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The Crystal Structure of $La_3Ru_3O_{11}$: A New Cubic $KSbO_3$ Derivative Oxide with No Metal–Metal Bonding

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$La_3Ru_3O_{11}$ was prepared by the reaction of La_2O_3, RuO_2, and $NaClO_3$ in a KCl flux under vacuum at 950°C. The crystal structure of this new cubic $KSbO_3$ derivative oxide was determined from single-crystal X-ray diffraction data collected on an automated diffractometer with Mo*Kα* radiation. Principal crystallographic data: Cubic, space group *Pn*3; $a = 9.451(2)$ Å; $V = 844.2$ Å^3; $d_X = 7.049$ g cm^{-3}. Final discrepancy indices $R = 0.036$, $R_w = 0.042$. $La_3Ru_3O_{11}$ is isomorphous with $Bi_3Ru_3O_{11}$, but is notably different in showing no direct bonding between ruthenium atoms; the closest Ru–Ru contact in this new oxide is 2.994(1) Å.

Introduction

Recently two ternary ruthenium oxides were reported which exhibit the first known evidence in oxide systems of metal-to-metal bonding between Ru atoms. $La_4Ru_6O_{19}$ (*1*) and $Bi_3Ru_3O_{11}$ (*2*), despite their dissimilar stoichiometries, adopt closely related structures derived from the cubic $KSbO_3$ structure type. In both compounds the short Ru–Ru distances (2.448 and 2.60 Å, respectively), as well as the displacement of the paired Ru atoms from the centers of their coordination octahedra toward each other, clearly indicate the presence of a bonding interaction.

In the course of our study of compounds in the lanthanide–ruthenium–oxide system, we have synthesized $La_3Ru_3O_{11}$, a third ternary Ru oxide structurally related to $KSbO_3$. Our investigation of the crystal structure of this new compound revealed one surprising difference between it and that of the isomorphous Bi compound: $La_3Ru_3O_{11}$ exhibits a repulsive rather than a bonding interaction between the ruthenium atoms. In this paper we present the details of the $La_3Ru_3O_{11}$ crystal structure along with a structural comparison of ternary transition metal $KSbO_3$ derivative oxides.

Experimental

All starting materials were reagent grade chemicals and, with the exception of La_2O_3, were used without further purification. Lanthanum oxide was roasted in air at 800°C for a few hours, cooled in an inert atmosphere, and weighed quickly to avoid contamination with carbonate or hydroxide.

$La_3Ru_3O_{11}$ was obtained as one product of the reaction of a 1:1 molar mixture of La_2O_3 and RuO_2 with enough $NaClO_3$ to oxidize Ru from the 4^+ to the 4.5^+ oxidation state, using a large molar excess of KCl as a flux. (Hexagonal $La_8Ru_4O_{21}$, described in a previous paper (*3*), was another crystalline product obtained). After being sealed under vacuum in a Vycor tube, the reaction mixture was heated

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at 950°C for 1 day, cooled to 700°C over a 12-hr period, then quenched to room temperature. The solidified KCl flux was removed from the products by leaching with water.

$\mathrm{La_3Ru_3O_{11}}$ was obtained as black cuboctahedral crystals up to 2 mm across. A crystal of dimensions 0.15 × 0.15 × 0.15 mm was mounted for X-ray study.

X-ray Data Collection

All data were collected at room temperature on a Syntex P$\bar{1}$ automated diffractometer using graphite-monochromated Mo$K\alpha$ radiation. The automatic centering and indexing procedures used have been described elsewhere (*4*). Preliminary photographs revealed $m3$ (cubic) Laue symmetry. The systematic absence ($0kl$, $k + l \neq 2n$, etc.) established $Pn3$ (No. 201) as the space group. The principal crystallographic data are as follows: $a = 9.451\,(2)$ Å; $V = 844.18$ Å^3; $d_x = 7.049$ g/cm^{-3} for $Z = 4$ and a formula weight of 895.93.

