JOURNAL OF SOLID STATE CHEMISTRY **24**, 359–365 (1978)

$La_8Ru_4O_{21}$: A Mixed-Valence Ternary Ruthenium Oxide of a New Hexagonal Structure Type

F. A. COTTON* AND C. E. RICE

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received September 19, 1977

Crystals of the title compound were obtained by reaction of La_2O_3, RuO_2, and $NaClO_3$ in a KCl melt at 950°C under vacuum. $La_8Ru_4O_{21}$ forms hexagonal crystals, space group $P6_3cm$; $a = 9.885(2)$, $c = 10.805(2)$ Å; $V = 914.3(5)$ Å^3; $Z = 2$. Single crystal X-ray intensity data were collected on an automated diffractometer using graphite monochromated Mo$K\alpha$ radiation. Using 486 unique reflections ($6° \leq 2\theta \leq 60°$), the structure has been refined to a conventional $R = 0.027$ ($R_w = 0.031$). The significant motif in this new structure is the $Ru_4O_{21}^{24-}$ group with $3m$ symmetry, composed of a central RuO_6 octahedron that shares three mutually *cis* oxygen atoms with adjacent RuO_6 octahedra. The mean ruthenium oxidation number is 4.5, but the averaged Ru–O distances for the two types of ruthenium atom, Ru(1), 1.96 Å and Ru(2), 1.98 Å, provide no support for the assignment of integral oxidation states to individual Ru ions. It is proposed that there is extensive delocalization of $d\pi$ electrons across the bridging oxygen atoms.

Introduction

A limited number of ternary ruthenium oxides containing lanthanide ions have been reported. These include the cubic pyrochlores $Ln_2Ru_2O_7$ (*1–3*) (Ln = Pr–Lu; Y), the orthorhombic perovskite $LaRuO_3$ (*4*) and $La_4Ru_6O_{19}$ (*5*), which is isostructural with $La_4Re_6O_{19}$ (*6*) and has a cubic structure related to $KSbO_3$. However, no lanthanide-rich ternary ruthenium oxides have been made. By contrast, a large number of ternary rhenium oxides with Ln:Re ratio greater than unity are known, several of which exhibit considerable Re–Re bonding. For example, the $Re_2O_8^{8-}$ structural units in $La_4Re_2O_{10}$ (*7*) bear a striking resemblance to the $Re_2Cl_8^{2-}$ ions in $K_2Re_2Cl_8 \cdot 2H_2O$ (*8*), both in configuration and short Re–Re distance (2.259 vs 2.24 Å, respectively). Re and Ru have similar ionic radii in their various oxidation states and in many cases form isomorphous oxides. Therefore we undertook to determine whether some of the lanthanide-rich lanthanide ruthenium oxides might also exhibit strong metal–metal bonding. In our exploration of the lanthanum ruthenium oxide system we have synthesized and determined the crystal structure of $La_8Ru_4O_{21}$, a new mixed-valence oxide crystallizing in a previously unknown type of hexagonal structure. Though this compound contains no direct Ru–Ru bonding, there is evidence to suggest the presence of indirect interactions between the ruthenium cations via oxygen atoms bridging the metals.

Experimental

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

---

* Author to whom correspondence should be addressed.

0022-4596/78/2434-0359$02.00/0
Copyright © 1978 by Academic Press, Inc.
All rights of reproduction in any form reserved.
Printed in Great Britain

Preparation. Ruthenium(IV) oxide (0.100 g), lanthanum(III) oxide (0.245 g), $NaClO_3$ (0.0065 g), and about 3 g of KCl were loaded into a Vycor tube (14-mm diameter × 10 cm long), which was then evacuated and sealed. The reaction tube was heated at 950°C for 2 days, allowed to cool to 700°C over a period of 12 hr, then quenched to room temperature. Excess alkali halide was removed from the reaction mixture by leaching with water.

The product thus obtained was not homogeneous, containing several distinguishable crystalline phases. The compound chosen for this study was present chiefly as thin black hexagonal plates, along with a few approximately hemispherical crystals having one large hexagonal face. Because it was difficult and tedious to separate out enough of this compound for chemical analysis, single-crystal X-ray diffraction was used to identify the phase. Attempts at grinding a spherical crystal were unsuccessful, so one of the hemispherical crystals of approximate diameter 0.18 mm was mounted for X-ray study.

A two-probe resistance measurement on a single crystal of $La_8Ru_4O_{21}$ showed it to be an insulator.

