Hence

$$\begin{aligned}&\{\Pi(1,p)-\Pi(-1,p)\}-\{\Pi(1,p-1)-\Pi(-1,p-1)\}\\&=n_a+n_b-n_e-n_f-n_d-n_e+n_b+n_c\\&=(n_a+n_c+n_e)-(n_b+n_d+n_f)\ (\mathrm{mod.}\ 3)\\&=\{\Pi(1,1)-\Pi(-1,1)\}\ (\mathrm{mod.}\ 3)\ .\end{aligned}$$

This is just another way of expressing formula (5), since hexagonal and trigonal SiC structures (space groups $P6_3mc$ and $P3m1$) are characterized by $\{\Pi(1,1)-\Pi(-1,1)\}=0$ (mod. 3), and rhombohedral structures ($R3m$) by $\{\Pi(1,1)-\Pi(-1,1)\}=\pm1$ (mod. 3). The positive sign refers to the obverse setting, the negative sign to the reverse one.

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The Crystal Structure of Lanthanum Rhenium Oxide, $La_4Re_6O_{19}$

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Lanthanum rhenium oxide, $La_4Re_6O_{19}$, is a body centered cubic phase, $a=9{\cdot}0325\pm0{\cdot}0014$ Å, space group $I23$, $Z=2$. It is formed by reacting La_2O_3, ReO_3, and Re at 1000° in vacuum. The structure contains a three-dimensional network of ReO_6 octahedra in which pairs of octahedra share an edge; the pairs in turn are linked to each other through corner sharing. The Re–Re distance in each pair is 2·42 Å, indicating metal–metal bonding. The Re–O distances range from 1·98–2·01 Å. The lanthanums are present as tetrahedral La_4O groups in open spaces of the network. The lanthanum coordination number is 10 with La–O distances of 2·50 Å (1); 2·51 Å (3); 2·60 Å (3); and 2·88 Å (3).

Introduction

If lanthanum sesquioxide, rhenium trioxide, and rhenium metal, in proportions corresponding approximately to $La_2Re_2O_7$, are heated to 1000° in vacuum, a heterogeneous product is formed (Longo, 1964). The major component of this product is a body centered cubic phase. No technique was found to separate this phase from the others present, so the stoichiometry could not be determined reliably in the normal way from density and chemical analysis. Microscopic examination of the material showed crystals apparently suitable for single-crystal study, so it was decided to solve the structure and from it establish the composition of the cubic phase.

Experimental

Longo (1964) obtained a good powder pattern for the cubic lanthanum rhenium oxide, which was indexed using a body centered cell with $a=9{\cdot}05$ Å. A more accurate cell length was obtained by Cohen's least-squares method (Klug & Alexander, 1954), using a program of Leipold & Pauly (1963). The value for a obtained is $9{\cdot}0325\pm14$ Å.

Under the microscope a number of black (or dark blue) crystals were observed. Their habit was multifaceted with one large face–apparently the face which had been in contact with the walls of the capsule–so that the crystals roughly approximated hemispheres. The radii of these 'hemispheres' were in the range 0·05–0·20 mm. The crystal which was selected had base diameters ranging from 0·130 to 0·165 mm and a height of 0·135 mm.

A precession camera study revealed directions with C_6 zero level symmetry and C_3 upper level symmetry as well as directions showing C_{2l} symmetry for both zero and upper levels. This establishes Laue group $m3$ (Buerger, 1942). All of the photographs showed absences for odd values of $h+k+l$. The probable space group is therefore one of $I23$, $I2_13$ and $Im3$.

The crystal was aligned with the c axis vertical when $\chi=0$ on a General Electric single crystal orienter. Zr-filtered Mo radiation was used with pulse height discrimination, a scintillation counter, and a 2° take-off angle to align the crystal and collect data. A total of 2634 reflections were measured by the moving-crystal moving-counter technique. Background was measured on each side (in θ) of each reflection. Averaging equiv-

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alent reflections gave a total of 772 independent reflections. Using an approximate density and cell content, a linear absorption coefficient of 600 cm^{-1} was estimated. (The actual value, $\mu = 650$ cm^{-1}, was used in the final refinement.) Because of the large absorption coefficient of the material, an unusual collection scheme was employed. All accessible reflections for which $l \leq 3$ and all their higher orders were measured. For this crystal and orientation, almost all of the collected reflections occur at low values of $\chi (< 20°)$ and in a small range of φ (about 30°). The need for an absorption correction dependent on χ and φ is thus reduced.

The data were corrected for Lorentz and polarization effects, and a sharpened three-dimensional Patterson map was generated using programs of Penfold (1959) and Sly, Shoemaker & Van den Hende (1962). The Patterson map was consistent with rhenium atoms in positions 12(*e*) of space groups *I*23 and *Im*3 with x approximately $\frac{1}{8}$ or $\frac{3}{8}$, but was not consistent with any position of $I2_13$. To resolve the ambiguity in x, two cycles of isotropic least-squares calculation (Busing & Levy, 1959) were run; only the value $x = \frac{3}{8}$ refined. With the Re atoms located, the Re–La peaks on the Patterson were identified. These indicated either position 8(*c*) of *I*23 or 16(*f*) of *Im*3 for lanthanum with $x = \frac{1}{6}$ or $\frac{2}{6}$. However, the preparations indicated that the number of lanthanum atoms could not exceed the number of rhenium atoms and was probably smaller, so 8(*c*) of *I*23 was chosen. *I*23 was confirmed as the proper space group by the structure determination. It was impossible to decide at this stage between $x = \frac{1}{6}$ and $x = \frac{2}{6}$ because the only difference is the sign of the imaginary part of the structure factor; *i.e.* the two values correspond to two enantiomorphs. The $x = \frac{1}{6}$ value was arbitrarily chosen.

Least-squares refinement of the rhenium and lanthanum positions gave an unreasonably high R value, though the convergence was regular. A spherical absorption correction of the data was made with $\mu R = 4{\cdot}3$. Refinement of the corrected data gave an R value of 12·4%.

