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The Crystal and Molecular Structure of Trirhenium Nonaiodide[1]

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Received February 19, 1968

Rhenium(III) iodide has been obtained as well-formed single crystals by a modification of published preparative procedures. From X-ray diffraction data obtained with a counter diffractometer, the structure has been solved and refined to a final value for the conventional, unweighted residual of 4.4% for the 623 significant reflections. The substance is composed of Re_3I_9 molecules essentially similar in structure to the Re_3Cl_9 and Re_3Br_9 cluster complexes which are already well characterized. The Re–Re distances are 2.440 (twice) and 2.507 Å. The Re_3I_9 groups are linked into zigzag chains by bridging halogen atoms in a manner similar to that in which Re_3Cl_9 molecules are linked into sheets. Variations in Re–I bond lengths correlate well with the structural functions of the various I atoms in the molecule and crystal. Trirhenium nonaiodide crystallizes in the monoclinic system, space group $P2_1/m$, with unit cell dimensions $a = 9.234$, $b = 11.309$, $c = 8.799$ Å, $\beta = 110.25°$. The measured density was 6.37 g cm^{-3} (in fact, a lower limit because of iodine loss) while that calculated for two formula units (Re_3I_9) per cell is 6.55 g cm^{-3}. An important feature of the structure is that the off-plane I–Re–I angle at the Re atom not involved in intermolecular bridging is much smaller (131°) than the corresponding angles (150–160°) at Re atoms which have a fifth coordinated atom in many other Re_3X_9 derivatives. A similar reduction in angle in $Re_3Br_{11}^{2-}$ was reported earlier by Penfold. A reexamination of the Re_3Br_9 unit which shows no such reduction in $(C_9H_7NH)_2Re_4Br_{15}$ suggests that coordinated water molecules may be present. The limited chemistry of Re_3I_9 including a possible structural relation to "ReI_2" is briefly discussed.

Introduction

It was reported independently in 1963 by Robinson, Fergusson, and Penfold[2] in New Zealand and by Bertrand, Cotton, and Dollase[3] in this laboratory that the long known, red "$CsReCl_4$" contains $Re_3Cl_{12}^{3-}$ groups with triangular Re_3 metal atom clusters (Re–Re = 2.48 Å). This discovery constitutes the point of departure for what might be called the modern period in the study of the chemistry of rhenium in its lower oxidation states. Following quickly upon this key result came chemical and structural studies[4–10] of a host of compounds derived from the chloride and bromide of rhenium(III) as well as a structural study of rhenium(III) chloride itself.[11] This body of work clearly established that rhenium(III) chloride and nearly all, if not all, compounds derived therefrom under thermally mild, nonredox conditions, as well as all of the bromo analogs of these chloro compounds, contain the Re_3Cl_9 (or Re_3Br_9) group as the characteristic structural unit. Several studies[9,12] have shown that although the entire Re_3X_9 moiety generally persists through chemical reactions, the six nonbridging X atoms can be displaced while the Re_3X_3 unit consisting of the Re_3 triangular cluster and its three bridging X atoms remains intact. It has even been shown that in the gas phase at temperatures over 600° and at pressures much less than 1 torr the Re_3Cl_9 and Re_3Br_9 molecules predominate.[13,14]

While several of the studies cited above[6,7,9,14] provide good indirect reasons for believing that crystalline rhenium(III) bromide must be built up of Re_3Br_9 molecules, no conclusive crystallographic evidence for this has yet been published.[15] Moreover, there has been no evidence whatever concerning the structural nature of rhenium(III) iodide. If one considers the fact that iodides often differ from the stoichiometrically analogous chlorides and bromides for a number of obvious reasons (the reducing nature, the polarizability, and the greater size of I and I^- compared to Cl, Cl^- and Br, Br^-) and if, in particular, one notes that the Re_3X_9 structure involves a number of fairly close $X \cdots X$ nonbonded contacts, it becomes a very real question whether rhenium(III) iodide could be expected to be structurally homologous to the chloride and bromide.

In order to find out if rhenium(III) iodide does have a structure built of Re_3I_9 molecules, we undertook the preparation of the crystalline compound and then, upon being successful in this, carried out an X-ray crystallographic investigation of the structure of the compound.

Experimental Section

Single crystals suitable for X-ray diffraction work were obtained with some difficulty. Two preparative methods are de-

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[1] Supported by the United States Atomic Energy Commission.

