Volume 8
Number 1
January 2, 1969

Inorganic Chemistry

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Structure of Tetra-*n*-butyratodiruthenium Chloride, a Compound with a Strong Metal–Metal Bond[1]

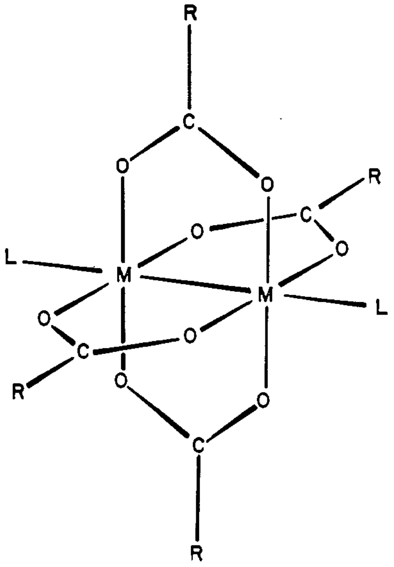
BY M. J. BENNETT, K. G. CAULTON,[2] AND F. A. COTTON

Received July 22, 1968

The crystal and molecular structures of tetra-*n*-butyratodiruthenium chloride, $Ru_2(O_2CC_3H_7)_4Cl$, have been determined using the intensities of 708 independent, statistically significant reflections collected with a counter diffractometer. The compound crystallizes in the tetragonal space group $I\bar{4}2d$ with unit cell dimensions $a = 13.265 \pm 0.005$ Å and $c = 24.453 \pm 0.008$ Å ($\rho_{obsd} = 1.76 \pm 0.03$ g cm^{-3} and $\rho_{calcd} = 1.81$ g cm^{-3} for $Z = 8$). The structure, excluding hydrogen atoms, was solved using Patterson and Fourier methods and refined by full-matrix least-squares methods to a conventional unweighted residual of 7.3%. The compound contains the dinuclear, carboxylate-bridged species $Ru_2(O_2CC_3H_7)_4{}^+$ with a very short Ru–Ru distance of 2.281 Å. This short bond length and the reported presence of three unpaired electrons on the cation may be rationalized in terms of molecular orbital theory. The two ruthenium atoms of a given molecule are equivalent by virtue of a crystallographic twofold axis and therefore, barring disorder, for which we find no evidence, exist in the common, nonintegral oxidation state of +2.5. Chloride ions bridge adjacent dinuclear cations in the crystal to form infinite zigzag chains parallel to the *a* and *b* crystallographic axes.

Introduction

Several transition metals are already known to form binuclear, carboxylato-bridged compounds. The general structure of these molecules is shown as I. Compounds with this type of structure are of interest because they afford examples of homonuclear metal–metal interactions ranging from weak, antiferromagnetic spin–spin couplings to strong, multiple bonds.



I

The structure in its general features demands propinquity of the metal atoms but does not of itself assure or require a bonding interaction between them, as emphasized elsewhere.[3] It is, in fact, precisely this property which makes this type of structure particularly interesting. It establishes a framework within which metal–metal interaction may readily occur, but the nature and extent of the interaction can vary over the widest limits, depending upon the properties of the metal atoms concerned.

The occurrence of the structure has been definitely established by X-ray crystallography for the acetates of copper(II),[4] chromium(II),[5] molybdenum(II),[6] and rhodium(II),[7] in all of which, except $Mo_2(O_2CCH_3)_4$, neutral ligands, L, are present. For the trivalent metal, Re^{III}, the same structure has been found in $Re_2(O_2CC_6H_5)_4Cl_2$,[8] the terminal ligands being Cl^- ions. There are various known homologs, *i.e.*, compounds $M_2(O_2CR)_4L_2$, with other R groups for each of these metals except rhodium, all of which seem certain to have the

---

[1] Research supported by the U. S. Atomic Energy Commission.

[2] National Science Foundation Postdoctoral Fellow, 1967–1969.

[3] F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

[4] J. N. van Niekerk and F. R. L. Schoenig, *Acta Cryst.*, **6**, 227 (1953).

[5] J. N. van Niekerk, F. R. L. Schoenig, and J. F. de Wet, *ibid.*, **6**, 501 (1953).

[6] D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

[7] M. A. Porai-Koshits and A. S. Antschishkina, *Proc. Acad. Sci. USSR, Chem. Sect.*, **146**, 902 (1962).

[8] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

same type of structure. It has been proposed[9] that $V_2(O_2CR)_6$ compounds also have such a structure, with the terminal ligands being O_2CR groups, but X-ray evidence for this has not yet been presented.

On the basis of the structural data for the Cr^{II}, Mo^{II}, Cu^{II}, Rh^{II}, and Re^{III} compounds mentioned, one would tend to believe that for the heavier metals, the formation of metal–metal bonds would be likely to occur within the $M_2(O_2CR)_4L_2$ structure; thus, extremely short M–M distances of 2.11 and 2.222 Å are found for the Mo^{II} and Re^{III} compounds, respectively, and even for Rh^{II} the distance (~2.45 Å) is short enough to imply a significant amount of Rh–Rh bonding.

In view of the above considerations, the synthesis by Stephenson and Wilkinson[10] of compounds with the unusual stoichiometry $Ru_2(O_2CR)_4Cl$ aroused our interest. We naturally considered a structure of type I, but polymeric, to be a likely possibility, as did Stephenson and Wilkinson. Moreover, with 11 electrons to be placed in molecular orbitals of the $Ru_2(O_2CR)_4{}^+$ unit, as compared with eight for $Mo_2(O_2CR)_4$, where a very strong quadruple bond is believed to exist,[3,11] and 14 for $Rh_2(O_2CCH_3)_4(H_2O)_2$, where there is also significant metal–metal bonding, it seemed natural to us that an appreciable degree of Ru–Ru bonding would be expected in the $Ru_2(O_2CR)_4{}^+$ units (assuming, of course, that these dinuclear cations actually do occur in the compounds in question). On the other hand, Stephenson and Wilkinson, noting that several of the compounds possess three unpaired electrons per (dinuclear) molecule, formulated them as Ru^{II}–Ru^{III} species and concluded that "...the metal–metal distance in these systems is large enough to prevent direct orbital overlap."