Using the corrected data and the refined rhenium and lanthanum parameters, a difference electron density map was calculated. Three crystallographically different sets of oxygen atom positions were located. These positions are 2(*a*), 12(*d*), and 24(*f*). Thus the total unit cell formula for the material was established as $La_8Re_{12}O_{38}$. The density calculated from this formula, 8·91 $g.cm^{-3}$, agrees well with the observed density, $8{\cdot}92 \pm 0{\cdot}06$ $g.cm^{-3}$. Introduction of the oxygen atoms into the least-squares refinement, treating temperature factors anisotropically, led to an R value of 7·4%.

The ten largest reflections showed obvious extinction effects. Omitting these and the next five largest reflections and introducing the weighting scheme $\sqrt{w} = 1$ for $|F|_{obs} > 60$ and $\sqrt{w} = |F|_{obs}/60$ for $|F|_{obs} \leq 60$ led to an R value of 6·6% (weighted $R = 6{\cdot}6\%$ also) as the final result. The scattering factors used throughout were those of Re^{4+} and La^{3+} (Thomas & Umeda, 1957) and O^{2-} (*International Tables*, 1962). Both the real and imaginary anomalous dispersion corrections were made for rhenium and lanthanum (Cromer, 1965). All refinements were based on F.

To confirm the stoichiometry another difference map was calculated using the final parameters. It showed no peaks of height greater than one-fifth of an oxygen. In addition a least-squares refinement was carried out with the atom multipliers, except for rhenium and the twofold-axis oxygen, as variables. No significant changes from full occupancy occurred. The atomic position and thermal parameters are given in Table 1, and the corresponding structure factors are given in Table 2.

The data are reported with only positive values of h, k, and l. In general these are averages of measurements of hkl and $\bar{h}\bar{k}l$ reflections. Such reflections may properly be averaged since they are related by genuine twofold symmetry. The Friedel related reflections were not recorded. Effectively, the one octant of data listed represents half of the available sphere in reciprocal space: hkl, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$. Since the structure does not have a center of symmetry, it remained to be deter-

Table 1. *Atomic parameters*

Position parameters × 10^5 (standard errors in parentheses)

	x	y	z
Re	36632 (7)	$\frac{1}{2}$	0
La	15986 (9)	15986 (9)	15986 (9)
O(1)	32247 (155)	0	0
O(2)	34136 (130)	28390 (113)	97389 (122)
O(3)	0	0	0

The temperature factor expression used was: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

Thermal parameters × 10^5 (standard errors in parentheses)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	76 (4)	82 (4)	82 (4)	0	0	3 (7)
La	165 (4)	165 (4)	165 (4)	15 (5)	15 (5)	15 (5)
O(1)	144 (79)	120 (69)	228 (91)	0	0	−37 (139)
O(2)	205 (70)	119 (57)	194 (67)	31 (66)	159 (75)	21 (59)
O(3)	236 (130)	236 (130)	236 (130)	0	0	0

Table 2. *Observed and calculated structure factors*

Asterisks mark the reflections omitted from the final refinement.