A total of 630 unique reflections with $5° \leqslant 2\theta \leqslant 70°$ were collected using the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from $2\theta(\mathrm{Mo}K\alpha_1) - 0.8°$ to $2\theta(\mathrm{Mo}K\alpha_2) + 0.8°$. The intensities of three standard reflections measured after every 100 reflections showed no significant variation during data collection. Lorentz and polarization corrections[1] were applied. The crystal was measured with a micrometer eyepiece, and a numerical absorption correction (linear absorption coefficient $\mu = 202.8$ cm^{-1}) was applied to the data. Transmission coefficients ranged from 8.60 to 12.89%.

Solution and Refinement of the Structure

A three-dimensional Patterson function was used to determine the positions of the metal atoms (Ru, La(1) and La(2)). These atoms were used to calculate approximate phases for

TABLE I

POSITIONAL AND THERMAL PARAMETERS[a] WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.09160(7)	0.75[b]	0.25	0.00065(5)	0.00075(5)	0.00073(5)	0.0	0.0	0.0000(1)
La(1)	0.5	0.5	0.5	0.00111(9)	β_{11}	β_{11}	−0.0002(2)	β_{12}	β_{12}
La(2)	0.1129(1)	x	x	0.00112(6)	β_{11}	β_{11}	−0.0004(2)	β_{12}	β_{12}
O(1)	0.6203(7)	0.25	0.25	0.0015(6)	0.0022(6)	0.0016(6)	0.0	0.0	0.0003(11)
O(2)	0.4169(5)	0.7462(6)	0.0397(5)	0.0011(4)	0.0026(4)	0.0011(4)	−0.0003(8)	−0.0011(7)	−0.0007(8)
O(3)	0.3559(5)	x	x	0.0013(9)	β_{11}	β_{11}	−0.0009(21)	β_{12}	β_{12}

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

[b] Entries with no *esd's* are fixed by the symmetry of the space group.

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[1] Computer programs used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, were those of the Enraf–Nonius structure determination package.

a Fourier map, from which the three oxygen atoms were located. The origin of the unit cell was chosen at the $\bar{3}$ special position, which is $\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$ from that used by Abraham *et al.* (*2*) for $Bi_3Ru_3O_{11}$. Three cycles of least-squares refinement of a scale factor, all variable positional parameters, and isotropic temperature factors gave discrepancy indices:

$$R_1 = \sum||F_o| - |F_c||/|F_o| = 0.052,$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.061$$

The function minimized during all least-squares cycles was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor $w = 4F_o^2/\sigma(F_o^2)^2$, with σ determined from counting statistics. Only those 568 reflections with $F_o^2 > 3\sigma(F_o^2)$ were included in the refinements. Scattering factors used were those of Cromer and Waber (*5*) for neutral atoms, and anomalous dispersion corrections (*6*) were included for all atoms.

Five subsequent refinement cycles in which the scale factor, all variable atomic positions, anisotropic temperature factors, and an isotropic extinction correction were varied reduced R_1 to 0.036 and R_2 to 0.042. Final shifts in the parameters were less than 10% of the estimated standard deviations of the individual parameters. The esd of an observation of unit weight was 2.60. The extinction correction was of the form $F^2_{corr} = F_c^2/(1 + sI_0)$, with a final s value of $4.88(6) \times 10^{-7}$. A final Fourier difference map showed no significant residual electron density.

The final atomic parameters listed in Table I were used along with the variance-covariance matrix to calculate the interatomic distances and angles and their *esd*'s reported in Table II. Observed and calculated structure factor amplitudes are listed in Table III.