The other crystalline phases obtained from the reaction mixture are now under study.

X-ray data collection. All data were collected at room temperature on a Syntex P$\bar{1}$ automated diffractometer using Mo$K\alpha$ radiation monochromatized with a graphite crystal in the incident beam. The automatic centering and autoindexing procedures have been described elsewhere (*9*). Preliminary photographs revealed $6/mmm$ Laue symmetry. The systematic absence ($h\bar{h}0l$, $l \neq 2n$) indicated $P\bar{6}c2$, $P6_3cm$, and $P6_3/mcm$ as possible space groups. The principal crystallographic data are as follows: $a = 9.885(2)$, $c = 10.805(2)$ Å; $V = 914.3(5)$ Å^3; $d_{calc} = 6.725$ for $Z = 2$ and a formula weight of 1851.55.

A total of 516 unique reflections with $6° \leq 2\theta \leq 60°$ were collected using the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from $2\theta(\text{Mo}K\alpha_1) - 0.8°$ to $2\theta(\text{Mo}K\alpha_2) + 0.8°$. Intensities of three standard reflections measured after every 100 reflections showed no significant variations during data collection. Lorentz and polarization corrections were applied.[1] The crystal was measured with a micrometer eyepiece and a numerical absorption correction (linear absorption coefficient $\mu = 218.06$ cm^{-1}) was applied, with transmission coefficients varying from 10.89 to 23.25%.

Structure solution and refinement were successful only in the non-centrosymmetric space group $P6_3cm$ (no. 185). Patterson methods were used to solve the structure; it was necessary to locate all five crystallographically independent metal atoms, two ruthenium atoms and three lanthanum atoms from the Patterson map in order to phase satisfactorily a Fourier difference map showing the locations of the five independent oxygen atoms. Three subsequent weighted refinement cycles of the scale factor, all variable positional parameters, and isotropic temperature factors reduced the discrepancy factor R_1 ($R_1 = \sum | |F_0| - |F_c| | / |F_0|$) to 0.045 and R_2 ($R_2 = [\sum w(| |F_0| - |F_c| |)^2 / \sum w |F_0|^2]^{1/2}$) to 0.058. Only those 489 reflections with $F_0 > 3\sigma(F_0)$ were included in the refinement. The atomic scattering factors used were those of Cromer and Waber (*10*) for neutral atoms; anomalous dispersion terms (*11*) were included for all atoms. The quantity minimized in all least-squares cycles was $\sum w(|F_0| - |F_0|)^2$, with weights assigned as $w = 4F_0^2/\sigma(F_0^2)^2$, and σ was determined from counting statistics.

Attempts to refine the anisotropic temperature factors of the oxygen atoms were not successful, always resulting in some non-positive definite thermal ellipsoids. This problem is often encountered in oxides whose very heavy metal atoms dominate the X-ray scattering; in this case the difficulty is aggravated