In order to resolve the uncertainties and differences in viewpoint just discussed and provide a precise structural basis for a discussion of the electronic structure of $Ru_2(O_2CR)_4Cl$ compounds, a single-crystal X-ray structure determination of one of them, namely, the *n*-butyrato compound, $Ru_2(O_2CCH_2CH_2CH_3)_4Cl$, was carried out.

Experimental Section

Tetra-*n*-butyratodiruthenium chloride was prepared according to the method of Stephenson and Wilkinson.[10] Tetragonal-prismatic crystals were grown by slowly cooling a hot, saturated solution of the compound in *n*-butyric acid. *Anal.* Calcd for $Ru_2(O_2CC_3H_7)Cl$: Ru, 34.5; C, 32.8; H, 4.9; Cl, 6.1. Found: Ru, 34.4; C, 33.7; H, 4.8; Cl, 6.0.

Precession photographs (*h0l, h1l, h2l, hk0, hhl*) indicated Laue symmetry 4/mmm. The observed systematic absences, *hkl* for $h + k + l \neq 2n$ and *hhl* for $2h + l \neq 4n$, are compatible with space groups $I4_1$ md and $I\bar{4}2$d. The Patterson function, and in particular the Harker section $z = 0$, was consistent only with $I\bar{4}2$d, and this was taken as the correct space group. The unit cell dimensions, determined by a method previously described[12] with Cu radiation [$\lambda(K\alpha_1)$ 1.5405 Å, $\lambda(K\alpha_2)$ 1.5443 Å] on a General Electric XRD-5 manual diffractometer (24°) are $a = 13.265 \pm 0.005$ Å and $c = 24.453 \pm 0.008$ Å. The uncertainties quoted represent maximum estimated errors based on previous calibrations with NaCl. The observed density, measured by flotation in carbon tetrachloride–iodobenzene, is 1.76 ± 0.03 g cm^{-3}, while that calculated for eight formula units per unit cell is 1.81 g cm^{-3}.

The intensities of 1372 independent reflections [$(\sin \theta)/\lambda < 0.65$] were measured using Mo Kα radiation filtered by zirconium foil. The diffractometer geometry and method of data collection have been described previously.[12] The crystals were decomposed by molybdenum radiation, the decomposition being retarded somewhat by coating the crystal with a thin layer of shellac. Nine standard reflections, distributed over a wide range of θ, were monitored, and the crystal was discarded when any intensity dropped to 85% of its initial value. Four crystals were used in collecting the data. All were morphologically similar with well-developed {100}, {010}, and {001} faces.

Experimental data were corrected for background, assuming linear variation over the scan range. Of the 1372 observed intensities (I) 708 were judged to be statistically significant using the criteria $I > 0$ and $I/[P + (t_p/t_b)^2(B_1 + B_2)]^{1/2} \geq 3$, where t_p and t_b are the total counting time for peak and background; P, B_1, and B_2 are total counts in the peak and two backgrounds, respectively; and $I = P - B_1 - B_2$. Only these statistically significant reflections were used in the subsequent refinement. The intensities of these 708 reflections were then corrected for Lorentz and polarization effects. Absorption corrections were neglected ($\mu = 15.5$ cm^{-1}, average crystal dimensions $0.027 \times 0.027 \times 0.152$ mm).

Solution and Refinement of Structure[13]

The positions of the ruthenium and chlorine atoms were determined by examination of a three-dimensional map of the Patterson function. After one cycle of least-squares refinement, the locations of all carbon and oxygen atoms were found from a difference Fourier map. Three cycles of refinement of the scale factor and the positional and isotropic thermal parameters of the 14 independent nonhydrogen atoms yielded a discrepancy index, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.076. At this point, a weighting scheme with the weights, $w(F_o)$, equal to $\sigma^{-2}(|F_o|)$ was introduced. Standard deviations were derived from the standard deviations of the observed intensities according to Doedens and Ibers,[14] using an "uncertainty factor," p, of 0.045. Two more cycles of least-squares refinement resulted in convergence at $R_1 = 0.077$ and $R_2 = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2} = 0.074$. The validity of the weighting scheme is reflected in the lack of dependence of $w(|F_o| - |F_o|)^2$ on $|F_o|$ and $(\sin \theta)/\lambda$. Although no parameter changed as much as one standard deviation upon chang-

---

[9] N. N. Greenwood, P. V. Parish, and P. Thornton, *J. Chem. Soc.*, 320 (1966).

[10] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).

[11] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

[12] M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90,** 903 (1968).

[13] (a) Computer programs used for data processing and in the solution and refinement of this structure were as follows: D. P. Shoemaker, MIXG2 (calculates diffractometer settings) and DISTAN (orthogonal cell coordinates, inter- and intramolecular contacts and angles); R. C. Elder, PDATA2 (corrects MIGX2 output for ϕ_0 and scan width and prints diffractometer settings in convenient format) and PUBTAB (prepares structure factors in proper format for publication); A. Zalkin, FORDAP (Fourier and Patterson maps); C. T. Prewitt, SFLS5 (least-squares refinement); M. J. Bennett, PMMO (general data reduction); J. S. Wood, MGEOM (bond lengths and angles with standard deviations, and best least-squares planes). (b) Sources of atomic scattering factors: Ru, Cl: D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 17, 104 (1965); C, O: J. A. Ibers, "International Cables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

[14] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10, IN ELECTRONS) FOR $Ru_2(O_2CC_3H_7)_4Cl$