TABLE II

BOND DISTANCES (Å) AND ANGLES (°) WITH STANDARD DEVIATIONS IN PARENTHESES

Bond Distances	
Ru–O(1)(X2)	1.935(3)
–O(2a)(X2)	1.990(3)
–O(2b)(X2)	2.007(3)
La(1)–O(2)(X6)	2.551(3)
–O(3)(X2)	2.359(5)
La(2)–O(1)(X3)	2.866(3)
–O(2)(X3)	2.665(3)
–O(3)(X3)	2.334(1)
Angles	
O(1)–Ru–O(1)′	78.6(2)
O(1)–Ru–O(2a)	91.1(1)
O(1)–Ru–O(2a)′	92.4(1)
O(1)–Ru–O(2b)	167.5(1)
O(1)–Ru–O(2b)′	88.9(1)
O(2a)–Ru–O(2a)′	175.4(2)
O(2a)–Ru–O(2b)	90.4(2)
O(2b)–Ru–O(2b)′	86.8(2)

Results

$La_3Ru_3O_{11}$ crystallizes in a structure derived from that of cubic $KSbO_3$, which is also adopted by $Bi_3Ru_3O_{11}$ (*2*), $Bi_3GaSb_2O_{11}$ (*7*), and a number of related compounds. The basic structural unit in all $KSbO_3$ derivatives is the $M_{12}O_{36}$ three-dimensional network (M = Ru, Ga, Sb, and other octahedral ions) consisting of edge-sharing pairs of MO_6 octahedra, further linked through their remaining vertices to other M_2O_{10} moieties. The resulting framework is quite open and admits a variety of counter ion configurations. In $KSbO_3$ the interstices of this network are occupied by 12 K^+ ions, although this compound generally shows nonintegral K^+ ion occupancy and is an ionic conductor (*8*). In $La_4Ru_6O_{19}$ (*1*) the interstices contain two tetrahedral La_4O groupings, while in $La_3Ru_3O_{11}$ there is a $La_{12}O_8$ network. The reader is referred to other works (*1*, *2*, *7–9*) for drawings and overall description of $KSbO_3$-type structures; we will confine structural description to the immediate environments of the metal ions.

The unique Ru atom in $La_3Ru_3O_{11}$ has a distorted octahedral coordination geometry, with Ru–O distances varying from 1.935(3) to 2.007(3) Å, and *cis* O–Ru–O angles ranging from 78.6(2) to 92.4(1)°. Two RuO_6 octahedra share an edge to form the $Ru_2O_{10}^{11\,1/3-}$ unit shown in Fig. 1. The group lies on a position

TABLE III

VALUES OF 10*FOBS AND 10*FCALC   LA3 RU3 011

H	K	L	FOBS	FCALC
0	1	3	3640	3486
0	1	5	2467	2627
0	1	7	941	1011
0	1	9	1841	1968
0	1	11	2098	2166
0	1	13	264	191
0	1	15	561	580
0	2	0	331	304
0	2	2	1896	1060
0	2	4	1187	1154
0	2	6	2364	2428
0	2	8	932	945
0	2	10	1155	1202
0	2	14	1094	1146
0	3	1	1063	974
0	3	3	2319	2441
0	3	5	1594	1615
0	3	7	914	916
0	3	9	733	750
0	3	11	1685	1750
0	3	13	519	506
0	4	0	513	439
0	4	2	1971	1905
0	4	4	3298	3355
0	4	6	1023	1011
0	4	8	656	659
0	4	10	244	201
0	4	12	2201	2343
0	4	14	1309	1442
0	5	1	1788	1782
0	5	3	1202	1210
0	5	5	355	327
0	5	7	1042	1043
0	5	9	2027	2016
0	5	13	207	153
0	6	0	3128	3271
0	6	2	2742	2799
0	6	4	710	665
0	6	6	3813	3984
0	6	8	1314	1327
0	6	10	1285	1293
0	6	12	468	435
0	6	14	2490	2531
0	7	1	204	119
0	7	3	3758	3799
0	7	5	2410	2385
0	7	7	1156	1111