---

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

TABLE I

VALUES OF 10*FOBS AND 10*FCALC

H	K	L	FOBS	FCALC
0	0	2	993	979
0	0	4	1928	1995
0	0	8	3202	3456
0	0	10	2832	2966
0	0	12	1729	1792
0	0	14	2443	2513
0	1	0	260	229
0	1	2	1208	1109
0	1	4	2234	2281
0	1	6	598	609
0	1	8	788	778
0	1	10	1157	1197
0	1	12	673	704
0	1	14	596	631
0	2	0	842	800
0	2	2	2556	2484
0	2	4	1456	1417
0	2	6	1176	1173
0	2	8	733	701
0	2	10	1421	1442
0	2	12	1499	1532
0	3	2	2298	2338
0	3	4	2713	2724
0	3	6	2965	3021
0	3	8	1851	1852
0	3	10	2725	2768
0	3	12	1424	1459
0	3	14	1211	1227
0	4	0	1281	1257
0	4	2	2239	2355
0	4	4	3550	3600
0	4	6	672	621
0	4	8	1664	1640
0	4	10	2104	2052
0	4	12	1006	1000
0	4	14	1014	1021
0	5	0	3647	3676
0	5	2	2055	2046
0	5	4	723	698
0	5	6	2458	2398
0	5	8	2052	2039
0	5	10	1737	1710
0	5	12	2004	1956
0	6	0	2445	2439
0	6	2	2938	3069
0	6	4	2151	2215
0	6	6	1570	1536
0	6	8	2320	2355
0	6	10	1817	1822
0	6	12	1017	961
0	7	0	1291	1300
0	7	2	1750	1757
0	7	4	1384	1400
0	7	6	726	707
0	7	8	1093	1077
0	7	10	405	401
0	7	12	1057	1073
0	8	0	2915	2992
0	8	2	1184	1177
0	8	4	960	938
0	8	6	2037	2014
0	8	8	1608	1572
0	8	10	1566	1547
0	9	0	2456	2453
0	9	2	1806	1847
0	9	4	1271	1276
0	9	6	1958	1956
0	9	8	1851	1847
0	9	10	556	528
0	10	0	288	327
0	10	2	2136	2119
0	10	4	1253	1260
0	10	6	1154	1137
0	10	8	1473	1417
0	11	0	833	806
0	11	2	750	749
0	11	4	533	570
0	12	0	2729	2750
1	1	0	662	656
1	1	1	692	645
1	1	2	2113	2102
1	1	4	365	354
1	1	5	1419	1441
1	1	6	2208	2283
1	1	7	1816	1894
1	1	8	1520	1586
1	1	9	2587	2649
1	1	10	1044	1055
1	1	11	1432	1443
1	1	12	1133	1150
1	1	13	1730	1764
1	1	14	283	270
1	1	15	984	1000
1	2	0	978	982
1	2	1	2430	2432
1	2	2	1500	1485
1	2	3	1216	1178
1	2	4	1455	1444
1	2	5	1631	1643
1	2	6	1771	1737
1	2	7	2125	2112
1	2	8	839	866
1	2	9	1183	1230
1	2	10	247	196
1	2	11	529	496
1	2	12	919	957
1	2	13	1216	1214
1	2	14	1035	1028
1	3	0	1595	1488
1	3	1	1776	1709
1	3	2	878	845
1	3	3	2563	2514
1	3	4	2826	2863
1	3	5	1114	1085
1	3	6	1451	1460
1	3	7	1291	1279
1	3	9	1306	1362
1	3	10	1482	1480
1	3	11	776	790
1	3	12	464	494
1	3	13	1131	1134
1	3	14	987	988
1	4	0	2187	2126
1	4	1	1442	1443
1	4	2	1152	1139
1	4	3	1561	1536
1	4	4	1096	1075
1	4	5	1243	1187
1	4	6	1565	1572
1	4	7	1220	1186
1	4	8	1810	1800
1	4	9	874	841
1	4	10	368	370
1	4	11	853	802
1	4	12	949	932
1	4	13	813	812
1	4	14	961	961
1	5	0	1030	1028
1	5	1	1392	1354
1	5	2	819	826
1	5	3	229	172
1	5	4	742	651
1	5	5	1461	1454
1	5	6	1300	1280
1	5	7	1227	1174
1	5	8	365	364
1	5	9	484	508
1	5	10	436	356
1	5	11	957	1010
1	5	12	619	616
1	5	13	791	816
1	6	0	1995	2005