ℓ= 0

H	K	FOBS	FCAL	A	B
2	0	326	368	366	45
4	0	132	96	95	15
*6	0	630	830	825	85
*8	0	464	473	466	77
10	0	91	72	68	24
12	0	281	302	298	47
14	0	305	313	305	68
16	0	152	138	129	49
18	0	165	165	161	35
20	0	135	125	120	36
22	0	125	121	111	48
24	0	152	141	133	45
1	1	180	175	-174	-22
*3	1	552	776	-772	-85
*5	1	426	453	-449	-58
7	1	33	12	-0	-12
9	1	318	327	-324	-47
11	1	330	344	-337	-70
13	1	134	126	-121	-36
15	1	116	107	-104	-22
17	1	171	159	-153	-43
19	1	160	152	-143	-51
21	1	96	92	-87	-30
23	1	61	55	-52	-16
2	2	239	231	229	26
4	2	132	117	117	3
6	2	138	112	107	25
8	2	325	319	315	51
10	2	148	144	143	16
12	2	58	53	-53	-4
14	2	178	177	172	39
16	2	191	190	185	42
18	2	32	14	-13	-3
20	2	28	17	15	7
22	2	149	139	133	40
1	3	0	8	-7	2
3	3	248	250	250	-7
5	3	223	210	-209	-25
7	3	26	9	-8	[illegible]
9	3	218	225	224	21
11	3	156	150	-147	-32
13	3	151	152	-150	-21
15	3	185	180	177	32
17	3	33	7	-5	-4
19	3	166	161	-156	-37
21	3	66	56	55	10
2	4	35	21	21	3
4	4	85	74	-71	-18
6	4	84	71	-71	-3
8	4	175	167	165	27
10	4	48	34	34	-3
12	4	169	166	-163	-29
14	4	86	79	77	15
16	4	120	120	118	24
18	4	90	85	-82	-24
20	4	48	41	-40	-12
22	4	105	94	90	25
1	5	100	92	92	8
3	5	329	353	-350	-44
5	5	178	170	-168	-25
7	5	154	145	144	15
9	5	111	92	-91	-11
11	5	188	176	-172	-38
13	5	25	17	-14	-10
15	5	18	23	21	8
17	5	58	54	-52	-15
19	5	89	78	-73	-28
21	5	23	15	-14	-5
2	6	180	159	157	25
4	6	36	43	-43	-3
*6	6	473	520	515	66
8	6	328	305	299	56
10	6	23	11	-9	5
12	6	179	179	177	27
14	6	210	211	205	50
16	6	101	86	79	32
18	6	102	92	90	19
20	6	80	70	67	20
22	6	91	83	75	34
1	7	169	149	-147	-27
*3	7	537	631	-624	-93
5	7	357	361	-355	-62
7	7	84	42	-39	-16
9	7	322	313	-308	-55
11	7	341	329	-321	-73
13	7	136	124	-117	-38
15	7	136	123	-120	-29
17	7	181	166	-158	-48
19	7	155	145	-136	-52
21	7	109	104	-98	-35
2	8	301	315	311	51
4	8	179	178	176	27
6	8	299	301	296	56
*8	8	390	391	383	77
10	8	203	193	189	37
12	8	104	100	97	24
14	8	257	244	236	62
16	8	222	225	216	59
18	8	72	68	65	20
20	8	96	85	80	28
1	9	172	168	-166	-27
3	9	129	112	-105	-39
5	9	278	291	-286	-53
7	9	140	138	-136	-22
9	9	35	20	17	-10
11	9	256	247	-240	-57
13	9	212	204	-199	-41
15	9	59	44	44	4
17	9	97	94	-90	-28
19	9	201	193	-185	-56
21	9	17	22	-19	-12
2	10	115	112	111	16
4	10	21	21	21	-3
6	10	29	15	-13	6
8	10	188	183	179	37
10	10	94	84	84	9
12	10	101	94	-92	-18
14	10	101	96	93	25
16	10	165	152	148	34
18	10	56	51	-49	-14
20	10	20	8	-8	-2
1	11	95	89	87	17
3	11	106	101	-98	-22
5	11	58	58	-57	-12
7	11	109	105	103	23
9	11	33	39	38	6
11	11	91	92	-89	-23
13	11	30	2	-2	-1
15	11	91	78	75	21
17	11	10	7	-6	-2
19	11	65	55	-52	-19
2	12	38	24	-24	-4
4	12	152	157	-154	-29
6	12	188	187	185	27
8	12	106	100	97	24
10	12	97	95	-95	-18
12	12	33	25	25	-2
14	12	76	67	64	20
16	12	23	12	9	8
18	12	15	6	-3	-6
1	13	37	39	39	1
3	13	290	320	-314	-58
5	13	122	116	-111	-31
7	13	91	80	79	10
9	13	143	138	-135	-27
11	13	165	161	-155	-43
13	13	32	12	2	-11
15	13	43	34	-34	-6
17	13	84	73	-69	-23
19	13	57	52	-44	-28
2	14	169	168	163	39
4	14	66	59	57	16
6	14	221	224	218	50
8	14	236	241	233	62
10	14	94	88	84	25
12	14	92	86	84	20
14	14	176	169	160	51
16	14	143	143	135	45
18	14	51	48	46	16
1	15	171	172	-167	-39
3	15	175	174	-165	-56
5	15	245	252	-244	-63
7	15	150	152	-148	-33
9	15	56	64	-57	-28
11	15	245	239	-230	-67
13	15	194	189	-181	-52
15	15	23	22	-18	-13
17	15	124	119	-112	-40
2	16	182	190	185	42
4	16	131	122	120	24
6	16	91	85	78	32
8	16	224	221	213	59
10	16	168	152	148	34
12	16	15	12	8	8
14	16	148	140	132	46
16	16	201	189	182	53
1	17	37	26	-26	-6
3	17	113	116	-110	-35
5	17	109	108	-104	-31
7	17	39	14	-14	-0
9	17	19	16	-13	-10
11	17	125	124	-118	-38
13	17	79	67	-63	-21
15	17	0	18	17	4
2	18	28	14	-14	-3
4	18	102	101	-98	-24
6	18	107	103	102	19
8	18	71	63	60	20
10	18	67	64	-62	-14
12	18	29	10	8	-6
14	18	48	41	37	16
1	19	99	91	89	20
3	19	142	135	-132	-29
5	19	25	11	-8	-7
7	19	122	110	107	27
9	19	42	30	-30	-4
11	19	74	58	-54	-19
13	19	57	48	48	6
2	20	33	25	24	7
4	20	54	44	-42	-11
6	20	80	77	74	20
8	20	95	88	83	28
10	20	25	13	-12	-2
1	21	70	63	-60	-17
3	21	95	90	-81	-37
5	21	123	121	-115	-39
7	21	57	54	-52	-13
9	21	31	22	-16	-14
2	22	141	133	126	40
4	22	95	88	84	25
6	22	87	84	77	34
1	23	83	76	-71	-26