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[6] F. A. Cotton and S. J. Lippard, *ibid.*, **4**, 59 (1965).

[7] F. A. Cotton, S. J. Lippard, and J. T. Mague, *ibid.*, **4**, 508 (1965).

[8] M. Elder and B. R. Penfold, *Nature*, **205**, 276 (1965); *Inorg. Chem.*, **5**, 1763 (1966).

[9] (a) J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 189 (1964); (b) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).

[10] J. H. Hickford and J. E. Fergusson, *ibid.*, *A*, 113 (1967).

[11] F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.*, 233 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

[12] F. A. Cotton and S. J. Lippard, *J. Am. Chem. Soc.*, **88**, 1882 (1966).

[13] (a) K. Rinke and H. Schäfer, *Angew. Chem. Intern. Ed. Engl.*, **4**, 148 (1965); (b) K. Rinke, M. Klein, and H. Schäfer, *J. Less-Common Metals*, **12**, 497 (1967).

[14] A. Buchler, P. E. Blackburn, and J. L. Stauffer, *J. Phys. Chem.*, **70**, 685 (1966).

[15] Crystallographic examination of rhenium(III) bromide was undertaken in this laboratory early in 1964 by Lippard[7] and by Gelinek and Rüdorff.[16] The two studies were in agreement as to the monoclinic unit cell dimensions ($a = 8.10$ Å, $b = 10.62$ Å, $c = 8.65$ Å, $\beta = 111°$), the space group (either $P2_1$ or $P2_1/m$), and the marked tendency of the crystals to twinning along a plane in the [010] zone. Upon inquiry, Professor Rüdorff informed one of the authors (F. A. C.) that the structure had been solved and was being refined.

[16] J. Gelinek and W. Rüdorff, *Naturwissenschaften*, **51**, 85 (1964).

scribed in the recent literature. In one[17a] (method A) perrhenic acid is reduced directly to ReI_3 by the action of concentrated hydriodic acid and ethyl alcohol at elevated temperatures. Method B[17b] utilizes a controlled thermal decomposition of rhenium(IV) iodide in an atmosphere of iodine.

Method A provided crystalline material consistently superior to that of method B. However, the material obtained from the hydriodic acid–ethanol reduction consisted of dendritic clusters of very small crystals and was thus not suitable for our purposes. The material was only sparingly soluble in and could not be successfully recrystallized from 55% aqueous HI, and it was virtually insoluble in all other solvents. Attempts to improve the quality of material through variation of reaction time and solution concentration were unsuccessful. The next step was to vary reaction temperature; it was found that use of higher-boiling alcohols produced the desired results. Substitution of *n*-hexyl alcohol for ethanol in the preparation drastically reduced the yields of material, but much larger single crystals were obtained. Unfortunately, this reaction does not appear to be particularly reproducible; only about 100 mg of crystallographically suitable material could be obtained.

The material was tentatively identified by comparison of powder patterns of samples prepared by the literature method with those of samples prepared using *n*-hexyl alcohol–hydriodic acid reduction. X-Ray absorption effects were minimized by grinding the samples with silica gel. Analytical figures (provided by Galbraith Laboratories, Knoxville, Tenn.) for the sample prepared by the literature method are given below.

Anal. Calcd for ReI_3: Re, 32.85; I, 67.15; atom ratio, I/Re, 3.00. Found: Re, 34.25; I, 66.39; atom ratio, I/Re, 2.85.

A preliminary optical examination showed the crystals to be needlelike monoclinic prisms. Further examination by Weissenberg (levels $h0l$–$h6l$) and precession photography (levels $0kl$, $1kl$, $hk0$, $hk1$) showed the crystals to be monoclinic with well-developed (100) and ($\bar{1}01$) faces. The only observed set of systematic absences was $0k0$ for $k \neq 2n$. This suggested the probable space groups $P2_1$ (C_2^2, no. 4) and $P2_1/m$ (C_{2h}^2, no. 11).