H	K	L	FOBS	FCALC
0	7	9	1674	1673
0	7	11	2512	2612
0	7	13	246	228
0	8	0	4235	4499
0	8	2	1067	1090
0	8	4	450	419
0	8	6	1172	1083
0	8	8	2717	2754
0	8	10	1505	1530
0	8	12	826	838
0	9	1	842	829
0	9	3	915	886
0	9	7	985	925
0	9	9	625	637
0	10	0	1137	1162
0	10	2	885	831
0	10	4	402	289
0	10	6	1174	1122
0	10	8	1674	1720
0	10	10	1001	1039
0	11	1	1451	1503
0	11	3	452	424
0	11	7	1644	1567
0	11	9	1105	1130
0	12	0	1761	1790
0	12	2	368	316
0	12	4	2618	2634
0	12	6	419	445
0	12	8	1125	1123
0	13	1	781	763
0	13	3	1859	1835
0	13	5	1140	1086
0	13	7	409	325
0	14	0	1874	1919
0	14	2	905	863
0	14	4	1540	1532
0	14	6	2455	2404
0	15	1	936	979
1	1	1	428	368
1	2	1	437	413
1	2	2	2250	2198
1	2	3	2128	2175
1	2	4	909	851
1	2	5	1176	1147
1	2	6	1783	1751
1	2	7	265	253
1	2	8	1045	1008

H	K	L	FOBS	FCALC
1	2	9	1310	1315
1	2	10	1021	1045
1	2	11	908	951
1	2	12	1068	1108
1	2	14	548	548
1	2	15	578	610
1	3	1	2411	2449
1	3	2	1321	1273
1	3	3	1224	1164
1	3	4	362	295
1	3	5	457	417
1	3	6	2691	2743
1	3	7	1407	1362
1	3	8	2215	2212
1	3	9	1861	1924
1	3	11	978	1023
1	3	12	875	862
1	3	14	1621	1685
1	4	1	1249	1197
1	4	2	867	841
1	4	3	3469	3553
1	4	4	230	200
1	4	5	1784	1729
1	4	6	620	590
1	4	7	1472	1425
1	4	8	231	195
1	4	9	1390	1391
1	4	10	327	335
1	4	11	1759	1800
1	4	12	277	272
1	5	1	2712	2835
1	5	2	538	514
1	5	3	404	378
1	5	4	1163	1187
1	5	5	385	342
1	5	6	1524	1459
1	5	7	1608	1526
1	5	8	478	457
1	5	9	2407	2382
1	5	10	669	664
1	5	11	917	913
1	5	12	564	537
1	5	13	269	251
1	5	14	481	483
1	6	1	775	775
1	6	2	1712	1727
1	6	3	179	152

H	K	L	FOBS	FCALC
1	6	4	631	600
1	6	5	781	729
1	6	6	1380	1336
1	6	7	651	587
1	6	8	889	862
1	6	9	360	399
1	6	10	889	858
1	6	11	769	742
1	6	12	876	874
1	6	13	685	690
1	6	14	454	450
1	7	1	1044	1049
1	7	2	193	194
1	7	3	1345	1369
1	7	4	1061	1020
1	7	5	1561	1558
1	7	7	1077	1037
1	7	8	1251	1191
1	7	9	575	550
1	7	10	267	221
1	7	11	656	654
1	7	12	861	858
1	7	13	983	988
1	8	1	1035	1057
1	8	2	1077	1082
1	8	3	314	236
1	8	4	226	214
1	8	6	929	914
1	8	7	868	865
1	8	8	423	381
1	8	9	1152	1127
1	8	10	525	527
1	8	11	326	306
1	8	12	421	421
1	9	1	205	200
1	9	2	862	842
1	9	3	1805	1916
1	9	4	978	1000
1	9	5	2326	2347
1	9	6	1862	1879
1	9	7	559	540
1	9	8	749	709
1	9	9	392	388
1	9	10	400	454
1	9	11	753	712
1	9	12	1330	1366
1	10	2	1049	1066