ℓ= 1

H	K	FOBS	FCAL	A	B
2	1	275	249	5	-249
4	1	280	273	132	239
6	1	77	65	19	63
8	1	236	236	-159	-175
10	1	107	102	17	100
12	1	161	163	136	89
14	1	126	126	-71	-105
16	1	91	85	-84	10
18	1	105	95	70	65
20	1	59	55	41	-36
22	1	75	70	-67	-17
*3	2	429	424	424	-11
5	2	310	333	229	241
7	2	174	168	-59	-157
9	2	138	134	121	-57
11	2	250	263	200	171
13	2	88	92	81	-42
15	2	63	57	0	-57
17	2	108	105	53	87
19	2	119	118	116	23
21	2	47	42	33	-25
2	3	274	246	-236	-70
4	3	37	33	-19	26
*6	3	434	445	-441	-63
8	3	355	369	-361	-76
10	3	61	57	-56	-10
12	3	133	134	-134	-12
14	3	230	239	-229	-66
16	3	129	136	-130	-40
18	3	77	76	-76	-9
20	3	83	78	-72	-30
22	3	116	111	-103	-40
*3	4	574	674	666	103
*5	4	428	404	394	-92
7	4	153	137	33	132
9	4	278	290	273	98
11	4	318	331	330	-26
13	4	155	158	135	82
15	4	108	111	87	65
17	4	152	153	152	-18
19	4	167	167	153	66
21	4	105	96	79	55
2	5	294	304	-253	169
4	5	199	184	-52	-177
6	5	276	249	-222	-113
8	5	348	357	-343	99
10	5	148	150	-94	-116
12	5	72	70	-16	-68
14	5	207	211	-207	41
16	5	162	173	-155	-76
18	5	46	49	-11	-48
20	5	62	62	-54	30
22	5	124	123	-116	-42
3	6	115	88	86	18
5	6	211	191	191	-9
7	6	34	22	-7	21
9	6	70	69	-69	9
11	6	159	163	162	13
13	6	115	111	108	25
15	6	106	99	-99	1
17	6	24	30	29	-8
19	6	139	135	129	40
21	6	27	21	-20	6
2	7	137	129	26	-125
4	7	200	194	122	151
6	7	110	96	91	31
8	7	150	141	-96	-103
10	7	82	72	27	65
12	7	172	180	163	75
14	7	81	78	-33	-71
16	7	76	71	-71	6
18	7	110	109	93	57
20	7	59	60	56	-21
3	8	120	115	112	-24
5	8	149	162	4	162
7	8	223	221	-166	-144
9	8	98	86	-45	-74
11	8	139	137	53	126
13	8	57	64	-19	-61
15	8	124	115	-90	-71
17	8	63	59	-25	53
19	8	47	44	43	6
21	8	46	49	-24	-43
2	9	71	68	15	-66
4	9	176	174	155	79
6	9	186	183	-182	-18
8	9	161	152	-136	-67
10	9	79	85	80	30
12	9	40	33	-10	32
14	9	110	106	-92	-53
16	9	37	30	-29	-8
18	9	29	27	4	27
20	9	0	17	-1	-17
3	10	347	381	375	67
5	10	201	204	203	-25
7	10	67	65	-27	59
9	10	167	159	160	54
11	10	209	216	216	5
13	10	78	78	63	45
15	10	63	56	42	37
17	10	100	99	99	-8
19	10	110	110	98	49
2	11	238	247	-234	81
4	11	149	150	-87	-122
6	11	235	239	-218	-99
8	11	284	307	-304	44
10	11	149	150	-113	-99
12	11	87	90	-62	-65
14	11	192	202	-202	12
16	11	167	177	-160	-75
18	11	55	62	-37	-49
20	11	72	74	-73	12
3	12	204	207	200	55
5	12	238	249	249	1
7	12	123	123	108	59
9	12	79	74	59	45
11	12	210	225	224	25
13	12	162	172	162	56
15	12	48	35	1	35
17	12	92	96	95	7
19	12	162	170	159	60
2	13	113	116	-93	-70
4	13	63	52	-15	49
6	13	60	51	-49	-10
8	13	165	177	-160	-75
10	13	64	58	-57	11
12	13	42	44	37	24
14	13	99	111	-93	-60
16	13	112	118	-115	-25
18	13	16	26	20	17
3	14	85	87	87	-2
5	14	99	105	19	103
7	14	121	123	-83	-91
9	14	61	51	-22	-46
11	14	114	107	55	92
13	14	51	35	3	-35
15	14	82	78	-58	-52
17	14	52	44	-7	43
2	15	82	79	67	-40
4	15	165	171	149	84
6	15	40	39	-38	9
8	15	66	62	-33	-53
10	15	101	107	96	48
12	15	69	68	50	46
14	15	43	40	-16	-36
16	15	0	9	4	8
3	16	128	127	124	29
5	16	41	34	31	-13
7	16	100	98	-98	-2
9	16	16	14	12	7
11	16	72	71	71	3
13	16	34	20	-19	7
15	16	45	38	-37	-7
2	17	90	91	-74	52
4	17	52	60	23	-55
6	17	102	104	-90	-50
8	17	135	142	-140	22
10	17	48	46	-9	-45
12	17	44	29	-2	-29
14	17	100	96	-96	12
3	18	168	163	153	55
5	18	148	156	156	4
7	18	71	74	56	48
9	18	68	71	57	42
11	18	153	159	158	21
13	18	109	112	99	51
2	19	133	131	-122	-49
4	19	74	65	-65	-5
6	19	96	101	-95	-33
8	19	166	176	-163	-66
10	19	89	86	-85	-18
12	19	22	27	-25	-10
3	20	118	117	113	31
5	20	106	119	88	79
7	20	44	41	28	-29
9	20	38	37	37	-3
11	20	116	125	98	77
2	21	42	36	-2	-36
4	21	62	62	42	44
6	21	47	47	-47	-2
8	21	73	78	-56	-54
3	22	67	65	62	17
5	22	22	2	1	-2

