The Re-Re distance is 2.259 (1) Å, which agrees well with the short distance (2.24 Å) found in the $\text{Re}_2\text{Cl}_8^{2-}$ ion (Cotton & Harris, 1965; see also Kuznetsov & Koz'min, 1963), with the conformation similar to the Re_2O_8 unit.

The eight La-O distances range from 2.406 to 2.600 Å with the mean value 2.53 Å (see Table 3), comparable with those found in $\text{La}_4\text{Re}_6\text{O}_{19}$. The La coordination polyhedron is illustrated in Fig. 2(b).

Each O(1) atom is coordinated to four La atoms to form a perfect tetrahedron, while the O(2) atom is bonded to one Re and three La atoms in a rather distorted tetrahedral arrangement. As a result of this difference in function of the two O atoms, a significant shortening of the La-O(1) distance (2.406 Å) compared to the La-O(2) bond lengths (2.537–2.600 Å) is observed, resulting in a deformed cubic environment of the lanthanums.

It is interesting to compare the structure of $\text{La}_4[\text{Re}_2]\text{O}_{10}$ with $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$ (Wilhelmi *et al.*, 1970) and $\text{La}_4\text{Re}_6\text{O}_{19}$ (Morrow & Katz, 1968; Longo & Sleight, 1968). The structures of $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$ and $\text{La}_4\text{Re}_6\text{O}_{19}$ both contain double octahedra Re_2O_{10} occurring in edge-shared pairs with short Re-Re contacts (2.42 Å). In $\text{La}_4\text{Re}_6\text{O}_{19}$, the dimeric units Re_2O_{10} are further linked by sharing corners to form a three-dimensional network in which there are voids containing La_4O tetrahedra. The La-O coordination is a trigonal prism which is capped on all three rectangular

faces and one triangular face. In $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$ the double octahedra are joined together by two crystallographically different neodymiums. One half of the Nd atoms, together with the O atoms, are in a somewhat deformed fluorite arrangement. The environment around the remaining Nd atoms is a bicapped trigonal prism.

The number of d electrons per Re in $\text{Nd}_4[\text{Re}_2]\text{O}_{11}$ and $\text{La}_4\text{Re}_6\text{O}_{19}$ is 2 and $2\frac{2}{3}$ respectively. Extended Hückel calculations (Sleight, Hare & Sleight, 1968) showed the presence of a Re=Re double bond across the edge-shared octahedra. The significantly shorter Re-Re bond length of 2.26 Å, observed in $\text{La}_4[\text{Re}_2]\text{O}_{10}$ with three d electrons per Re, indicates that the bonding conditions are more similar to those in the $\text{Re}_2\text{Cl}_8^{2-}$ cluster (five d^4 configuration) with an estimated quadruple bond (Cotton, 1965).

I am thankful to Dr Karl-Axel Wilhelmi for his interest in this investigation. The crystals of $\text{La}_4[\text{Re}_2]\text{O}_{10}$ were supplied by Dr A. W. Sleight (Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898, U.S.A.). I wish to thank Professor Arne Magnéli for valuable discussions and Dr Don Koenig for linguistic corrections to the English text. This investigation has been supported by the Swedish Natural Science Research Council.

References

- BAUD, G. & CAPESTAN, M. (1968). *Bull. Soc. Chim. Fr.* pp. 3999–4004.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst. A* **26**, 71–83.
- COTTON, F. A. (1965). *Inorg. Chem.* **4**, 334–336.
- COTTON, F. A. & HARRIS, C. B. (1965). *Inorg. Chem.* **4**, 330–333.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KUZNETZOV, V. G. & KOZ'MIN, P. A. (1963). *Zh. Strukt. Khim.* **4**, 55–62.
- LONGO, J. M. & SLEIGHT, A. W. (1968). *Inorg. Chem.* **7**, 108–111.
- MCMASTER, W. H., KERR DEL GRANDE, N. & HUBBELL, J. H. (1969). *Compilation of X-ray Cross Sections*, UCRL-50174 Sec. II, Rev. 1.
- MORROW, N. L. & KATZ, L. (1968). *Acta Cryst. B* **24**, 1466–1471.
- MULLER, O. (1968). Dissertation, Pennsylvania State Univ.
- MULLER, O. & ROY, R. (1969). *Mater. Res. Bull.* **4**, 349–360.
- SLEIGHT, T. P., HARE, C. R. & SLEIGHT, A. W. (1968). *Mater. Res. Bull.* **3**, 437–444.
- WILHELMI, K.-A., LAGERVALL, E. & MULLER, O. (1970). *Acta Chem. Scand.* **24**, 3406–3408.