The unit cell parameters were determined at 21° as $a = 9.234 \pm 0.003$, $b = 11.309 \pm 0.003$, $c = 8.799 \pm 0.003$ Å, and $\beta = 110.25 \pm 0.05°$ from measurements on a General Electric XRD-5 manual diffractometer using copper Kα radiation (λ_{α_1} 1.5405 Å, λ_{α_2} 1.5443 Å). The quoted values for a, b, and c were derived[18] by plotting the magnitudes obtained for each one at 21° for various 2θ settings against the function $1/2[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$ and linearly extrapolating these plots to $\theta = 90.0°$. The uncertainty intervals quoted for a, b and c do not represent the precision but rather are the estimated maximum errors judged by the results obtained on the same instrument employing the same procedure for several standard crystals whose unit cell dimensions are accurately known.[19] The uncertainty in β represents the estimated precision of the measurements made on the diffractometer. The density of a sample prepared by the hydriodic acid–ethanol method was measured by displacement of toluene in a specific gravity bottle, thermostated to $24.90 \pm 0.05°$, as 6.37 ± 0.02 g cm^{-3}. Loss of iodine into the toluene was rapid at room temperature, and the solution became strongly colored in a few minutes. The value calculated from the formula weight of 566.93, the unit cell volume of 862.1 Å^3, and $Z = 6$ (*i.e.*, $Z = 2$ for Re_3I_9) is 6.55 g cm^{-3}. Considering the observed iodine loss, it is probable that the observed density does not differ significantly from the calculated value. For Re_3I_9, with $Z = 2$ in space group $P2_1$, no crystallographic symmetry elements are imposed upon the molecule; with $Z = 2$ in space group $P2_1/m$, however, the crystallographic mirror planes at $y = {}^1/_4$ and ${}^3/_4$ must bisect the molecules.

Cu Kα radiation was chosen for use in the data collection; normally it would be desirable to use Mo Kα radiation in order to minimize absorption effects ($\mu_{Cu} = 1680$ cm^{-1}; $\mu_{Mo} = 384$ cm^{-1}). However, because of the small size of the largest single crystals available ($\sim 0.003 \times 0.01 \times 0.1$ mm), the lower background and increased intensity obtained with Cu Kα radiation made it preferable.

Preliminary data collection was carried out using the equi-inclination Weissenberg method with nickel-filtered Cu Kα radiation; the crystal used was a monoclinic prism mounted about the needle axis, b. Reciprocal lattice levels ($h0l$–$h6l$) were recorded using the multiple-film technique; the intensities of 702 independent reflections were estimated visually using a graduated intensity strip. No further data were collected with this crystal, since Laué photographs taken after collection of the above data indicated that the crystal had decomposed. These data were used only to compute the Patterson function and one set of structure factors (the individual levels were scaled by exposure times); a new set of data was collected on a General Electric XRD-5 diffractometer, in order that decomposition could be more carefully monitored.

A new crystal was selected (monoclinic prism elongated on b, dimensions $0.002 \times 0.008 \times 0.130$ mm) and aligned on the diffractometer with its b axis coincident with the ϕ axis of the goniometer. The intensities of 970 independent reflections (index sets hkl and $\bar{h}kl$) accessible within the range θ(Cu Kα) $\leq 50.5°$ were measured using nickel-filtered Cu Kα radiation. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα radiation with the window centered on the Cu Kα peak. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively. A θ–2θ scan technique was employed. Each intensity ($I = P - B_1 - B_2$) was obtained from a 2θ scan (P) at 4°/min from $2\theta_{calcd} - 1.33°$ to $2\theta_{calcd} + 1.33°$ and stationary background counts for 20 sec at the limits of the scan (B_1, B_2).[20] A take-off angle of 2° was used. No reflections exceeded the linear response range of the counter. Three reflections were checked at frequent intervals and showed a maximum variation of ±2%, which was random with time. Thus, there was no evidence for significant crystal decomposition. The intensities of 19 $\bar{h}\bar{k}\bar{l}$ reflections were measured to investigate the effect of the large imaginary anomalous dispersion terms of rhenium and iodine. Since no significant variation between I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$ was observed, the space group was considered likely to be the centrosymmetric $P2_1/m$.