H	K	L	FOBS	FCALC
1	10	3	2424	2490
1	10	4	316	327
1	10	5	1058	1055
1	10	6	877	857
1	10	7	569	526
1	10	8	582	580
1	10	9	1453	1408
1	10	10	566	576
1	10	11	1383	1379
1	11	1	867	881
1	11	3	1014	1054
1	11	4	1042	1037
1	11	5	945	913
1	11	6	1380	1389
1	11	7	707	691
1	11	8	1006	999
1	11	9	680	666
1	11	10	774	756
1	12	1	1025	1085
1	12	2	1075	1099
1	12	3	811	807
1	12	4	291	271
1	12	6	854	856
1	12	7	1302	1301
1	12	8	437	306
1	13	1	1669	1694
1	13	2	503	491
1	13	4	394	398
1	13	5	320	294
1	13	6	227	164
1	13	7	990	999
1	14	1	299	299
1	14	2	562	549
1	14	3	259	198
1	14	4	253	183
1	14	6	349	414
1	15	1	951	972
1	15	2	676	634
2	2	2	2493	2513
2	3	2	1400	1380
2	3	3	272	249
2	3	4	588	643
2	3	5	1574	1562
2	3	6	1089	1056
2	3	7	1862	1004
2	3	8	866	829
2	3	9	496	474

H	K	L	FOBS	FCALC
2	3	10	730	675
2	3	11	593	613
2	3	12	825	797
2	3	13	1272	1340
2	3	14	410	349
2	4	2	260	256
2	4	3	644	613
2	4	4	3345	3400
2	4	5	751	731
2	4	6	1503	1463
2	4	7	349	278
2	4	8	1802	1755
2	4	9	610	595
2	4	10	777	756
2	4	12	1067	1068
2	4	13	410	413
2	4	14	393	350
2	5	2	2352	2426
2	5	3	1070	1066
2	5	4	755	746
2	5	5	837	815
2	5	6	1930	1949
2	5	7	1000	951
2	5	8	1176	1123
2	5	9	673	589
2	5	10	1210	1197
2	5	12	1154	1155
2	5	13	780	789
2	5	14	612	619
2	6	2	1293	1300
2	6	3	1073	1053
2	6	4	1011	995
2	6	5	1853	1925
2	6	7	358	328
2	6	8	1285	1220
2	6	9	1692	1631
2	6	10	1222	1210
2	6	11	210	156
2	6	12	1578	1558
2	6	13	1267	1277
2	7	2	394	403
2	7	3	728	710
2	7	4	249	264
2	7	6	359	353
2	7	8	490	444
2	7	9	822	769
2	7	11	246	52

H	K	L	FOBS	FCALC
2	7	12	440	409
2	7	13	306	241
2	8	2	714	715
2	8	3	850	854
2	8	4	1716	1737
2	8	5	1126	1124
2	8	6	1309	1310
2	8	7	468	412
2	8	8	1344	1308
2	8	9	1000	959
2	8	12	417	389
2	9	2	2087	2127
2	9	3	167	38
2	9	4	620	618
2	9	5	1146	1138
2	9	6	1655	1673
2	9	7	1202	1157
2	9	8	962	926
2	9	9	204	96
2	9	10	1140	1106
2	9	11	688	701
2	9	12	1051	1006
2	10	2	2164	2198
2	10	3	671	688
2	10	4	753	761
2	10	5	1253	1222
2	10	6	897	907
2	10	7	273	248
2	10	8	300	168
2	10	9	1175	1110
2	10	10	2035	2043
2	10	11	236	148
2	11	2	205	194
2	11	3	421	419
2	11	4	207	62
2	11	5	496	432
2	11	7	1009	971
2	11	8	215	165
2	12	2	774	765
2	12	3	790	786
2	12	4	1314	1300
2	12	5	1156	1141
2	12	6	1417	1408
2	12	7	492	408
2	12	8	509	440
2	12	9	1024	998
2	13	2	1541	1540