1	6	1	505	503
1	6	2	738	737
1	6	3	3041	3155
1	6	4	1048	1029
1	6	5	1451	1431
1	6	6	2162	2170
1	6	7	739	718
1	6	8	658	678
1	6	9	1926	1863
1	6	10	438	399
1	6	11	1528	1482
1	6	12	574	566
1	7	0	1338	1340
1	7	1	1308	1317
1	7	2	687	654
1	7	3	371	372
1	7	4	293	289
1	7	5	1297	1293
1	7	6	978	973
1	7	7	769	739
1	7	8	1336	1320
1	7	9	819	772
1	7	10	647	616
1	7	11	915	911
1	8	1	1267	1252
1	8	2	525	538
1	8	3	645	625
1	8	4	2046	2018
1	8	5	1212	1238
1	8	6	524	487
1	8	7	895	896
1	8	8	377	311
1	8	9	849	836
1	8	10	1223	1167
1	9	0	1035	1021
1	9	1	509	549
1	9	2	572	571
1	9	3	1613	1647
1	9	4	1431	1407
1	9	5	365	445
1	9	6	1337	1336
1	9	7	633	685
1	9	9	1167	1132
1	10	1	1015	977
1	10	2	1244	1232
1	10	3	1224	1246
1	10	4	669	664
1	10	5	747	762
1	10	6	958	983
1	10	7	961	938
1	11	0	411	330
1	11	1	832	844
1	11	3	904	933
1	11	4	1107	1095
2	2	1	1170	1300
2	2	2	1860	1771
2	2	3	2131	2174
2	2	4	944	938
2	2	5	1084	1092
2	2	6	1608	1622
2	2	7	1375	1372
2	2	8	1159	1140
2	2	9	1116	1122
2	2	10	1431	1452
2	2	11	569	573
2	2	12	701	775
2	2	13	1414	1456
2	2	14	624	536
2	3	0	593	606
2	3	1	1953	1995
2	3	2	2220	2213
2	3	3	996	978
2	3	4	1060	1040
2	3	5	1258	1228
2	3	6	1060	1056
2	3	7	1508	1470
2	3	8	652	623
2	3	9	646	691
2	3	10	1326	1324
2	3	11	731	713
2	3	12	1516	1529
2	3	13	659	702
2	4	0	1818	1813
2	4	1	1125	1133
2	4	2	640	657
2	4	3	1932	1966
2	4	4	1532	1470
2	4	5	1024	1005
2	4	6	2066	2037
2	4	7	1368	1346
2	4	8	923	941
2	4	9	1439	1438
2	4	10	526	534
2	4	11	873	878
2	4	12	426	427
2	4	13	1178	1100
2	5	0	1620	1614
2	5	1	2061	2063
2	5	2	1467	1497
2	5	3	361	377
2	5	4	1991	2000
2	5	5	1762	1742
2	5	6	336	324
2	5	7	1646	1623
2	5	8	1088	1068
2	5	10	2052	1986
2	5	11	1257	1224
2	5	12	641	659
2	5	13	953	961
2	6	0	455	419
2	6	1	1117	1109
2	6	2	1111	1131
2	6	3	328	391
2	6	4	243	157
2	6	5	931	968
2	6	6	927	918
2	6	7	895	868
2	6	8	650	612
2	6	9	695	690
2	6	10	688	642
2	6	11	543	498
2	6	12	770	751
2	7	0	1308	1254
2	7	1	302	262
2	7	2	813	860
2	7	3	2260	2267
2	7	4	848	818
2	7	5	671	665
2	7	6	1558	1545
2	7	7	595	600
2	7	8	334	284
2	7	9	1471	1412
2	7	11	721	671
2	8	0	1479	1540
2	8	1	577	565
2	8	2	1043	1058
2	8	3	628	627
2	8	4	1373	1378
2	8	5	488	431
2	8	7	483	474
2	8	8	818	740
2	8	9	804	699
2	9	0	1041	970
2	9	1	1608	1578
2	9	2	832	838
2	9	3	425	410
2	9	4	595	578
2	9	5	987	1019
2	9	6	1094	1080
2	9	7	1333	1288
2	9	8	906	888
2	10	0	472	454
2	10	1	971	940
2	10	2	1477	1454
2	10	4	959	922
2	10	5	910	935
3	3	0	2019	2128
3	3	1	2294	2275
3	3	2	2869	3185
3	3	3	895	844
3	3	4	2254	2281
3	3	5	1461	1505
3	3	6	1231	1195
3	3	7	1770	1767
3	3	8	2138	2188
3	3	9	1271	1338