The experimental data were converted to values of $|F_o|$ and $|F_o|^2$ (on a relative scale) by the Fortran II program PMMO written by M. J. B. As the intensities were calculated, 347 reflections were rejected using two criteria: (1) $I \leq 0$; (2) $I < 3(P + B_1 + B_2)^{1/2}$. The remaining 623 reflections were used to solve and refine the structure. In the final stages of refinement absorption corrections were applied to these data. The calculated transmission factors fell into the range 0.311–0.774. The very small crystal size and consequent uncertainty in the measurement of its dimensions precludes a highly accurate absorption correction. The calculated and experimental absorption curves for the $0k0$ reflections, obtained by rotation about the ϕ axis at $\chi = 90°$, may be used as an estimate of the accuracy. An over-all variation of 50% in I_{0k0} was reduced to 15% by the corrections.

Solution and Refinement of the Structure

The symmetry of the three-dimensional Patterson function[21] supported the choice of $P2_1/m$ as the space group. The appearance of Re–Re and I–I vectors along the Harker line (0, v, 0) implied that there were both rhenium and iodine atoms related by a mirror

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[17] (a) M. Freni and V. Valenti, *Gazz. Chim. Ital.*, **90**, 1436 (1960); *Inorg. Syn.*, **7**, 185 (1963); (b) R. D. Peacock, A. J. E. Welch, and L. T. Wilson, *J. Chem. Soc.*, 2901 (1958); *Inorg. Syn.*, **7**, 187 (1963).

[18] A. Taylor and H. Sinclair, *Proc. Phys. Soc.*, **57**, 126 (1945); J. B. Nelson and D. P. Riley, *ibid.*, **57**, 160 (1945).

[19] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, p 122.

[20] D. P. Shoemaker's "MIXG-2, MIT X-Ray Goniometer Package," 1962, was used to compute the $2\theta_{calcd}$ values.

[21] Computed using the program of W. G. Sly, D. P. Shoemaker, and J. H. van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, ERFR-2," 1962.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR Re_3I_9