H	K	L	FOBS	FCALC
2	13	3	817	795
2	13	4	353	386
2	13	6	1293	1286
2	14	2	989	992
2	14	3	365	331
2	14	4	390	370
2	14	5	625	614
2	15	2	516	507
3	3	3	1710	1695
3	4	3	1006	986
3	4	4	181	80
3	4	5	1757	1790
3	4	6	446	424
3	4	7	849	857
3	4	8	204	172
3	4	9	599	532
3	4	10	233	254
3	4	11	1559	1532
3	4	13	589	443
3	5	3	1901	1971
3	5	4	1132	1134
3	5	5	2282	2307
3	5	6	456	456
3	5	7	850	868
3	5	8	1797	1764
3	5	10	1302	1231
3	5	11	775	763
3	5	12	327	270
3	5	13	1429	1433
3	5	14	1091	1091
3	6	3	397	355
3	6	4	450	429
3	6	5	1453	1473
3	6	6	875	849
3	6	7	2468	2532
3	6	8	629	626
3	6	9	806	800
3	6	10	583	559
3	6	11	279	331
3	6	12	672	659
3	6	13	1520	1535
3	7	3	1186	1208
3	7	4	3208	3449
3	7	5	911	900
3	7	6	414	38
3	7	7	944	905
3	7	9	1202	1156

H	K	L	FOBS	FCALC
3	7	10	2497	2516
3	7	11	902	887
3	7	12	1184	1195
3	7	13	459	472
3	8	3	1586	1614
3	8	5	303	258
3	8	6	636	625
3	8	7	2225	2241
3	8	8	314	232
3	8	9	298	214
3	8	10	441	426
3	8	11	699	608
3	8	12	324	262
3	9	3	447	435
3	9	4	301	965
3	9	6	686	677
3	9	7	1157	1147
3	9	8	239	156
3	9	9	1624	1627
3	9	10	832	815
3	9	11	726	720
3	10	3	199	83
3	10	4	249	258
3	10	5	784	785
3	10	6	571	562
3	10	7	320	350
3	10	8	409	399
3	10	9	501	517
3	10	10	349	330
3	10	11	794	789
3	11	3	750	761
3	11	4	334	304
3	11	5	767	777
3	11	6	743	707
3	11	7	920	920
3	11	8	1697	1635
3	11	9	726	725
3	11	10	326	249
3	12	3	1161	1193
3	12	5	1495	1474
3	12	6	680	659
3	12	7	601	571
3	12	8	237	269
3	13	3	1236	1221
3	13	4	1704	1695
3	13	5	1386	1417
3	13	6	493	470

H	K	L	FOBS	FCALC
3	13	7	492	475
3	14	3	918	935
3	14	5	483	463
4	4	4	3103	3332
4	5	4	213	168
4	5	5	239	230
4	5	6	668	624
4	5	7	1526	1570
4	5	8	332	274
4	5	9	398	378
4	5	10	443	347
4	5	11	360	299
4	5	12	328	311
4	5	13	826	831
4	6	4	790	780
4	6	5	562	572
4	6	6	1657	1652
4	6	7	262	211
4	6	8	1345	1354
4	6	9	400	467
4	6	10	1011	949
4	6	12	231	293
4	6	13	367	369
4	7	5	765	763
4	7	6	197	212
4	7	7	1601	1602
4	7	9	803	809
4	7	11	1195	1159
4	8	4	1408	1439
4	8	5	283	266
4	8	6	1526	1556
4	8	7	223	47
4	8	8	801	774
4	8	9	230	292
4	8	10	1033	1012
4	8	12	1289	1258
4	9	4	245	178
4	9	5	1520	1556
4	9	6	530	457
4	9	7	1323	1348
4	9	8	260	240
4	9	9	230	247
4	9	10	369	344
4	9	11	995	963
4	10	4	3333	3350
4	10	5	396	365
4	10	6	951	1016

H	K	L	FOBS	FCALC
4	10	7	207	141
4	10	8	1049	1006
4	10	9	293	328
4	10	10	1491	1453
4	11	7	2090	2106
4	12	4	502	448
4	12	5	346	285
4	12	6	224	167
4	12	8	1428	1395
4	13	6	334	359
4	14	4	432	423
5	5	5	2706	2815
5	6	5	690	669
5	6	6	1483	1507
5	6	7	1643	1631
5	6	8	889	898
5	6	9	249	137
5	6	10	1002	979
5	6	11	231	92
5	6	12	955	955