ℓ= 2

H	K	FOBS	FCAL	A	B
2	2	298	276	-74	-266
4	2	349	347	-307	161
6	2	108	93	52	77
8	2	198	194	109	-160
10	2	157	156	-137	73
12	2	117	118	-110	40
14	2	96	98	47	-85
16	2	58	44	22	38
18	2	89	89	-85	24
20	2	83	74	-39	-62
22	2	41	35	32	14
3	3	113	94	-94	-1
5	3	141	118	108	46
7	3	358	376	374	35
9	3	138	125	124	14
11	3	35	17	-7	16
13	3	145	151	150	22
15	3	165	160	157	26
17	3	65	65	58	30
19	3	35	32	32	-0
21	3	70	66	64	16
*4	4	506	517	-463	-230
6	4	81	64	-38	-52
8	4	148	134	-58	121
10	4	269	280	-256	-114
12	4	195	196	-167	-98
14	4	91	92	-58	72
16	4	83	73	-62	-37
18	4	149	147	-121	-79
20	4	108	105	-104	13
22	4	33	26	-23	-11
3	5	69	54	-26	47
5	5	226	210	19	-209
7	5	287	272	207	176
9	5	177	163	132	95
11	5	157	155	-49	-147
13	5	85	81	35	72
15	5	170	169	141	92
17	5	77	69	35	-58
19	5	37	33	-33	0
21	5	92	75	47	58
4	6	131	106	-73	-77
6	6	29	2	2	1
8	6	182	181	167	68
10	6	61	30	24	-17
12	6	111	111	-101	-45
14	6	96	95	81	49
16	6	120	120	118	19
18	6	79	70	-60	-36
20	6	33	25	-23	10
22	6	96	89	86	22
3	7	194	171	-165	-47
5	7	259	252	-239	79
7	7	98	91	-28	-86
9	7	50	45	1	-45
11	7	218	223	-221	31
13	7	141	135	-123	-57
15	7	71	59	48	-34
17	7	90	86	-79	33
19	7	155	149	-138	-55
21	7	37	32	-12	-30
4	8	152	148	-59	136
6	8	193	191	167	92
8	8	244	245	218	-111
10	8	92	95	8	95
12	8	57	55	-1	55
14	8	140	143	132	-54
16	8	114	117	99	62
18	8	57	42	-8	42
20	8	55	43	22	-37
3	9	236	238	-235	-36
5	9	89	89	-80	38
7	9	162	155	154	-14
9	9	44	46	-39	-25
11	9	123	120	-120	6
13	9	31	31	29	-11
15	9	34	47	44	-15
17	9	38	35	-29	19
19	9	38	45	-36	-27
21	9	10	14	1	-14
4	10	261	277	-243	-132
6	10	25	36	33	-14
8	10	76	73	12	72
10	10	167	166	-151	-69
12	10	107	109	-91	-60
14	10	46	53	-4	53
16	10	39	31	-26	-18
18	10	90	90	-74	-51
20	10	64	64	-63	12
3	11	72	60	47	37
5	11	130	142	71	-123
7	11	235	247	202	142
9	11	169	164	141	84
11	11	99	101	12	-100
13	11	103	97	67	70
15	11	171	171	149	85
17	11	78	73	64	-34
19	11	29	9	-0	9
4	12	192	200	-173	-99
6	12	117	119	-114	-32
8	12	54	45	0	45
10	12	105	98	-84	-49
12	12	181	181	-166	-72
14	12	37	34	-20	28
16	12	21	18	17	-8
18	12	123	123	-107	-63
3	13	25	13	-6	-11
5	13	57	64	-50	39
7	13	96	91	89	-16
9	13	80	82	82	1
11	13	82	76	-74	17
13	13	41	23	-14	-18
15	13	96	99	98	7
17	13	36	30	-2	30
4	14	91	93	-59	72
6	14	112	101	84	55
8	14	139	144	132	-57
10	14	52	57	-9	56
12	14	44	38	-22	31
14	14	92	94	89	-32
16	14	82	78	63	46
18	14	33	29	-17	24
3	15	197	202	-195	-52
5	15	127	129	-128	17
7	15	50	46	34	-31
9	15	81	81	-70	-39
11	15	131	139	-139	-6
13	15	48	47	-36	-31
15	15	26	27	-0	-27
17	15	53	60	-60	3
4	16	71	62	-46	-42
6	16	111	109	107	22
8	16	112	115	101	55
10	16	0	21	-12	-17
12	16	39	10	3	-10
14	16	79	81	67	45
16	16	50	48	46	13
3	17	49	50	-50	-1
5	17	80	77	-17	-75
7	17	112	108	77	75
9	17	52	44	26	36
11	17	86	84	-42	-72
13	17	34	29	4	29
15	17	75	75	58	47
4	18	147	147	-124	-79
6	18	60	65	-58	-30
8	18	43	41	-8	40
10	18	87	86	-71	-48
12	18	119	120	-105	-58
14	18	36	28	-16	23
3	19	62	56	55	10
5	19	46	38	31	22
7	19	113	122	119	27
9	19	104	109	105	27
11	19	12	10	1	10
4	20	93	103	-102	11
6	20	35	31	-30	6
8	20	31	42	21	-36
10	20	58	60	-59	6
3	21	77	76	-69	-31
5	21	55	54	-49	23
7	21	45	50	49	-11
9	21	29	19	-1	-18
4	22	25	16	-15	-7
6	22	80	89	85	25

ℓ= 3

H	K	FOBS	FCAL	A	B
4	3	92	65	64	9
6	3	239	230	230	8
8	3	174	169	-166	-27
10	3	56	56	-56	-4
12	3	219	232	229	34
14	3	60	51	-49	-16
16	3	144	153	-150	-31
18	3	137	133	130	27
20	3	56	51	49	13
22	3	110	103	-98	-29
5	4	171	151	149	-18
7	4	0	6	-5	-2
9	4	120	121	-120	-13
11	4	159	155	155	6
13	4	104	101	100	18
15	4	122	122	-120	-20
17	4	30	20	20	-5
19	4	132	127	122	34
21	4	36	23	-23	-0
4	5	318	314	312	32
6	5	73	69	-69	-4
8	5	83	78	-76	16
10	5	168	168	166	25
12	5	90	87	84	21
14	5	44	34	-33	7
16	5	0	6	5	-3
18	5	81	74	72	16
20	5	54	44	39	20
22	5	15	15	-12	-9
5	6	170	160	-158	-25
*7	6	417	429	-423	-74
9	6	55	32	-22	-22
11	6	36	15	-15	-7
13	6	195	204	-199	-43
15	6	117	110	-103	-39
17	6	63	60	-56	-21
19	6	76	69	-68	-15
21	6	44	51	-45	-22
*4	7	509	551	543	94
6	7	105	93	90	20
8	7	140	131	131	4
10	7	340	363	357	68
12	7	206	202	195	54
14	7	90	96	95	12
16	7	150	149	145	34
18	7	160	159	149	54
20	7	127	125	119	38
5	8	185	173	-173	-5
7	8	320	327	-320	-69
9	8	254	266	-260	-54
11	8	79	74	-74	2
13	8	140	135	-130	-35
15	8	229	240	-231	-67
17	8	107	115	-112	-26
19	8	39	34	-31	-12
21	8	125	122	-112	-46
4	9	220	214	208	50
6	9	258	270	268	35
8	9	0	9	5	-6
10	9	101	96	92	26
12	9	263	281	275	58
14	9	37	40	40	2
16	9	52	25	-25	-3
18	9	153	176	169	49
20	9	105	104	100	29
5	10	75	65	65	0
7	10	67	57	-53	-21
9	10	145	149	-146	-29
11	10	70	74	73	11
13	10	59	57	57	4
15	10	143	144	-140	-33
17	10	21	18	-16	-7
19	10	95	93	89	24
4	11	102	99	98	15
6	11	54	50	-49	-13
8	11	118	114	-113	-4
10	11	31	36	36	7
12	11	64	60	59	13
14	11	56	67	-66	-7
16	11	64	53	-50	-17
18	11	37	39	39	8
20	11	27	16	16	8
5	12	40	30	29	-5
7	12	162	167	-164	-28
9	12	75	71	71	5
11	12	77	77	76	10
13	12	51	49	-48	-9
15	12	22	20	-17	-10
17	12	27	14	14	-4
19	12	28	20	17	10
4	13	241	260	255	52
6	13	36	54	-53	-7
8	13	0	6	3	-5
10	13	178	187	184	36
12	13	72	67	63	24
14	13	15	3	-3	-1
16	13	75	69	68	11
18	13	61	63	57	27
5	14	94	96	-95	-4
7	14	228	242	-234	-62
9	14	131	135	-126	-41
11	14	45	42	-41	[illegible]
13	14	114	107	-104	[illegible]
15	14	152	156	-147	-52
17	14	67	75	-72	[illegible]
4	15	206	216	205	[illegible]
6	15	215	225	221	[illegible]
8	15	69	63	63	4
10	15	132	134	126	46
12	15	231	243	239	46
14	15	65	67	66	11
16	15	33	35	32	13
5	16	50	51	-47	-21
7	16	120	131	-124	-44
9	16	187	145	-138	[illegible]
11	16	44	32	-31	-10
13	16	34	23	-21	-13
15	16	165	179	-170	[illegible]
4	17	98	115	112	26
6	17	44	52	51	[illegible]
8	17	16	21	-18	11
10	17	62	66	63	19
12	17	104	110	105	[illegible]
14	17	23	10	-2	10
5	18	16	26	26	-2
7	18	90	103	-101	-21
9	18	56	40	45	7
11	18	43	53	52	[illegible]
13	18	22	25	-24	[illegible]
4	19	95	103	[illegible]	[illegible]
6	19	94	93	[illegible]	[illegible]
8	19	60	58	-13	[illegible]
10	19	73	71	69	17
12	19	10	4	-1	4
5	20	0	15	7	14
7	20	95	94	-89	-30
9	20	16	17	-14	[illegible]
11	20	41	35	30	24
4	21	110	106	98	[illegible]
6	21	96	92	89	22
8	21	15	3	7	[illegible]
5	22	59	54	-49	-23