H	L	FOBS	FCAL
K = 0**			
0	4	5254	5281
0	8	1933	1934
0	12	3457	3461
0	16	3764	3770
0	20	1551	1688
1	1	5217	4802
1	3	4728	4235
1	5	3033	2703
1	7	1720	1569
1	9	958	1004
1	11	2332	2336
1	13	1104	967
1	15	3600	3614
1	17	642	515
1	19	2141	2188
1	23	1205	1176
1	27	650	776
1	31	464	480
2	0	5530	5377
2	2	808	855
2	4	4257	4013
2	6	1753	1777
2	8	1353	1557
2	10	1325	1315
2	12	2085	1950
2	14	557	555
2	16	1613	1634
2	18	413	622
2	20	713	737
2	24	461	276
3	1	1298	1123
3	3	2511	2276
3	5	2494	2299
3	7	1462	1486
3	9	1412	1348
3	11	1321	1233
3	15	853	919
4	0	2224	2201
4	2	975	935
4	6	1632	1679
4	8	1764	1734
4	10	1506	1489
4	14	551	540
5	7	728	711
5	9	1814	1832
5	13	673	798
5	15	969	1068
5	17	1304	1271
5	19	573	534
5	21	650	769
5	23	662	684
5	25	670	604
5	27	551	587
6	0	2616	2745
6	2	2771	2812
6	4	1821	1885
6	6	2935	3165
6	8	1904	1976
6	10	2415	2351
6	12	1416	1361
6	14	1350	1439
6	16	783	852
6	18	713	695
6	20	670	631
6	22	658	589
6	26	433	183
7	1	607	537
7	9	883	842
7	11	1133	1044
7	13	1427	1420
7	15	540	580
7	17	958	955
7	19	594	648
7	21	682	632
7	23	903	820
7	25	946	941
7	27	755	794
8	0	1201	1170
8	2	634	740
8	4	901	979
8	6	421	597
8	8	1545	1587
8	10	678	784
8	12	747	789
8	14	487	545
8	16	434	398
9	1	813	778
9	3	776	810
9	5	640	584
9	7	818	738
9	11	632	765
9	15	765	718
9	23	448	410
10	0	1464	1450
10	2	1234	1204
10	4	1308	1316
10	6	1008	985
10	12	772	753
10	14	391	361
10	16	596	742
10	18	454	353
11	1	1775	1775
11	3	1304	1440
11	5	1175	1158
11	9	1223	1094
11	13	956	1112
11	15	375	443
11	17	1034	1100
11	21	563	611
12	0	559	640
12	2	2590	2681
12	6	2079	2111
12	8	559	625
12	10	2010	2018
12	14	1492	1507
12	18	921	944
12	22	439	473
13	1	1221	1316
13	3	765	896
13	5	1135	1192
13	9	1427	1379
13	13	1053	1283
13	17	704	825
14	2	1153	1302
14	6	1451	1504
14	10	1262	1232
15	7	520	686
15	9	746	861
15	13	697	720
16	2	598	537
16	6	540	640
16	10	518	603
K = 1**			
1	2	1061	1126
1	6	2231	2249
1	10	1658	1752
1	14	3149	3134
1	18	2501	2795
1	22	1486	1524
1	26	1254	1209
1	30	980	1052
2	1	2606	2387
2	3	2502	2324
2	5	3034	2899
2	7	1181	1275
2	9	1156	1023
2	11	1704	1647
2	13	899	997
2	15	1741	1804
2	17	692	578
2	19	1331	1406
2	21	876	1026
2	25	759	601
2	27	922	520
3	0	2895	2659
3	2	1011	882
3	6	1695	1761
3	8	1511	1427
3	10	1598	1543
3	12	889	810
3	14	1007	963
3	16	682	639
3	18	959	986
3	22	912	971
3	26	1013	651
4	1	772	752
4	3	510	646
4	5	1689	1755
4	7	1513	1406
4	9	2119	2104
4	11	688	674
4	13	940	1110
4	17	674	750
4	19	348	427
4	21	857	898
4	23	492	504
4	25	409	430
4	27	472	383
5	0	517	495
5	2	1440	1445
5	4	763	844
5	6	1442	1372
5	8	1714	1689
5	10	1124	1122
5	12	887	876
5	14	982	1009
5	16	1238	1237
5	18	658	647
5	20	1136	1062
5	24	925	929
5	28	693	696
6	1	2686	2714
6	3	2504	2453
6	5	1963	1948
6	7	2018	2036
6	9	2133	2099
6	11	1732	1735
6	13	1562	1632
6	15	1086	1094
6	17	1067	1166
6	19	674	667
6	21	571	634
7	2	670	520
7	4	1264	1233
7	6	857	953
7	8	1495	1532
7	10	956	979
7	12	1477	1545
7	14	980	918
7	16	735	749
7	18	855	846
7	20	516	524
7	22	808	831
7	24	780	852
7	26	883	824
7	28	583	642
8	1	1161	1211
8	3	1258	1349
8	5	1112	1189
8	7	1661	1691
8	9	810	799
8	11	1473	1502
8	13	731	683
8	15	595	671
8	17	524	477
8	19	520	604
8	21	405	129
8	23	423	417
9	0	703	645
9	2	938	950
9	4	1067	988
9	6	514	563
9	8	1005	986
9	10	840	837
9	12	699	699
9	14	794	725
9	16	445	473
9	18	526	586
9	20	484	414
9	22	538	636
10	1	915	816
10	3	796	826
10	5	366	478
10	7	776	833
10	11	534	618
10	13	644	552
10	15	770	757
10	17	563	570
10	19	642	730
10	21	543	492
10	23	468	469
11	0	561	687
11	4	954	1041
11	8	920	1041
11	12	921	937
11	16	980	1022
11	20	913	903
11	24	782	716
12	1	984	973
12	3	934	947
12	5	1345	1414
12	7	1057	1064
12	9	1600	1554
12	11	565	575
12	13	1215	1281
12	17	919	1016
12	21	705	684
13	2	367	362
13	4	454	501
13	6	465	242
13	8	693	785
13	12	1004	1041
13	16	1021	984
13	20	863	846
14	1	705	751
14	3	407	444
14	5	1057	955
14	7	417	395
14	9	562	979
14	13	834	820
15	12	573	578
K = 2**			
2	0	2012	2051
2	4	3500	3414
2	8	1667	2008
2	12	2201	2288
2	16	1163	1163
2	20	1161	1242
2	24	919	786
3	1	1053	976
3	3	1115	1108
3	5	2834	2761
3	7	2456	2398
3	9	2136	2131
3	11	1468	1496
3	13	667	613
3	17	704	806
4	0	1056	982
4	2	1751	1740
4	4	837	751
4	6	2533	2447
4	8	2380	2270
4	10	1623	1792
4	12	1032	951
4	14	1100	1078
4	16	1220	1213
4	18	746	807
4	20	1185	1263
5	1	2084	1974
5	3	1483	1353
5	5	2126	2063
5	9	1782	1870
5	13	1882	1843
5	17	1578	1474
5	21	1431	1377
6	0	1171	1223
6	2	2320	2383
6	4	1854	1949
6	6	1750	1775
6	8	1615	1485
6	10	1977	1985
6	12	1582	1579
6	14	1418	1383
6	16	986	1160
6	20	825	946
6	22	866	727
6	26	1164	959
7	3	697	679
7	5	310	368
7	7	1937	1870
7	11	2227	2183
7	13	1063	1079
7	15	1114	1141
7	17	741	718
7	19	1161	1072
7	21	887	818
7	23	1175	1116
7	25	776	798
7	27	1015	951
8	0	784	863
8	2	776	846
8	4	1612	1664
8	6	552	906
8	8	2085	2191
8	10	782	867
8	12	1159	1165
8	14	887	911
8	16	851	902
8	18	980	879
8	20	666	650
8	22	693	876
8	26	834	819
9	1	395	414
9	3	729	729
9	5	535	623
9	7	1408	1452
9	11	1027	955
9	15	798	871
9	17	599	623
9	19	786	751