H	K	L	FOBS	FCALC
5	6	13	967	967
5	7	5	595	570
5	7	6	465	469
5	7	7	1002	1000
5	7	9	1257	1265
5	7	10	1222	1198
5	7	11	853	828
5	7	12	286	261
5	8	5	665	672
5	8	6	922	913
5	8	7	774	747
5	8	8	527	464
5	8	9	786	792
5	8	10	599	601
5	8	11	804	783
5	8	12	524	503
5	9	5	620	622
5	9	6	1469	1527
5	9	7	1261	1231
5	9	8	701	702

H	K	L	FOBS	FCALC
5	9	9	2073	2093
5	9	10	325	294
5	9	11	712	701
5	10	5	575	591
5	10	6	1005	1011
5	10	7	544	571
5	10	8	623	619
5	10	9	1273	1233
5	10	10	595	626
5	11	5	723	744
5	11	6	304	263
5	11	7	831	813
5	11	8	429	444
5	11	9	746	722
5	12	5	577	603
5	12	6	950	942
5	12	7	575	559
5	12	8	518	492
5	13	5	1775	1812
6	6	6	1210	1222

H	K	L	FOBS	FCALC
6	7	6	411	299
6	7	8	257	302
6	7	9	1565	1552
6	7	10	274	162
6	7	11	1594	1576
6	7	12	361	339
6	8	6	2359	2417
6	8	7	332	354
6	8	8	289	218
6	8	9	777	768
6	8	10	474	463
6	9	6	1373	1380
6	9	7	615	618
6	9	8	792	773
6	9	9	808	798
6	9	10	906	899
6	10	6	252	232
6	10	7	210	156
6	10	8	351	284
6	10	9	964	307

H	K	L	FOBS	FCALC
6	11	6	209	133
6	11	7	550	575
6	12	6	1803	1036
6	12	7	322	319
7	7	7	992	1002
7	8	7	1163	1210
7	8	8	199	59
7	8	9	1073	1054
7	9	7	690	687
7	9	8	655	650
7	9	9	373	340
7	9	10	571	556
7	10	7	716	657
7	10	9	1216	1101
7	11	7	632	597
8	8	8	1566	1539
8	9	8	400	444
8	10	8	1731	1774

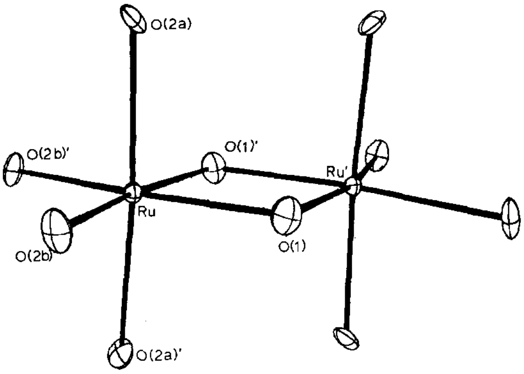

FIG. 1. The $Ru_2O_{10}^{11\,1/3-}$ unit.

of 222 symmetry, with one crystallographic two-fold axis passing through both metal atoms. The two ruthenium atoms of this group are displaced from ideal octahedral geometry away from each other, resulting in an acute O(1)–Ru–O(1)' angle of 78.6°, and the closest approach between Ru atoms is 2.994(1) Å.

Two crystallographically independent lanthanum atoms occupy the cavities in the $Ru_{12}O_{36}$ network; their coordination environments are shown in Fig. 2. La(1) lies on a site of 23 symmetry and is coordinated by an approximate cube of eight oxygen atoms; six of these are at La–O distances of 2.551(3) Å and two more at 2.359(3) Å. Nine-coordinate La(2) lies on a threefold axis, with La–O distances ranging from 2.334(1) to 2.866(3) Å. The O–La–O angles are not particularly unusual and were omitted from Table II in the interest of brevity.