3	3	10	2248	2217
3	3	11	616	569
3	3	12	763	734
3	3	13	996	1027
3	4	0	680	703
3	4	1	923	907
3	4	2	986	1013
3	4	3	877	864
3	4	4	1736	1750
3	4	5	519	563
3	4	6	1115	1095
3	4	7	1123	1120
3	4	8	657	693
3	4	9	719	750
3	4	10	756	750
3	4	11	411	365
3	4	12	471	447
3	4	13	761	795
3	5	0	2265	2354
3	5	1	437	390
3	5	2	1231	1258
3	5	4	727	716
3	5	6	1324	1288
3	5	7	400	354
3	5	8	728	662
3	5	9	362	236
3	5	10	1209	1165
3	5	12	1392	1399
3	6	0	1247	1266
3	6	1	1732	1728
3	6	2	2499	2634
3	6	3	563	554
3	6	4	1326	1306
3	6	5	1048	1015
3	6	6	1359	1290
3	6	7	1709	1671
3	6	8	2285	2190
3	6	9	1148	1098
3	6	10	1106	1064
3	7	0	753	715
3	7	1	1436	1432
3	7	2	1772	1842
3	7	3	724	702
3	7	4	1030	1049
3	7	5	1349	1346
3	7	6	1444	1407
3	7	7	1162	1139
3	7	8	1067	998
3	7	9	703	656
3	7	10	693	644
3	8	0	665	609
3	8	1	659	663
3	8	2	615	578
3	8	3	449	446
3	8	4	572	583
3	8	5	434	349
3	8	7	709	695
3	8	8	325	313
3	9	0	1812	1754
3	9	1	485	517
3	9	2	1248	1225
3	9	3	876	837
3	9	4	754	739
3	9	5	604	562
3	9	6	1280	1261
3	10	1	552	511
3	10	2	1280	1251
3	10	3	421	386
4	4	0	1640	1750
4	4	1	1657	1743
4	4	2	1640	1798
4	4	3	839	873
4	4	4	1967	2026
4	4	5	1704	1732
4	4	6	1917	1948
4	4	7	989	964
4	4	8	1920	1941
4	4	9	1176	1174
4	4	10	814	811
4	4	11	1141	1165
4	4	12	1593	1559
4	5	1	803	804
4	5	2	924	936
4	5	3	706	692
4	5	4	2129	2135
4	5	5	345	352
4	5	6	393	379
4	5	7	862	813
4	5	8	690	666
4	5	9	686	621
4	5	10	1176	1155
4	5	11	393	304
4	6	0	1293	1347
4	6	1	790	812
4	6	2	735	762
4	6	3	476	471
4	6	4	1161	1189
4	6	5	536	523
4	6	6	1615	1573
4	6	7	845	805
4	6	8	437	357
4	6	9	497	450
4	6	10	472	360
4	7	0	531	571
4	7	1	1169	1154
4	7	2	1148	1180
4	7	3	692	701
4	7	4	389	423
4	7	5	1357	1370
4	7	6	1336	1302
4	7	7	657	657
4	7	8	1129	1145
4	7	9	873	781
4	8	0	938	881
4	8	1	807	846
4	8	2	1170	1188
4	8	3	294	242
4	8	4	1931	1965
4	8	5	931	934
4	8	6	402	322
4	8	7	565	528
4	9	1	1012	1035
4	9	2	937	951
4	9	4	1905	1925
5	5	0	2273	2410
5	5	1	1242	1303
5	5	2	1321	1375
5	5	4	1848	1874
5	5	5	1206	1178
5	5	6	861	871
5	5	7	1054	1047
5	5	8	1343	1324
5	5	10	1826	1874
5	6	1	903	966
5	6	2	1100	1090
5	6	3	879	918
5	6	5	810	774
5	6	6	588	614
5	6	7	975	950
5	6	8	978	955
5	6	9	905	849
5	7	0	533	539
5	7	1	720	745
5	7	2	1233	1209
5	7	3	454	436
5	7	4	856	860
5	7	5	745	795
5	7	6	588	552
5	7	7	648	629
5	8	0	2433	2423
5	8	1	339	298
5	8	3	595	555
5	8	4	347	402
5	8	5	418	358
6	6	0	538	550
6	6	1	689	719
6	6	2	2049	2015
6	6	3	1644	1801
6	6	4	1229	1278
6	6	5	845	805
6	6	6	1023	1016
6	6	7	497	530
6	7	0	487	514
6	7	1	834	867
6	7	2	910	875
6	7	3	480	535
6	7	4	752	761
6	7	5	1189	1204