9	21	419	462
9	23	435	576
10	0	391	525
10	2	915	933
10	6	646	658
10	10	733	750
10	14	798	820
10	18	913	977
10	22	735	770
11	1	859	914
11	3	905	864
11	5	780	824
11	7	958	924
11	9	891	827
11	11	699	717
11	13	676	721
11	15	597	599
11	17	587	525
11	19	607	695
11	23	583	527
12	2	1434	1456
12	4	624	568
12	6	1219	1218
12	8	666	781
12	10	1067	1055
12	12	476	404
12	14	845	803
12	18	518	611
13	1	737	792
13	3	579	576
13	5	747	683
13	9	749	762
13	13	869	831
13	17	662	717
14	0	484	392
14	2	1112	1165
14	6	1100	1164
14	10	1015	1040
14	14	692	686
14	18	630	457
15	1	470	539
15	5	512	598
15	7	480	432
15	9	628	652
15	11	451	322
15	13	459	442
16	2	447	418
17	3	514	443
K = 3**			
3	2	1727	1801
3	6	2956	3163
3	10	2414	2319
3	14	1065	1047
4	1	2505	2553
4	3	1890	1930
4	5	2361	2357
4	7	1689	1619
4	9	2629	2826
4	11	1145	1126
4	13	1429	1600
4	15	934	799
4	17	1427	1563
4	21	938	1065
5	2	3630	3602
5	4	1011	1019
5	6	3581	3667
5	8	1360	1374
5	10	2454	2475
5	12	1224	1365
5	14	1870	1891
5	16	726	634
5	18	1468	1378
5	20	808	859
6	1	2362	2519
6	3	2308	2468
6	5	2808	2754
6	7	2674	2744
6	9	1838	1982
6	11	2010	2092
6	13	1791	1794
6	15	825	941
6	17	1342	1406
7	0	1640	1706
7	2	1888	1885
7	4	2351	2454
7	6	1059	1286
7	8	2448	2776
7	10	1027	1219
7	12	1925	2083
7	14	914	978
7	16	1352	1354
7	18	914	739
7	20	1131	1052
7	22	998	787
8	1	1979	2052
8	3	1997	2074
8	5	1704	1698
8	7	2324	2403
8	9	1061	1218
8	11	1716	1839
8	13	1005	764
8	17	922	676
8	19	860	842
8	21	897	331
9	0	1916	2070
9	2	348	420
9	4	1639	1704
9	6	413	408
9	8	1750	1811
9	10	488	470
9	12	870	1056
10	1	836	868
10	3	980	1113
10	5	666	712
10	7	1035	1117
10	9	356	265
10	11	656	675
10	15	838	893
10	19	701	765
10	23	534	540
11	0	1258	1374
11	4	1503	1555
11	8	936	993
11	10	378	345
11	12	869	890
11	14	474	322
11	16	782	748
11	20	520	486
12	1	818	801
12	3	838	865
12	5	656	661
12	7	729	665
12	9	524	476
12	11	620	561
12	13	662	473
13	2	609	683
13	12	500	478
13	16	486	505
13	18	611	498
14	1	689	770
14	3	826	775
14	5	646	689
14	7	654	666
14	9	634	654
14	11	435	438
14	17	466	473
15	0	772	681
15	4	644	603
15	8	443	463
16	3	496	452
16	7	459	491
K = 4**			
4	0	2903	3028
4	4	1628	1697
4	8	1841	2005
4	12	1928	1940
4	16	1756	1821
4	20	1392	1446
4	24	1356	1322
4	28	889	988
5	1	1878	1845
5	3	1309	1431
5	5	1155	1181
5	7	911	954
5	9	1394	1333
5	11	844	624
5	13	1614	1692
5	15	761	833
5	17	1261	1287
5	19	862	864
5	23	1017	769
5	25	842	876
6	2	1129	1180
6	4	1145	967
6	6	712	923
6	8	1424	1219
6	10	1088	1076
6	12	1502	1393
6	16	1165	1062
6	18	800	982
6	20	836	913
7	1	1141	1216
7	7	1348	1344
7	11	1043	1266
7	13	932	810
7	15	1088	1025
7	17	984	1081
7	21	877	916
7	25	1104	785
7	27	909	671
8	2	1896	1852
8	4	897	649
8	6	1195	1466
8	8	1125	1096
8	10	1160	1249
8	14	1420	1484
8	18	1414	1426
8	26	1005	903
9	1	1542	1656
9	3	1511	1681
9	7	1222	1322
9	11	1030	1077
9	15	1381	1398
9	19	1003	1127
9	25	872	307
10	0	1181	962
10	4	926	698
10	18	1437	1327
10	22	1197	927
11	1	1112	957
11	3	970	1002
11	11	949	872
12	0	678	682
12	4	567	547
12	8	466	501
12	12	411	449
13	7	407	433
13	11	535	499
13	15	468	419
14	0	913	907
14	4	558	950
14	8	814	772
14	12	595	595
14	16	549	551
15	1	780	695
15	3	705	700
15	5	482	471
15	7	630	664
15	11	502	499
15	13	417	329
16	6	506	362
K = 5**			
5	2	2381	2379
5	6	1273	1382
5	10	1266	1415
5	14	980	1199
5	18	858	842
6	1	1033	1110
6	3	759	884
6	5	895	919
6	7	801	894
6	11	903	647
7	0	1191	1490
7	2	838	925
7	4	1204	1131
7	8	893	819
7	16	801	813
8	1	1248	1193
8	3	1514	1439
8	5	1309	1125
8	7	1051	1048
8	11	1025	1212
8	15	994	1063
8	17	1033	829
8	19	877	849
9	0	3165	3144
9	2	885	902
9	4	2562	2433
9	8	1750	1687
9	12	1498	1436
9	16	1159	1321
10	7	967	1097
10	15	982	1297
10	19	1048	1133
11	0	1447	1556
11	2	986	646
11	4	1073	1283
11	12	874	831
14	3	1036	713
15	0	1027	963
15	2	441	534
15	4	954	913
15	8	786	760
15	10	545	475
15	12	628	546
K = 6**			
6	0	869	944
6	8	743	639
8	22	865	616
9	1	1918	1825
9	3	2024	1966
9	5	1234	1317
9	7	1256	1257
9	9	964	994
9	11	932	954
9	13	1074	1032
9	15	1311	1061
10	0	897	940
10	2	1055	949
10	10	958	742
10	12	982	794
10	14	944	924
10	18	929	1023
10	22	994	626
11	1	1792	1621
11	3	1457	1319
11	5	1120	994
11	7	968	926
11	9	921	833
11	11	942	955
11	13	1155	819
11	15	1061	773
12	0	1427	1350
12	8	1176	947
12	14	947	500
12	18	998	411
13	3	1195	876
13	9	934	668
15	1	1096	657
15	7	1116	843
15	9	1129	696
K = 7**			
7	6	838	584
8	7	824	703
8	13	824	640
9	0	1252	1209
9	2	1803	1848
9	4	1000	1053
9	6	1699	1488
9	8	801	514
9	10	1295	1395
9	14	998	1013
9	18	921	758
10	9	840	796
10	13	1080	1068
10	17	1009	929
11	2	1135	1182
11	6	854	718
11	10	954	691
12	13	862	511
K = 8**			
8	8	1596	1597
8	12	1082	978
8	16	960	887
9	1	1025	1158
9	3	1082	1008
9	5	1435	1285
9	7	1108	1045
9	9	1319	1395
9	13	1011	916
11	1	930	886
11	9	1035	926
11	15	475	278
13	9	881	500
K = 9**			
9	2	1116	1124
9	6	1681	1581
9	10	1549	1368
10	5	936	864
10	9	1206	1034
11	6	1277	1244
11	10	1199	960
K = 10**			
11	5	925	809
K = 11**			
11	6	1035	995
11	10	984	898
K = 12**			
12	0	1362	1078
12	4	1370	1190