Discussion

In $La_4Re_6O_{19}$ (*9*) the short Re–Re contact (2.415 Å) has been interpreted as denoting a double bond (*10*). The somewhat longer Ru–Ru distances in $La_4Ru_6O_{19}$ (*1*) and $Bi_3Ru_3O_{11}$ (*2*) (2.488 and 2.60 Å, respectively) betoken a substantial bonding interaction, while $Ba_{0.5}IrO_3$ (*11*) but slight, if any, metal–metal bonding ($d_{Ir-Ir} = 2.96$ Å). The trend toward decreasing metal–metal interaction along this series of $KSbO_3$-derived oxides is readily understandable as the result of the increase in nuclear charge going from $Re^{4.33+}$ to $Ru^{4.33+}$ to Ir^{5+}. However, it is not so easy to explain why, among the three oxides $La_4Ru_6O_{19}$, $Bi_3Ru_3O_{11}$ and $La_3Ru_3O_{11}$, all with Ru in the 4.33 formal oxidation state, two compounds should show Ru–Ru bonding while the third does not. Particularly puzzling is the comparison of $Bi_3Ru_3O_{11}$ with $La_3Ru_3O_{11}$, which raises the question of why the isomorphous replacement of Bi^{3+} with La^{3+} should result in such a dramatic change in Ru–Ru separation, from 2.60 to 2.994 Å.

Since neither Bi^{3+} nor La^{3+} is likely to participate in covalent interactions with the ruthenium atoms, the only factors likely to affect the structures are some difference in the over-

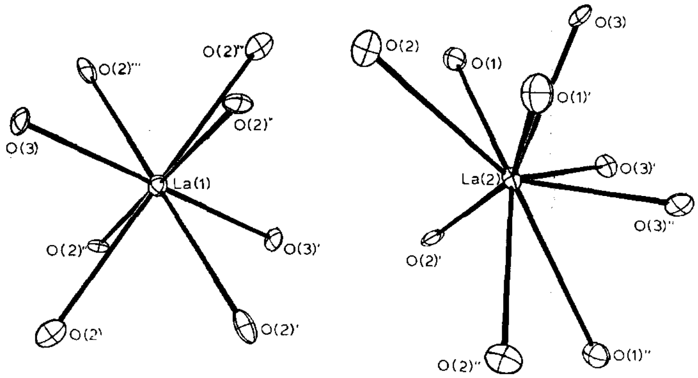

FIG. 2. The La(1) and La(2) coordination environments.

all size or some particular coordination geometry of the tripositive ions. However, a general dilation of the crystal lattice due to ionic size effects does not seem sufficient to explain the drastic increase in Ru–Ru distance observed. The unit cell volume of $Bi_3Ru_3O_{11}$ is fully 10% greater than that of $La_4Ru_6O_{19}$, yet its Ru–Ru distance is only 0.11 Å longer. By contrast, the 5% cell volume increase from $Bi_3Ru_3O_{11}$ to $La_3Ru_3O_{11}$ results in a 0.39 Å increase in d_{Ru-Ru}. Aside from general ionic size differences, the coordination geometries of La^{3+} and Bi^{3+} in the two compounds are roughly similar; if anything, the Bi^{3+} coordination is more regular than that of La^{3+}. Thus the structural differences between $La_3Ru_3O_{11}$ and $Bi_3Ru_3O_{11}$ are apparently not attributable to distortions due to a Bi^{3+} $6s^2$ lone pair effect.

In summary, there does not seem to be any single, simple reason why Ru–Ru bonding should be absent in $La_3Ru_3O_{11}$. We therefore suggest that those Ru–Ru bonds that are found in ruthenium oxides with Ru having oxidation numbers >4 are only barely favored energetically, so that even so subtle a change as the replacement of Bi^{3+} by La^{3+} can disfavor them. Perhaps this low stability is the reason why so few examples of metal–metal bonding have been found in ruthenium oxide systems.

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