ℓ= 4

H	K	FOBS	FCAL	A	B
*4	4	600	655	-652	58
8	4	216	212	-162	-136
12	4	243	249	-249	-15
16	4	146	144	-144	-11
20	4	141	158	-131	-86
6	6	152	157	-156	-17
10	6	65	61	-59	-13
14	6	25	15	-6	-14
18	6	130	141	-139	-25
8	8	155	155	78	133
12	8	97	88	-62	-62
16	8	58	44	42	-12
20	8	48	46	-40	22
6	10	70	58	-57	-10
10	10	251	262	-261	-27
14	10	69	73	-50	-53
18	10	119	121	-118	-25
8	12	90	87	-66	-57
12	12	249	257	-254	-40
16	12	30	36	-36	-7
6	14	33	30	8	-24
10	14	90	85	-55	-65
14	14	64	58	14	56
8	16	58	37	37	-6
12	16	46	41	-39	-13
16	16	23	9	-6	5
6	18	124	131	-128	-24
10	18	120	126	-124	-21
8	20	55	48	-39	27

ℓ= 5

H	K	FOBS	FCAL	A	B
10	5	109	105	40	97
20	5	46	49	30	-38
15	10	70	73	-52	-52
10	15	164	173	170	31

ℓ= 6

H	K	FOBS	FCAL	A	B
6	6	306	323	321	39
8	6	164	178	175	32
12	6	92	92	92	8
16	6	36	36	33	12
18	6	45	43	43	3
20	6	35	29	28	2
10	8	98	98	97	14
14	8	164	169	154	64
18	8	20	19	17	-2
9	9	86	83	83	5
15	9	99	97	95	21
8	10	92	96	95	7
12	10	142	145	-142	-30
16	10	65	86	84	19
10	12	141	144	-141	-30
12	12	34	24	-25	-14
14	12	35	23	19	-13
18	12	32	36	-35	-14
8	14	166	171	153	77
12	14	41	27	27	-0
16	14	85	95	91	29
9	15	0	11	-6	-4
15	15	0	23	21	7
10	16	89	89	87	16
14	16	88	89	84	29
8	18	37	21	18	-11
12	18	37	33	-29	-15

ℓ= 7

H	K	FOBS	FCAL	A	B
14	7	71	74	-44	-59

ℓ= 8

H	K	FOBS	FCAL	A	B
8	8	283	304	292	-84
16	8	168	174	156	77
12	12	77	69	-57	-36

ℓ= 9

H	K	FOBS	FCAL	A	B
12	9	144	148	144	35
18	9	97	94	90	24
15	12	53	57	52	21
12	15	147	148	140	48

ℓ= 10

H	K	FOBS	FCAL	A	B
10	10	183	162	-160	-30

ℓ= 12

H	K	FOBS	FCAL	A	B
12	12	95	97	-93	-28

mined whether for the model presented the recorded *hkl* should have been $\bar{h}\bar{k}\bar{l}$, or, alternatively, whether for the indices recorded the correct model should have been the center related one. To test the compatibility of the model and the indexing two new least-squares refinements were kindly carried out for us by Dr Arthur Sleight, one refinement with $\Delta f''$ and the other with $-\Delta f''$. This change of sign is equivalent to changing the signs of the indices or of changing the signs of all the position parameters in so far as the magnitudes of the structure factors are concerned. The results made it clear that our original assignment was correct. Using $\Delta f''$, R dropped to 69%, whereas with $-\Delta f''$ the lowest value for R was 85%. In addition, all the errors were larger with the changed signs of $\Delta f''$. The large values for $\Delta f''$ for Re (7·34) and for La (2·86) made it fairly easy to resolve the issue. Certainly the difference in R was more pronounced than for some cases already reported (Hamilton, 1965; Veki, Zalkin & Templeton, 1966; Zalkin, Hopkins & Templeton, 1966).

Since the structure belongs to the non-polar class 23, the anomalous atoms should not be misplaced relative to the others in the case of the refinement to the false minimum (Cruickshank & McDonald, 1967). Though there were differences in the final atomic positions for the two refinements, these differences were indeed small; all were less than their corresponding standard deviations. (Since 23 is an enantiomorphous class, the refinement with $-\Delta f''$ corresponds to the opposite absolute configuration to the true structure.)