ing from unit weights to $w = \sigma^{-2}(|F_o|)$, the standard deviations of these parameters decreased by 10–20%.

A difference Fourier map with all nonhydrogen atoms removed showed evidence for anisotropic motion of the heavy atoms particularly in the vicinity of the ruthenium atoms. The ruthenium and chlorine atoms were therefore assigned anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and three cycles of least-squares refinement varying all scale, positional, and thermal parameters resulted in convergence to $R_1 = 0.073$ and $R_2 = 0.072$. A statistical test[15] based on the R factors affirms the anisotropic model at the 99.5% confidence level.

A difference Fourier map, using only the data for which $(\sin\theta)/\lambda \leq 0.35$, was now computed in an attempt to locate hydrogen atoms. Although a number of peaks were found in positions where some of the hydrogen atoms might be expected, other expected hydrogen atoms were not resolved. This phase of the refinement was therefore abandoned.

For an acentric space group, $|F(hkl)| \neq |F(\bar{h}\bar{k}\bar{l})|$ when the effects of anomalous dispersion are important. In the absence of a complete data set, one might consider using the R-factor test to decide whether $F(hkl)$ or $F(\bar{h}\bar{k}\bar{l})$ was observed. However, since four crystals were used, such a test would have to be performed on each of the four data sets individually and in each case there would be an unfavorable ratio of data to parameters. Since the effect of anomalous dispersion is thus quite small, it was neglected, and the results reported here are based on the refinement neglecting anomalous dispersion.

A comparison of the observed and calculated structure amplitudes did not suggest that a correction for extinction was necessary. The final standard deviation of an observation of unit weight is 1.15. Calculation of the structure factors for the rejected reflections gave no $|F_o|$ greater than the minimum observable.

Results

In Table I are listed the final calculated and observed structure amplitudes. The final fractional coordinates and thermal parameters for the atoms of the asymmetric unit are given in Table II. Tables III–V contain data on molecular bond lengths, angles, and planes, respectively.

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS[a]

Atom	x	y	z	B,[b] Å^2
Ru	0.03738 (15)	0.07743 (15)	0.13358 (8)	2.21
Cl	0.1269 (7)	0.25	0.125	3.10
O_1	0.1326 (14)	0.0273 (15)	0.1929 (7)	3.31 (38)
O_2	0.1314 (14)	0.0290 (14)	0.0775 (6)	3.16 (37)
O_3	0.0541 (13)	−0.1228 (12)	0.1937 (6)	2.36 (34)
O_4	0.0615 (13)	−0.1228 (13)	0.0771 (6)	2.70 (36)
C_1	0.1204 (22)	−0.0627 (22)	0.2109 (10)	3.24 (58)
C_2	0.1289 (16)	−0.0606 (17)	0.0600 (8)	1.22 (42)
C_3	0.1806 (25)	−0.0943 (25)	0.2627 (12)	4.42 (74)
C_4	0.2098 (19)	−0.1012 (19)	0.0201 (10)	2.95 (54)
C_5	0.2902 (28)	−0.0578 (29)	0.2614 (13)	6.85 (97)
C_6	0.2908 (26)	−0.1601 (27)	0.0525 (14)	6.30 (90)
C_7	0.3442 (28)	−0.0967 (26)	0.3158 (14)	6.40 (94)
C_8	0.3476 (26)	−0.0896 (26)	0.0906 (12)	5.82 (85)

Anisotropic Temperature Parameters (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	33.8 (12)	27.5 (11)	9.95 (28)	2.4 (14)	0.0 (6)	0.1 (6)
Cl	48.7 (59)	28.8 (47)	16.3 (20)	0	0	0.7 (28)

[a] Numbers in parentheses are esd's in the last figure quoted.
[b] Equivalent isotropic B's are quoted here for the anisotropically refined atoms.