by the necessarily approximate nature of the absorption correction used. Therefore the anisotropic thermal parameters were refined for the metal atoms only. Three cycles of least-squares refinement of the scale factor, isotropic extinction parameter s ($F_{\text{corr}} = F_c/(1 + sI_c)$), all variable positional parameters and thermal parameters produced $R_1 = 0.031$, and $R_2 = 0.033$. Three reflections (006, 030, and 113) were very strongly affected by extinction and were given zero weight, giving $R_1 = 0.028$ and $R_2 = 0.032$. Changing the enantiomorphic specification by reversing the signs of the imaginary anomalous dispersion terms further reduced R_1 to 0.027 and R_2 to 0.031. Final shifts in the parameters were less than 10% of the estimated standard deviations of the individual parameters. A final difference Fourier synthesis revealed no peaks greater than $2e^-/\text{Å}^3$. The esd of an observation of unit weight was 1.92; the final value of the extinction parameter s was $4.0(1) \times 10^{-7}$. Values of observed and calculated structure factors are listed in Table I. Positional and thermal parameters for the atoms and their esd's (estimated standard deviations) are shown in Table II. These atomic positions along with the variance–covariance matrix were used to calculate the interatomic distances and angles listed in Table III.

Results

The structure of $La_8Ru_4O_{21}$ is shown in projection on the a–b plane in Fig. 1; a perspective drawing emphasizing the linkages of the ruthenium coordination octahedra is shown in Fig. 2. The structure can be described in terms of discrete assemblies of four RuO_6 octahedra linked by corners to form $Ru_4O_{21}^{24-}$ units, with lanthanum ions coordinated between these clusters.

The main structural motif of this compound, the $Ru_4O_{21}^{24-}$ cluster, is shown in detail in Fig. 3. The cluster has $3m(C_{3v})$ symmetry and contains a unique Ru(1) atom on a site of $3\,m$ symmetry and three equivalent Ru(2) atoms lying on mirror planes. Both kinds of ruthenium atoms are surrounded by octahedra of oxygen atoms with Ru–O distances ranging from 1.92(1) to 2.03(1) Å, and *cis*-O–Ru–O angles from 84.4(3) to 99.8(3)°. The average Ru–O distances for Ru(1) and Ru(2) are approximately the same (1.96 and 1.98 Å, respectively). The O(1) atoms form bridges between the ruthenium atoms so that Ru(1)

TABLE II

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La(1)	0.3333[b]	0.6667	0.3831(1)	0.00158(11)	0.00158	0.00127(8)	0.0016	0.0	0.0
La(2)	0.2420(1)	0.0	0.2321(1)	0.00207(8)	0.00147(9)	0.00190(6)	0.0015	–0.0017(2)	0.0
La(3)	0.6028(1)	0.0	0.0930(1)	0.00192(8)	0.00269(9)	0.00097(6)	0.0027	–0.0007(2)	0.0
Ru(1)	0.0	0.0	0.0	0.0010(2)	0.0010	0.00049(16)	0.0010	0.0	0.0
Ru(2)	0.6449(1)	0.0	0.4017(1)	0.0011(1)	0.0014(1)	0.00067(7)	0.0014	0.0001(2)	0.0
O(1)	0.8404(13)	0.0	0.3854(13)	0.7(2)[c]					
O(2)	0.8457(13)	0.0	0.1081(13)	0.7(2)					
O(3)	0.4364(8)	0.2730(9)	0.2700(8)	0.3(1)					
O(4)	0.5461(10)	0.7019(9)	0.0348(9)	0.9(1)					
O(5)	0.4415(13)	0.0	0.3754(13)	0.5(2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 - \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Numbers in parentheses are estimated standard deviations in the last significant digits.

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

[c] Isotropic B's.

TABLE III

INTERATOMIC DISTANCES AND ANGLES

Distances (Å)		Angles (deg)	
Ru(1)–O(1)(×3)	2.01(1)	O(1)–Ru(1)–O(1)′	85.9(4)
–O(2)(×3)	1.92(1)	O(1)–Ru(1)–O(2)	179.3(5)
Ru(2)–O(1)	1.94(1)	O(1)–Ru(1)–O(2)′	93.6(3)
–O(3)(×2)	2.00(1)	O(2)–Ru(1)–O(2)′	86.9(4)
–O(4)(×2)	1.97(1)	O(1)–Ru(2)–O(3)	86.2(3)
–O(5)	2.03(1)	O(1)–Ru(2)–O(4)	99.8(3)
La(1)–O(3)(×3)	2.382(6)	O(1)–Ru(2)–O(5)	166.8(4)
–O(4)(×3)	2.549(7)	O(3)–Ru(2)–O(3)′	89.0(4)
–O(5)(×3)	2.913(2)	O(3)–Ru(2)–O(4)	92.6(2)
La(2)–O(1)(×2)	2.680(7)	O(3)–Ru(2)–O(5)	84.4(3)
–O(2)(×2)	2.488(6)	O(4)–Ru(2)–O(4)′	85.1(4)
–O(3)(×2)	2.441(6)	O(4)–Ru(2)–O(5)	89.9(3)
–O(4)(×2)	2.842(7)		
–O(5)	2.508(10)	Ru(1)–O(1)–Ru(2)	136.7(6)
La(3)–O(2)	2.407(10)		
–O(3)(×2)	2.407(6)		
–O(4)(×2)	2.783(7)		
–O(4)′(×2)	2.683(7)		
–O(5)	2.391(10)		