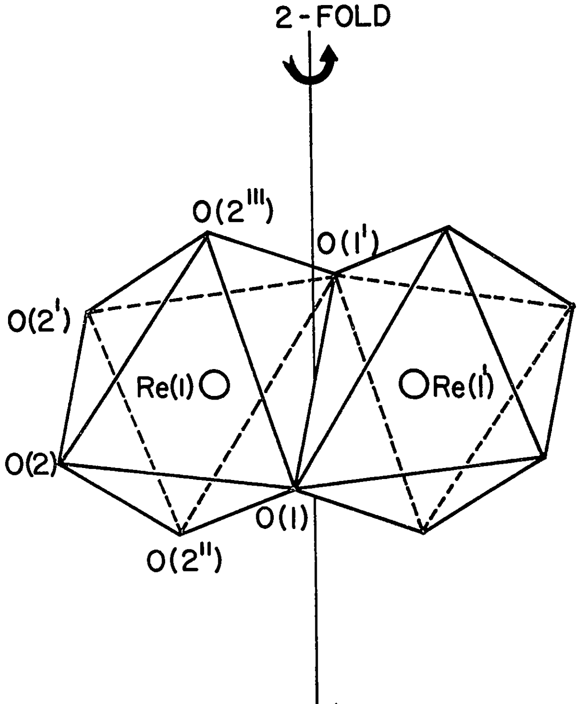

Fig. 1. Pair of edge sharing ReO_6 octahedra.

Discussion

A basic feature of the structure of $La_4Re_6O_{19}$ is the highly symmetric three-dimensional network of ReO_6 octahedra. The octahedra occur in edge-shared pairs; one such pair is shown in Fig. 1. These octahedra are quite distorted, as indicated by the distances and angles listed in Table 3. The rhenium atoms in the pairs are only 2·42 Å apart, which is appreciably closer than the distance in rhenium metal (about 2·75 Å), and is intermediate between the very short (2·24 Å) distance found in the $[Re_2Cl_8]^{2-}$ ion and the average Re–Re distance of 2·48 Å found in Re_3Cl_9 groups in Re(III) compounds derived from rhenium(III) chloride and in rhenium(III) chloride itself (Cotton & Harris, 1965).[*] Despite this

Table 3. *Interatomic distances and angles*[*]

Re–Re (in edge-shared octahedra)	2·415 (1) Å
	3·522 (1)
La–La (in La_4O tetrahedra)	4·084 (2)
	5·070 (1)
Re–La	3·403 (1)
Rhenium coordination (Fig. 1)	
Re—O(1), O(1′)	2·007 (10) Å
Re—O(2), O(2′)	1·979 (9)
Re—O(2″), O(2‴)	1·987 (10)
O(1)–O(1′)	3·207 (26)
O(2)–O(2′)	2·903 (22)
O(1)–O(2); O(1′)–O(2′)	2·581 (9)
O(1)–O(2‴); O(1′)–O(2″)	2·781 (11)
O(1)–O(2″); O(1′)–O(2‴)	3·040 (13)
O(2)–O(2‴); O(2′)–O(2″)	2·738 (5)
O(2)–O(2″); O(2′)–O(2‴)	2·647 (3)
O(1)—Re–O(1′)	106·0 (4)°
O(2)—Re–O(2′)	93·9 (6)
O(1)—Re–O(2); O(1′)–Re–O(2′)	80·5 (4)
O(1)—Re–O(2‴); O(1′)–Re–O(2″)	88·5 (3)
O(1)—Re–O(2″); O(1′)–Re–O(2‴)	99·4 (3)
O(2)—Re–O(2‴); O(2′)–Re–O(2″)	87·3 (2)
O(2)—Re–O(2″); O(2′)–Re–O(2‴)	83·8 (2)
O(2″)–Re–O(2‴)	167·0 (6)
O(1)—Re–O(2′); O(1′)–Re–O(2)	170·6 (3)
Lanthanum coordination (Fig. 3)	
La–O(1) O(1″) O(1‴)	2·515 (7) Å
La–O(2) O(2^{iv}) O(2^{v})	2·601 (9)
La–O(2‴) O(2^{vi}) O(2^{vii})	2·882 (10)
La–O(3)	2·501 (1)
O(1)—O(2); O(1″)–O(2^{v}); O(1‴)–O(2^{iv})	2·581 (9)
O(1)—O(2‴); O(1″)–O(2^{vii}); O(1‴)–O(2^{vi})	2·781 (11)
O(1)—O(2^{v}); O(1″)–O(2^{iv}); O(1‴)–O(2)	3·113 (11)
O(2)—O(2‴); O(2^{iv})–O(2^{vi}); O(2^{v})—O(2^{vii})	2·738 (5)
O(2‴)–O(2^{vi}); O(2^{vi})–O(2^{vii}); O(2^{vii})–O(2‴)	3·716 (20)
O(2)—O(2^{vi}); O(2‴)–O(2^{v}); O(2^{iv})–O(2^{vii})	2·647 (3)
O(3)—O(1); O(1″); O(1‴)	2·913 (13)

[*] Calculated using the program of Busing, Martin & Levy (1964). Parenthesized quantities are standard deviations.

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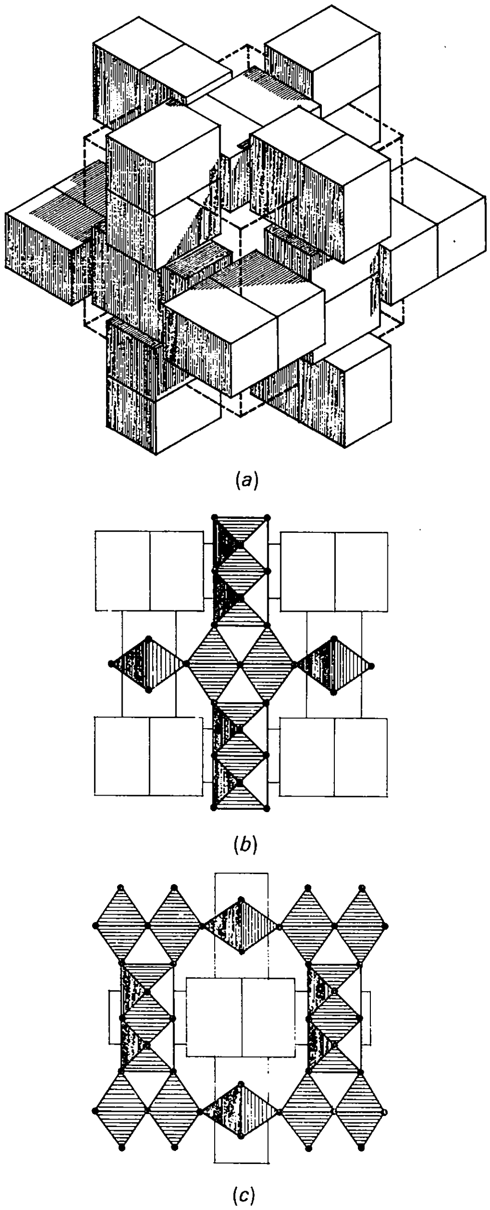
[*] An Re–Re distance of 2·48 Å is also reported by Magnéli (1957) in the monoclinic modification of ReO_2. The accuracy of this value is not known, however, since the Re positions were simply assumed to be the same as the Mo positions in the corresponding modification of MoO_2. For the Re–Re distance in orthorhombic ReO_2, Magnéli (1957) reports a value of 2·61 Å. In this case the Re positions were determined from Harker lines only, and again no estimate of accuracy is given.