Figure 1 shows a projection of the $Ru_2(O_2CC_3H_7)_4^+$ cation and two associated Cl^- anions onto the (100) plane. Unnumbered atoms are related by the twofold rotation axis shown in Figure 1 to the numbered ones and will be given corresponding numbers augmented with primes. Figure 2 is a packing diagram showing the projection of the structure on the (001) plane.

Discussion

Tetra-n-butyratodiruthenium chloride contains dinuclear units consisting of two ruthenium atoms

---

(15) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

Table III

Bond Lengths[a]

Atoms	Dist, Å	Atoms	Dist, Å	Atoms	Dist, Å
$Ru-Ru'$	2.281 (4)	O_2-C_2	1.26 (3)	C_1-C_3	1.55 (4)
$Ru-Cl$	2.587 (5)	O_1-C_1	1.28 (3)	C_3-C_5	1.53 (5)
$Ru-O_1$	2.04 (2)	O_4-C_2	1.29 (3)	C_5-C_7	1.60 (5)
$Ru-O_2$	1.96 (2)	O_3-C_1	1.26 (3)	C_2-C_4	1.55 (3)
$Ru-O_3'$	2.00 (2)			C_4-C_6	1.55 (4)
$Ru-O_4'$	2.00 (2)			C_6-C_8	1.52 (5)

[a] Standard deviations occurring in the last figure of each bond length are given in parentheses.

Table IV

Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
$Ru'-Ru-Cl$	175.1 (1)	$Ru-O_2-C_2$	122 (2)
$Ru'-Ru-O_1$	88.6 (5)	$Ru-O_1-C_1$	118 (2)
$Ru'-Ru-O_2$	88.9 (5)	$Ru'-O_4-C_2$	119 (1)
$Ru'-Ru-O_3'$	90.4 (4)	$Ru'-O_3-C_1$	119 (2)
$Ru'-Ru-O_4'$	89.2 (5)	$C_1-C_3-C_5$	110 (2)
O_2-Ru-O_1	89.8 (8)	$C_3-C_5-C_7$	110 (3)
O_1-Ru-O_3'	87.2 (6)	$C_2-C_4-C_6$	113 (3)
$O_3'-Ru-O_4'$	91.1 (7)	$C_4-C_6-C_8$	108 (3)
$O_4'-Ru-O_2$	91.9 (7)	$O_2-C_2-O_4$	121 (2)
$Cl-Ru-O_2$	86.6 (5)	$O_1-C_1-O_3$	124 (3)
$Cl-Ru-O_1$	93.6 (5)	$O_2-C_2-C_4$	122 (2)
$Cl-Ru-O_3'$	94.1 (5)	$O_4-C_2-C_4$	117 (2)
$Cl-Ru-O_4'$	88.8 (5)	$O_1-C_1-C_3$	118 (2)
		$O_3-C_1-C_3$	117 (2)

[a] Standard deviations occurring in the last figure quoted for each angle are given in parentheses.

Table V

Weighted Least-Squares Planes[a]

Plane no.	Atoms	Equation[b]
1	$RuRu'O_2O_4C_2C_4$	$0.6161x - 0.2973y + 0.7294z = -2.382$
2	$RuRu'O_1O_3C_1C_3$	$-0.6625x + 0.3210y + 0.6768z = 2.211$
3	$RuO_1O_2O_3'O_4'$	$-0.4454x - 0.8953y + 0.0049z = -1.115$

Distances of Atoms from Planes (Å)[c]

Plane 1: Ru′, 0.0004; Ru, 0.0006; O_2, −0.040; O_4, −0.019; C_2, −0.020; C_4, 0.091

Plane 2: Ru′, −0.0017; Ru, 0.0007; O_1, −0.067; O_3, −0.004; C_1, −0.045; C_3, 0.148

Plane 3: Ru, −0.0098; O_2, 0.004; O_4', 0.030; O_1, 0.030; O_3', −0.001

[a] Atoms weighted by the inverse of their standard deviations. [b] The orthogonal-coordinate system (x, y, z) corresponds to the crystal (a, b, c) axes. [c] Average esd's in atom positions derived from uncertainties in fractional coordinates are (Å): Ru, 0.0020; O, 0.018; C, 0.020.

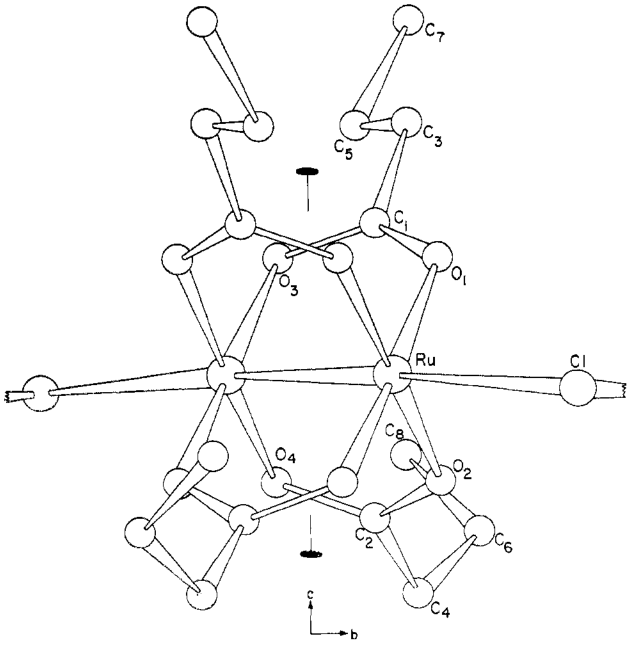


Figure 1.—A projection of the $Ru_2(O_2CC_3H_7)_4^+$ cation and two associated Cl^- anions onto the (100) plane.

bridged by four *n*-butyrato groups, a configuration which has also been found for various other $M_2(O_2CR)_4$ species as noted in the Introduction. In the crystal, these dinuclear units are linked by bridging chlorine atoms into infinite zigzag chains parallel to the *a* and *b* crystallographic axes. Although crystallographically the dinuclear unit possesses only a twofold axis perpendicular to the Ru–Ru axis, it has virtual D_{4h} symmetry if the alkyl chains are neglected.