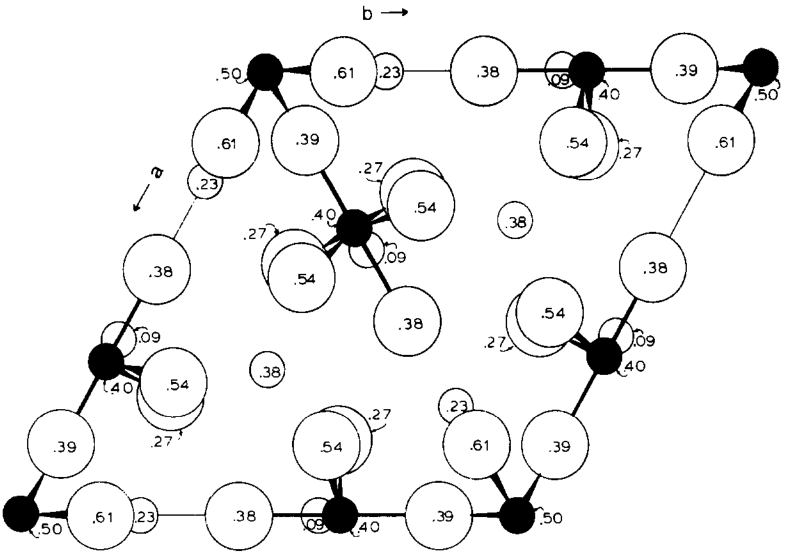

FIG. 1. A projection of the La$_8$Ru$_4$O$_{21}$ structure on the *a–b* plane. Half the atoms in the unit cell are shown. Small open circles: La; small closed circles: Ru; large circles: O atoms. Heights are given as fractions of the *c* axis.

shares three mutually *cis*-oxygen atoms with the Ru(2) atoms. The Ru(1)–O(1)–Ru(2) angle is 136.7(6)°, and the closest approach between ruthenium atoms is 3.67 Å. The two Ru$_4$O$_{21}^{24-}$ clusters in the unit cell are related by the 6_3 symmetry operation, and the shortest Ru–Ru distance between clusters is 5.40 Å.

The three crystallographically distinct lanthanum ions lie between the ruthenium clusters. Two of them (La(2) and La(3))

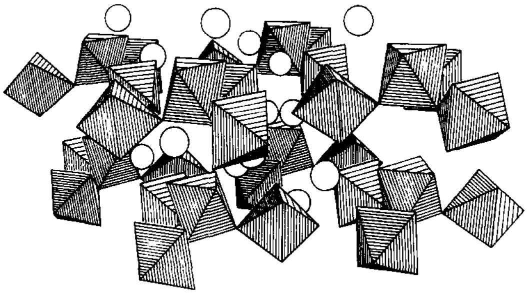

FIG. 2. A perspective view of the $La_8Ru_4O_{21}$ structure, with the *c* axis approximately vertical. The octahedra represent RuO_6 units, the open circles La ions.

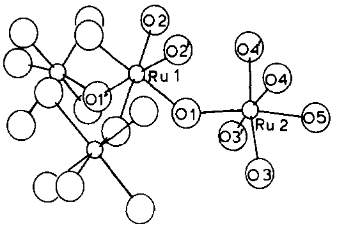

FIG. 3. The $Ru_4O_{21}^{24-}$ structural unit. The threefold axis of the cluster is approximately vertical.

interleave the $Ru(2)O_6$ octahedra along the *a*–*c* faces, while La(1) fills in the tunnels between clusters down the three fold axes along ($\frac{1}{3}$ $\frac{2}{3}$ *z*) and ($\frac{2}{3}$ $\frac{1}{3}$ *z*). The lanthanum coordination geometries are typical of those found in many La oxides and complex oxides; the O–La–O angles are unremarkable and were not listed in Table III in the interest of brevity. La(1), lying on a threefold axis, has six closely coordinated oxygens at distances of 2.382(6) and 2.549(7) Å, and three much longer La–O contacts at 2.913(2) Å; these nine oxygen atoms form a very distorted tricapped trigonal prism. La(2) and La(3) each lie on a mirror plane. La(2) is coordinated by nine oxygen atoms at distances from 2.441(6) to 2.842(7) Å, while La(3) is eight-coordinate with La–O distances from 2.391(10) to 2.783(7) Å.

Discussion

$La_8Ru_4O_{21}$ is the first lanthanide-rich lanthanide ruthenium oxide to be described. Its structure appears to be unprecedented, resembling no other known oxide, halide, or silicate structure; so far as we are aware, even its space group ($P6_3cm$) is but rarely encountered. $La_8Ru_4O_{21}$ is also the first mixed-valence ruthenium oxide found to contain finite groupings of ruthenium atoms rather than an infinitely extended arrangement of joined metal coordination polyhedra.