close Re–Re approach, the distortion of the octahedra results in nearly equal Re–O distances.

A representation of the three-dimensional network is shown in Fig. 2. In part (*a*), to emphasize the pattern of this network the octahedra have been replaced by rectangular parallelepipeds. The unit cell is outlined in broken lines. In part (*b*), the octahedra of the front (and back) face are shown. In part (*c*), the octahedra of the center section are shown. Large openings in the network of ReO_6 octahedra are clearly revealed at the corners and body center of the cell. This same type of network has been reported for a high temperature form of $KSbO_3$ (Spiegelberg, 1940) and in $KBiO_3$ (Zemann, 1950). These structures were determined from powder data, and the regularity of the octahedra is unknown.


(*a*)

(*b*)

(*c*)

Fig. 2. Representation of rhenium–oxygen network. In part (*a*) the three-dimensional network is shown with parallelepipeds representing inscribed octahedra. The unit cell is outlined with broken lines. In (*b*) the front (and back) section is shown as connected octahedra. In (*c*) the center section is shown.

In the holes in the network there are tetrahedral La_4O groups. Each group is a perfect tetrahedron of lanthanums with an oxygen at its center. The lanthanum–oxygen distance is 2·501 ± 10 Å and the lanthanum–lanthanum distance is 4·084 ± 2 Å. Since the tetrahedra surround lattice points, the tetrahedra are identical and have the same orientation.

The lanthanum environment is a modification of the seven-coordination found in lanthanum sesquioxide (Pauling, 1928; Koehler & Wollan, 1953). In $La_4Re_6O_{19}$, the sevenfold coordination is modified to add three additional oxygens so that the coordination is tenfold. An alternative description would be to say that the coordination polyhedron is a trigonal prism capped on four faces but not on one of the triangular faces. The lanthanum–oxygen bond distances are listed in Table 3, and the lanthanum coordination polyhedron is shown in Fig. 3.

The formal oxidation number for rhenium in $La_4Re_6O_{19}$ is $4\frac{1}{3}$. This suggested the possibility of interesting magnetic and electrical properties. These properties have in fact been studied and will be reported elsewhere, together with a detailed structure determination done from powder data, by Drs J. M. Longo and A. W. Sleight. This structure determination (Sleight & Longo, 1967) was carried out independently but agrees well with our single crystal results.

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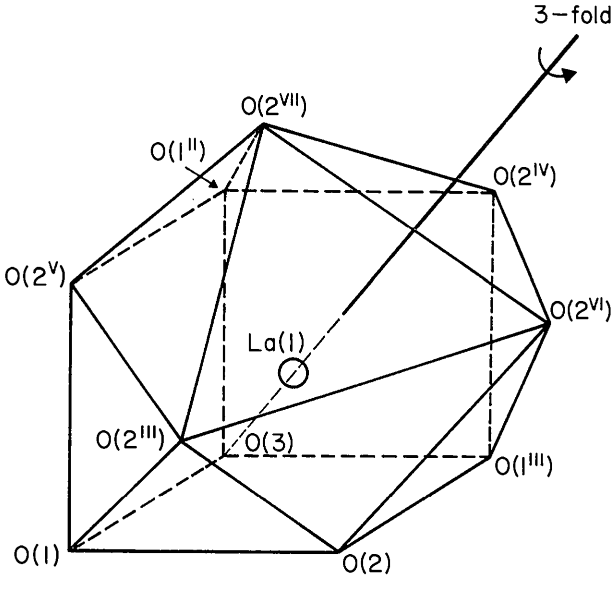

Fig. 3. Lanthanum environment.

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The Conformation of Non-Aromatic Ring Compounds XLVI.*
The Crystal and Molecular Structure of 2,2′-Dichlorotrimethylene Sulphite

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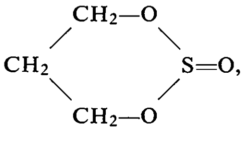
2,2′-Dichlorotrimethylene sulphite crystallizes in the form of monoclinic crystals with space group $P2_1$ and $Z=2$. The unit cell dimensions are $a=6{\cdot}173$, $b=6{\cdot}500$, $c=8{\cdot}986$ Å and $\beta=104{\cdot}7°$, at 20°C. The diffraction data were collected at room temperature with a diffractometer using Mo $K\alpha$ radiation. The structure was solved by the heavy-atom technique and refined by the least-squares method, the final R value being 5·0%. The molecule has the chair conformation with the S=O group pointing towards the axial direction. The conformation features are discussed and compared with those of analogous compounds.

Introduction

During the past decade the conformation of cyclic sulphites, notably trimethylene sulphite



TSU,

has been frequently investigated They have been mainly studied in the liquid phase by the application of a number of physical methods such as the infrared technique, nuclear magnetic resonance and electric dipole measurements. The interpretation of the physical properties was, however, difficult and resulted in conflicting conclusions concerning the conformation. The papers of van Woerden & Havinga (1967*a,b*) give details and further references.

Altona, Geise & Romers (1966) determined the crystal structure of TSU at −100°C and proved that in the solid state it has the chair conformation with

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* Part XLV, Altona, Hageman & Havinga, (1968).