H	L	FOBS	FCAL
****K = 0******			
1	0	1138	962
2	0	1004	964
3	0	729	707
4	0	3975	4103
5	0	3374	3444
6	0	1170	1187
7	0	1420	1585
8	0	2106	2039
0	1	2256	2283
-1	1	3600	3723
1	1	1814	1905
-2	1	1256	1101
2	1	2366	2506
-3	1	3466	3644
3	1	748	685
-4	1	3088	3267
4	1	1275	1235
5	1	2145	2256
-5	1	3100	3103
7	1	2165	2156
8	1	2170	2271
-8	1	2570	2373
0	2	1296	1335
1	2	2379	2307
-1	2	637	801
-2	2	2235	2385
-3	2	623	362
3	2	2666	2790
-4	2	1751	1764
4	2	2511	2561
-5	2	[illegible]	1404
5	2	2576	2626
-6	2	1480	1414
-7	2	2204	2111
-8	2	2800	2696
-9	2	1259	1141
0	3	9409	9812
-1	3	2507	2337
1	3	740	613
2	3	1774	1782
-2	3	901	897
-3	3	1380	1351
3	3	2358	2384
-4	3	3716	3868
4	3	2505	2559
-5	3	2830	2843
5	3	2177	2202
-6	3	1679	1609
6	3	1203	1215
7	3	1506	1626
-8	3	3194	3018
0	4	1747	1723
-1	4	4549	4550
1	4	1867	1912
2	4	1797	1789
-2	4	1322	1274
-3	4	3467	3423
-4	4	2738	2845
-5	4	3217	3242
5	4	1979	2075
-6	4	1195	1298
-8	4	2658	2557
0	5	727	858
-1	5	623	501
1	5	1044	1116
2	5	804	818
-2	5	1932	1995
3	5	1990	1994
-3	5	818	913
-4	5	1482	1482
4	5	2078	2009
-5	5	738	571
5	5	1699	1686
-6	5	1658	1686
-7	5	2173	2155
-8	5	2065	2009
0	6	5079	5158
-1	6	2409	2490
1	6	1111	1109
-2	6	1274	1079
2	6	1049	1101
3	6	2116	2188
-3	6	1457	1466
4	6	1461	1439
-4	6	1798	1851
-5	6	1147	1054
-6	6	1540	1647
-8	6	2889	2892
0	7	766	826
-1	7	4148	4185
1	7	1078	1081
-2	7	1449	1469
-3	7	2021	2029
-4	7	1334	1310
-5	7	2907	2989
-6	7	1576	1650
0	8	1225	1035
-1	8	959	611
-2	8	1416	1344
-3	8	1215	1329
-4	8	1559	1525
-6	8	1203	1194
****K = 1******			
1	0	3276	3175
3	0	1041	1035
5	0	1763	1889
6	0	1547	1523
0	1	2872	2783
1	1	969	962
-2	1	802	708
2	1	3316	3200
-3	1	4392	4472
3	1	512	446
-4	1	2976	3110
4	1	3109	3106
5	1	673	782
-5	1	1200	1093
-6	1	919	842
-7	1	1163	983
8	1	1549	1651
0	2	1135	1100
-1	2	1541	1458
-2	2	2558	2524
2	2	466	512
3	2	3224	3252
-4	2	2708	2691
4	2	2635	2663
-5	2	2326	2241
5	2	1149	1091
6	2	1134	1199
-8	2	1669	1703
-9	2	982	1023
-1	3	2847	2785
1	3	1995	1965
2	3	1123	1007
3	3	1363	1385
-4	3	596	548
-5	3	2237	2286
5	3	1181	1217
-6	3	1294	1375
6	3	731	931
-9	3	1451	1552
0	4	3718	3691
-1	4	778	823
1	4	517	420
2	4	1762	1736
-2	4	694	656
-3	4	3309	3210
-4	4	3530	3570
4	4	2425	2511
-7	4	870	995
0	5	626	580
-1	5	891	834
2	5	1005	864
-2	5	953	900
3	5	1745	1769
-4	5	2234	2252
4	5	2117	2145
-5	5	2476	2484
-8	5	1460	1467
-1	6	1247	1322
1	6	1418	1361
-2	6	821	723
2	6	1215	1177
3	6	1078	1139
-3	6	1036	1036
-4	6	653	556
-5	6	1423	1516
-8	6	807	915
0	7	2876	2917
1	7	764	775
-3	7	1303	1307
-4	7	3076	3132
-1	8	715	616
-4	8	1941	1938
-5	8	1887	2068
-6	8	710	648
****K = 2******			
0	0	1466	1111
1	0	1428	1146
3	0	733	811
4	0	2117	2081
5	0	913	1006
8	0	689	586
0	1	849	664
1	1	1579	1613
-2	1	960	844
2	1	2138	2204
-3	1	1917	2099
4	1	2115	2053
-6	1	824	860
7	1	1317	1228
8	1	941	884
1	2	983	910
-1	2	2053	2169
-2	2	2309	2435
2	2	1054	946
3	2	1449	1502
-4	2	1004	997
-5	2	979	1038
-6	2	775	940
6	2	1179	1182
-7	2	2035	2012
-8	2	947	978
0	3	647	396
-1	3	578	560
1	3	1613	1498
2	3	565	466
-2	3	804	838
3	3	1398	1380
-4	3	2660	2518
4	3	626	731
-5	3	1667	1627
5	3	904	817
-8	3	784	767
0	4	639	634
1	4	532	526
2	4	841	978
-2	4	1286	1202
-3	4	1322	1360
3	4	751	653
4	4	1596	1678
-6	4	824	662
-1	5	915	903
1	5	1284	1299
2	5	960	1074
-2	5	917	932
-5	5	1381	1353
-7	5	1820	1650
-1	6	1186	1205
1	6	755	822
-2	6	684	734
3	6	1044	936
-4	6	1646	1595
-5	6	1948	2009
-6	6	767	585
-2	7	1258	1035
2	7	640	443
-3	7	1088	894
-5	7	1151	1115
****K = 3******			
1	0	2598	2525
2	0	4404	4369
4	0	1730	1739
6	0	1118	1004
7	0	1314	1249
8	0	1071	944
0	1	1397	1358
-1	1	856	886
1	1	2725	2545
-2	1	3055	3085
-3	1	2304	2349
3	1	1873	1893
-4	1	2875	2922
4	1	1135	1189
5	1	1062	969
6	1	2001	1988
-8	1	1387	1273
0	2	1448	1372
1	2	717	609
-1	2	3517	3403
2	2	1535	1479
-3	2	1013	930
3	2	1986	2050
4	2	2436	2356
-5	2	1018	955
5	2	752	551
-6	2	2956	2842
7	2	992	911
0	3	674	379
-1	3	1664	1603
1	3	2886	2809
2	3	3894	3838
-2	3	2749	2719
3	3	620	615
-4	3	2251	2333
4	3	1034	1003
-5	3	1007	966
-6	3	1069	1009
6	3	684	595
-8	3	1224	1103
0	4	1246	1283
-1	4	1798	1803
2	4	596	396
-2	4	3099	3050
-3	4	3037	2946
3	4	1659	1661
-4	4	1892	1828
4	4	1345	1308
-5	4	787	758
5	4	955	924
-6	4	1195	1123
-8	4	1448	1408
0	5	1681	1710
-1	5	2271	2306
1	5	803	796
2	5	672	601
3	5	1561	1522
4	5	1070	1213
-5	5	1442	1418
-6	5	2464	2500
-1	6	986	1085
1	6	2002	1991
-2	6	867	655
2	6	2746	2792
3	6	741	812
-3	6	765	595
-4	6	1683	1761
-7	6	988	1026
-8	6	1026	1014
-1	7	1220	1204
1	7	968	1027
-2	7	1890	1672
2	7	989	937
-3	7	3117	3141
-6	7	869	805