The four independent Ru–O bond lengths show no significant deviations from the average value of 2.00 Å, and all four O–Ru–O angles are 90° within experimental error. The two crystallographically independent Ru_2O_2C groups deviate negligibly from planarity and are essentially orthogonal (89.5°) to each other. The α-carbon atoms, C_3 and C_4, show slight deviation from the planarity expected for the $C-CO_2$ group. The four oxygen atoms of the RuO_4 groups are planar, while the ruthenium atom is slightly out of the plane since the Ru–Ru distance (2.281 Å) slightly exceeds the mean O–O distance (2.24 ± 0.03 Å) in the carboxylate group.

The detailed geometry of the ruthenium–chlorine skeleton is a very interesting aspect of the crystal structure. The packing diagram given in Figure 2 shows that the dinuclear cations, $Ru_2(O_2CC_3H_7)_4^+$, are bridged symmetrically by chloride ions into infinite chains. The Ru–Ru–Cl angle deviates by a small but statistically significant amount (5°) from linearity. The Ru–Cl bond length of 2.587 Å is unusually large in comparison to the value of about 2.35 Å usually observed[16] in chloro complexes of Ru^{III}. The weakness of the Ru–Cl interaction indicated by the length of this bond is in accord with the observation that the compound behaves as a 1:1 electrolyte in solution. This weak interaction with ligands bonded along the metal–metal axis seems to be characteristic of carboxylate dimers. $Re_2(O_2CC_6H_5)_4Cl_2$ exhibits a long Re–Cl bond[8] with an appropriately low metal–chlorine stretching frequency,[17] and, in $Mo_2(O_2CCH_3)_4$, the axial groups are absent altogether. A closely related phenomenon is the ease of substitution of the axial ligands in the copper and rhodium acetates.

The Ru–Ru bond length, 2.281 Å, is very short; in ruthenium metal, the shortest Ru–Ru distance[18] is 2.65 Å. In the absence of detailed structural information, Stephenson and Wilkinson envisioned $Ru_2(O_2CC_3H_7)_4Cl$ as a complex containing ruthenium ion oxidation states +2 and +3 and interpreted the magnetism

---

(16) T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **5**, 1427, 1431 (1966).

(17) W. K. Bratton and F. A. Cotton, to be submitted for publication.

(18) A. Hellawell and W. Hume-Rothery, *Phil. Mag.*, **45**, 797 (1954).

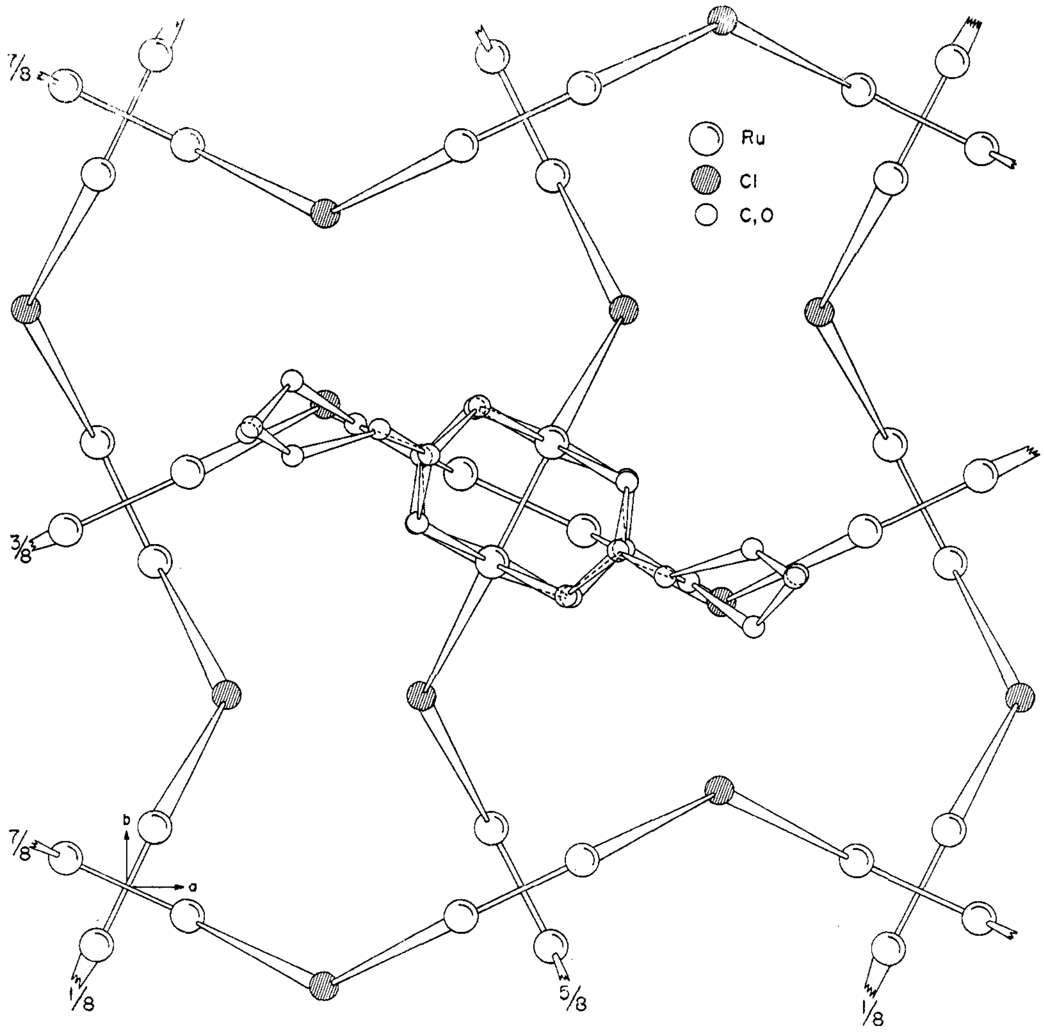


Figure 2.—A packing diagram of the contents of the unit cell projected onto the (001) plane. For clarity, the butyrate groups are pictured for only one dinuclear cation. The fractional *z* coordinate appears beside each ruthenium–chlorine chain.

of the compound on this basis. As Figure 1 shows, however, the two metal atoms of a given dinuclear cation are related by a crystallographic twofold axis. Since we see no indications of disorder, we believe that these atoms are structurally equivalent and therefore chemically equivalent and must be thought of as existing in the same nonintegral oxidation state of +2.5. The electronic structure of such a compound is best described by molecular orbitals.