Assuming that the lanthanum ions are present in their normal tripositive state, the mean oxidation number for the ruthenium atoms in $La_8Ru_4O_{21}$ is 4.5. This nonintegral average oxidation state brings up the question of how charge is distributed among the individual ruthenium atoms. Can we justify an assignment of two different, integral oxidation states for Ru(1) and Ru(2)? Since there are three Ru(2) atoms for every Ru(1), reasonable schemes, i.e., those employing only common oxidation numbers, for assigning integral oxidation states to the metals are few. Indeed, there are only two sets of reasonable oxidation numbers totaling +18: 3(+4) + (+6) and 3(+5) + (+3). However, even these schemes do not appear to pass additional tests of reasonableness. Thus, octahedrally coordinated Ru(VI) does not appear to be previously known in any oxide system, and both possibilities require the unlikely circumstance that two ruthenium atoms that differ by two units in oxidation number be bound to the same oxygen atoms and have the same coordination number.

Some clue as to the relative oxidation states of metal atoms in metal oxides should be provided by the metal–oxygen bond distances. As mentioned before, the average Ru(1)–O and Ru(2)–O distances in $La_8Ru_4O_{21}$ are quite similar, namely, 1.96 and 1.98 Å, respectively. According to Shannon and Prewitt's effective ionic radii (*12*) and Shannon's revised radii (*13*) both of these values are appropriate for oxidation states in the range +4 to +5. It might be argued that the distortions in the ruthenium coordination geometries, with Ru–O distances differing by more than 0.1 Å, are so great as to make judgements based on average distances unreliable. Indeed, Shannon (*13*) has shown that distortions definitely influence the average M–O distance for a metal in a given oxidation state. However, by Shannon's distortion index Δ (*13*) the distortions in the geometries of Ru(1) and Ru(2) are of essentially the same magnitude. Therefore, distortion may be assumed to affect the two sets of Ru–O distances equally and the Ru oxidation states, whatever they are, must be approximately the same. Even though the accuracy of our Ru–O distances (esd's ~ 0.01 Å) would not warrant differentiating between metals differing in oxidation state by one unit, in this case the only possible assignments of integral oxidation numbers require differences of two units. We therefore believe that our data argue against integral oxidation numbers and are better accommodated by postulating some form of charge delocalization.

Since in $La_8Ru_4O_{21}$ the ruthenium atoms are too far separated for direct metal to metal bonding, charge delocalization must be assumed to take place principally by π interactions across the Ru(1)–O(1)–Ru(2) chains. While it should be possible to develop this idea in some detail using a molecular orbital treatment, the low symmetry of the problem makes it unlikely that any firm conclusions could be reached from purely qualitative arguments. Moreover, without data on the magnetism and spectra, a quantitative computation could not be subjected to any cogent test of its validity. For these reasons we do not, at least for the present, plan to examine the electron distribution in more detail.

Acknowledgments

We would like to thank Professor R. A. Walton of Purdue University for experimental help in characterizing this compound. We thank the National Science Foundation for financial support.

References

1. E. F. Bertaut, F. Forrat, and M. C. Montmory, *C. R. Acad. Sci.* **249**, 829 (1959).
2. M. C. Montmory and E. F. Bertaut, *C. R. Acad. Sci.* **252**, 4171 (1961).
3. A. W. Sleight and R. J. Bouchard, *Nat. Bur. Stand. Spec. Publ.* **364**, 227 (1972).
4. R. J. Bouchard and J. F. Weiher, *J. Solid State Chem.* **4**, 80 (1972).
5. F. Abraham, J. Tréhoux, and D. Thomas, *Mater. Res. Bull.* **12**, 43 (1977).
6. N. L. Morrow and L. Katz, *Acta Crystallogr. B* **24**, 1466 (1968).
7. K. Waltersson, *Acta Crystallogr. B* **32**, 1485 (1976).
8. F. A. Cotton and C. B. Harris, *Inorg. Chem.* **4**, 330 (1965).
9. F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.* **50**, 227 (1973).
10. D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. 4, Table 2.2B, Kynoch Press, Birmingham, England (1974).
11. D. T. Cromer, "International Tables for X-ray Crystallography," Vol. IV, Table 2.3.1, Kynoch Press, Birmingham, England (1974).
12. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. B* **25**, 925 (1969).
13. R. D. Shannon, *Acta. Crystallogr. A* **32**, 751 (1976).