-1	8	1365	1418
-5	8	1531	1607
****K = 4******			
0	0	621	751
1	0	5396	5532
2	0	773	743
3	0	2375	2429
4	0	2211	2280
5	0	1137	1111
6	0	1963	1972
7	0	1233	1259
0	1	761	864
-1	1	1863	1912
-2	1	5306	5537
2	1	2384	2491
4	1	1881	1912
-5	1	2095	2122
6	1	2812	2790
-6	1	2829	2787
7	1	1374	1449
-7	1	1473	1443
-8	1	712	562
1	2	1465	1352
-2	2	1986	2152
2	2	4458	4385
-3	2	780	848
3	2	628	517
-4	2	1027	1070
5	2	2022	2038
-6	2	2762	2694
6	2	2495	2436
-7	2	2509	2362
7	2	1245	1142
-1	3	3216	3208
1	3	5145	5106
2	3	1427	1415
-2	3	823	751
-3	3	3152	3190
3	3	1104	1050
-4	3	2694	2805
5	3	717	613
-6	3	1210	1190
6	3	1770	1673
-7	3	2122	1957
-1	4	1414	1394
2	4	2356	2332
-2	4	5311	5437
3	4	799	673
4	4	1615	1569
-5	4	1301	1332
-6	4	2840	2802
-7	4	1755	1697
-1	5	905	862
1	5	710	696
2	5	2903	2879
-2	5	1972	2018
3	5	1020	954
-3	5	783	857
-6	5	2424	2415
-7	5	2296	2360
0	6	876	1072
-1	6	1091	1214
1	6	3112	3116
-2	6	1156	1100
2	6	843	847
3	6	625	588
-3	6	2236	2197
-4	6	1624	1646
-7	6	2063	2004
-1	7	981	881
-2	7	4061	4001
-4	7	715	642
-6	7	2239	2267
-1	8	1145	1162
-2	8	1730	1666
-3	8	893	954
****K = 5******			
2	0	3684	3727
3	0	588	545
4	0	692	726
5	0	771	878
6	0	3207	3356
0	1	553	420
-1	1	1415	1433
1	1	2171	2179
-2	1	2769	2845
2	1	3102	3087
3	1	2166	2199
5	1	1647	1621
-6	1	1351	1423
7	1	1341	1374
-7	1	1133	1224
0	2	1274	1235
1	2	506	488
-1	2	1725	1719
-2	2	3009	3031
2	2	2159	2038
-3	2	1575	1644
3	2	594	612
-5	2	954	927
5	2	656	761
-6	2	1027	947
6	2	975	903
-7	2	1452	1349
1	3	1142	1107
2	3	2708	2578
-2	3	3416	3352
-3	3	1751	1725
-4	3	1196	1124
5	3	1200	1082
-6	3	3501	3484
6	3	2403	2371
-7	3	737	611
-8	3	1085	1073
-1	4	1859	1845
1	4	2634	2682
2	4	1794	1667
-2	4	2286	2261
-3	4	1082	913
3	4	1761	1673
5	4	1867	1857
-6	4	1794	1798
-7	4	1252	1321
0	5	1041	1049
-1	5	1572	1559
2	5	1323	1325
-2	5	2043	2046
3	5	827	835
-3	5	1118	968
-4	5	678	508
-5	5	678	601
-6	5	741	683
-7	5	787	934
1	6	1060	1044
-2	6	2188	2107
2	6	1410	1459
-3	6	2262	2178
-4	6	921	865
-6	6	2287	2387
-7	6	1233	1266
-1	7	1214	1164
1	7	2249	2297
-2	7	1023	800
-3	7	1605	1533
-4	7	653	585
-6	7	1317	1288
****K = 6******			
0	0	3472	3239
1	0	725	758
2	0	671	585
3	0	756	690
4	0	994	1033
5	0	1906	1961
0	1	879	855
-1	1	822	784
1	1	1817	1761
2	1	2265	2228
3	1	3679	3608
-4	1	745	698
0	2	1812	1818
1	2	1177	1143
-1	2	2185	2249
-2	2	2307	2152
-3	2	3344	3360
4	2	863	908
-5	2	1571	1414
0	3	2484	2349
-1	3	868	1074
1	3	921	738
2	3	1278	1196
-3	3	1508	1641
-4	3	1600	1376
4	3	899	927
-5	3	1737	1802
5	3	1078	1262
-6	3	857	1040
-7	3	797	753
1	4	910	933
2	4	2068	2081
3	4	2602	2541
-6	4	1383	1424
-7	4	949	831
0	5	1751	1702
-1	5	1444	1441
1	5	1161	1153
2	5	1177	1288
-2	5	2247	2206
-3	5	1835	1849
-5	5	1628	1590
0	6	977	983
-1	6	806	838
1	6	817	913
2	6	975	957
-3	6	1526	1613
-4	6	1837	1876
-5	6	1022	1073
-6	6	1031	1018
-1	7	1153	1020
****K = 7******			
1	0	1202	1189
6	0	1702	1678
1	1	731	613
2	1	2504	2532
-3	1	2125	2124
-4	1	1749	1879
4	1	884	937
-5	1	1350	1251
0	2	696	623
-2	2	2110	2128
3	2	1502	1487
-4	2	838	666
4	2	1655	1803
-5	2	1465	1298
5	2	1255	1233
-1	3	1054	1075
1	3	896	776
-3	3	1062	1175
-5	3	747	734
-6	3	1412	1543
0	4	1254	1242
1	4	961	1055
2	4	1786	1684
-3	4	1695	1650
-4	4	1899	2018
4	4	776	864
0	5	702	663
-2	5	1212	1162
-4	5	724	695
-5	5	1525	1540
-3	6	1580	1531
****K = 8******			
0	0	3964	3977
1	0	974	947
4	0	3213	3227
5	0	726	477
0	1	1669	1656
-1	1	1380	1571
1	1	1193	1248
-2	1	1016	923
-3	1	1041	905
3	1	1283	1316
-4	1	1409	1452
4	1	1426	1429
5	1	1313	1374
-5	1	953	967
0	2	1543	1491
1	2	1516	1517
-1	2	925	949
2	2	783	816
-3	2	1250	1146
3	2	767	750
-4	2	1239	1342
4	2	1275	1325
-5	2	1079	1027
5	2	686	690
0	3	3261	3152
1	3	1245	1223
3	3	994	999
-4	3	3453	3476
4	3	2127	1994
0	4	1054	1104
-1	4	1631	1676
1	4	1213	1150
-2	4	1173	949
3	4	1437	1441
-3	4	952	974
-4	4	1198	1184
-5	4	1353	1343
-6	4	942	788
0	5	1211	1216
1	5	1210	1266
-3	5	1158	1114
-4	5	841	840
-5	5	750	588
-1	6	949	955
****K = 9******			
1	0	816	792
2	0	739	843
3	0	1381	1390
5	0	1941	1924
0	1	3301	3294
1	1	2775	2915
4	1	2708	2902
-5	1	1066	939
0	2	3151	3115
-1	2	3556	3593
3	2	787	726
-4	2	2306	2461
-5	2	974	665
-1	3	922	1023
2	3	917	864
-3	3	1336	1353
3	3	998	854
-5	3	2210	2302
0	4	2856	2928
-1	4	697	718
1	4	1492	1443
2	4	677	698
-2	4	992	842
-4	4	952	783
0	5	2756	2694
-1	5	3002	3138
-2	5	755	692
****K = 10******			
0	0	801	692
3	0	975	1063
4	0	2122	2265
0	1	968	911
2	1	1850	1918
-3	1	1107	984
3	1	1323	1475
0	2	903	836
1	2	1265	1267
-2	2	2037	1985
-3	2	1261	1292
1	3	835	901
****K = 11******			
1	1	612	496