Qualitative[19] and semiquantitative[20] discussions of the electronic structures of $Re_2Cl_8^{2-}$ and other species containing strong metal–metal bonds have been given and may be used as a point of departure in the present instance. Figure 3 shows a partial molecular orbital (MO) diagram for an M_2X_8 species, only those MO's which are of predominantly metal character being included.

The eleven electrons contributed by the two ruthenium atoms must be allocated to the most stable MO's. Eight of these electrons will completely fill the a_{1g}, e_u, and b_{2g} MO's, which have σ, π, and δ symmetry, respectively, relative to the metal–metal axis. The eight-electron configuration up to this point is analogous to the configurations in $Re_2Cl_8^{2-}$, $Re_2(O_2CC_6H_5)_4Cl_2$, and $Mo_2(O_2CCH_3)_4$. There are, however, still three electrons to be allocated.

The next available orbitals are those of a_{1g}, a_{2u}, and b_{1u} symmetry. Of these, the first two are essentially nonbonding in the metal–metal sense; they are directed outward along the metal–metal axis. The b_{1u} orbital is the δ-antibonding one. Since the paramagnetism of the $Ru_2(O_2CR)_4Cl$ compounds is indicative of three unpaired electrons per pair of metal atoms, it is clear that each of these three MO's contains one electron. The energy required to pair spins is evidently large compared to the separation of the orbital energies, and a high-spin system results.

It is unusual for a second-row transition metal to adopt a high-spin configuration, and this point therefore warrants discussion in terms of the molecular structure found here. From the electronic absorption spectrum of $Re_2Cl_8^{2-}$, to which a molecular orbital diagram quite similar to that of Figure 3 applies, it is believed[19,20] that the a_{2u} and a_{1g} nonbonding orbitals are about 18 kK below the b_{1u} orbital. If a separation of this magnitude existed in $Ru_2(O_2CR)_4Cl$, spin pairing

[19] F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

[20] F. A. Cotton and C. B. Harris, *ibid.*, **6**, 924 (1967).

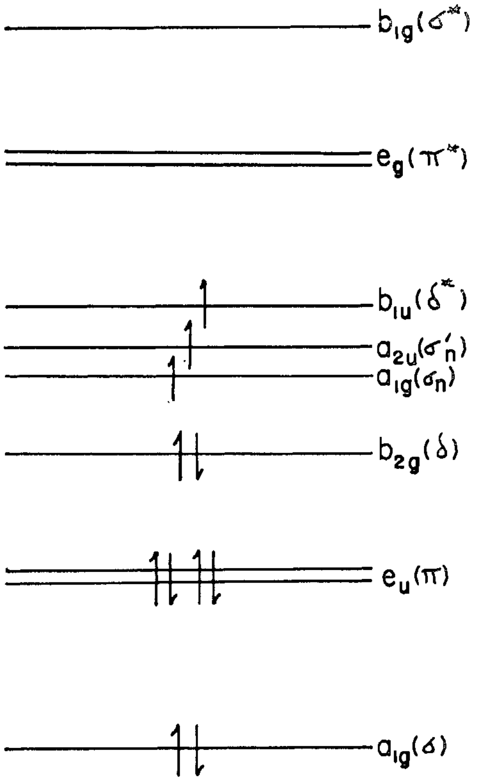


Figure 3.—A qualitative molecular orbital diagram for an M_2X_8 species of symmetry D_{4h}. The electron distribution shown is that for $Ru_2(O_2CR)_4Cl$.

would result leaving only one unpaired electron. However, the weakly bound, symmetrically bridging chloride ions in the ruthenium compound can interact with the axially directed a_{1g} and a_{2u} orbitals, thereby raising their energy somewhat. This effect moves the a_{1g} and a_{2u} orbitals closer to the b_{1u} orbital, and stabilizes the high-spin $^4B_{2g}$ ground state. The reported electronic spectrum[10] of $Ru_2(O_2CR)_4Cl$ species supports this reasoning. If the band at 425 mμ is assigned to the $b_{2g} \rightarrow a_{1g}$ and/or $b_{2g} \rightarrow a_{2u}$ transitions (both vibronically allowed) and the band at 310 mμ is taken as the $b_{2g} \rightarrow b_{1u}$ transition, then the b_{1u} orbital is only about 9 kK above the a_{1g} and a_{2u} orbitals. This is half the observed separation in $Re_2Cl_8^{2-}$ and is sufficiently small to allow the high-spin configuration to be stable.

It is of interest to compare the metal–metal distances in the series of isostructural molecules formed by metals of the second transition series, *viz.*, $Mo_2(O_2CCH_3)_4$, $Ru_2(O_2CC_3H_7)_4Cl$, and $Rh_2(O_2CCH_3)_4(H_2O)_2$. In the first, there are just enough electrons to fill the bonding orbitals σ, 2π, δ of Figure 3. A quadruple bond is formed, and the Mo–Mo distance is extremely short, 2.11 Å.

In the diamagnetic rhodium(II) carboxylates, there are fourteen electrons to be placed in the orbitals shown in Figure 3. After eight electrons have filled the bonding orbitals, there are still six electrons. These completely fill the next three orbitals, namely, the approximately nonbonding a_{1g} and a_{1u} orbitals and the δ-antibonding b_{1u} orbital. Filling of the a_{1g} and a_{1u} orbitals should not have a major effect on the metal–metal bond, although a small weakening effect appears likely, especially through the a_{1g} orbital, according to the calculations[20] on $Re_2Cl_8^{2-}$.

The two electrons in the δ-antibonding b_{1u} orbital should have a very marked effect on the bond, however. First, they will at the very least cancel the bonding effect of the electron pair in the b_{2g} orbital; the δ bond is effectively nullified and we have here only a triple (σ, 2π) Rh–Rh bond. Second, because of the constraint on rotation imposed by the carboxyl groups, the two δ-type d orbitals, one on each rhodium atom, remain directly opposite each other. Since each of these orbitals is now occupied by an electron pair, there is a substantial amount of repulsion tending to push the metal atoms apart. Thus, the Rh–Rh distance is considerably longer, ~2.45 Å, though still short enough to be consistent with the existence of strong metal–metal bonding.

For $Ru_2(O_2CC_3H_7)_4Cl$, we would expect a bond order and repulsive forces about halfway between those in the molybdenum and rhodium compounds. In agreement with this, the Ru–Ru distance, 2.281 Å, is about midway between those in the molybdenum and rhodium compounds.