plane. The coordinates of all independent atoms (two rhenium and six iodine atoms) were obtained from the Patterson function; a trial structure similar to that of the Re_3Cl_9 molecule was postulated, with the mirror plane perpendicular to the plane of the triangle of rhenium atoms. A structure factor calculation (using film data) at this point had a discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.450$ (where F_c's are the calculated and F_o's the observed structure factors); the weighted residual $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$ using unit weights was 0.468. Refinement did not proceed satisfactorily (converged to $R_1 = 0.264$, $R_2 = 0.306$); hence the film data were discarded and the refinement was carried out using the data collected with the diffractometer.

Four cycles of full-matrix least-squares refinement[22] of the scale factor and positional and isotropic thermal parameters for each atom led to $R_1 = 0.089$ and $R_2 = 0.107$. The experimental weighting scheme used was similar to that of Doedens and Ibers.[23] The atomic scattering factors used for rhenium and iodine are those of Cromer and Waber;[24] corrections[25] for the real and imaginary parts of anomalous scattering for rhenium and iodine were included in the calculated structure factors.[26] At this point absorption corrections[27] were introduced and one more cycle of full-matrix refinement resulted in $R_1 = 0.061$ and $R_2 = 0.069$. Two more cycles of full-matrix least-squares refinement in which the scale factor, positional parameters, and an anisotropic temperature factor (suggested by features in difference maps) of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were refined for each atom resulted in convergence, with $R_1 = 0.044$ and $R_2 = 0.053$. A comparison of $|F_o|$ and $|F_c|$ showed no evidence of serious extinction and no correction was made.

In the last cycle of refinement no parameter shift was greater than 0.01 esd. A final electron density difference map[28] ($F_o - F_c$) showed features as high as 2.0 $e^-/Å^3$ *near* the rhenium and iodine atoms; the major reason for these seemingly random features is probably the limited accuracy of the absorption corrections. Calculation of the structure factors for the rejected reflections gave no $|F_c|$ greater than twice the minimum observable $|F_o|$. The final standard deviation of an observation of unit weight is 0.92, indicating a slight overestimation in the standard deviation of the intensity data. This suggests a reduction in the "p factor" used for this work. Table I lists the observed structure amplitudes, $10|F_o|$ and the final calculated structure amplitudes, $10|F_c|$, each in electrons.

Results

The final fractional coordinates for all atoms are given in Table II, and the elements of the anisotropic temperature factor tensors are recorded in Table III. Estimated standard deviations were derived from the inverse matrix of the final least-squares refinement cycle. The crystal structure is shown in projection down the c^* and b axes in Figures 1 and 2, respectively.

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[22] C. T. Prewitt, "A Fortran-IV Full-Matrix Least-Squares Program, SFLS5," 1966. In this program the function minimized is $\Sigma w(|F_o| - |F_c|)^2$.

[23] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). Our weighting scheme differs only in that p, the "uncertainty factor," was assigned a value of 0.045.

[24] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[25] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[26] J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[27] Calculated using our local modification of the GONO9 program by W. C. Hamilton.

[28] Calculated using our local modification of the FORDAP program by A. Zalkin.

Table II

Final Atomic Positional Parameters[a] for Re_3I_9

Atom	Type of Position	x	y	z
Re(1)	4f	0.13660 (20)	0.36083 (17)	0.17201 (20)
Re(2)	2e	0.36599 (31)	0.25000	0.18045 (31)
I(1B)	4f	0.38909 (39)	0.49050 (32)	0.17661 (39)
I(2B)	2e	−0.13366 (47)	0.25000	0.15286 (50)
I(1T)	4f	0.19528 (31)	0.41018 (26)	0.48020 (29)
I(2T)	2e	0.56768 (51)	0.25000	0.46950 (50)
I(3T)	4f	0.01720 (31)	0.40885 (25)	−0.15359 (27)
I(4T)	2e	0.39833 (51)	0.25000	−0.10110 (49)

[a] Estimated standard deviations (in parentheses) in this and following tables occur in the least significant digits in each case.

Table III

Anisotropic Temperature Factors ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	13	β_{23}	Equivalent isotro ic B
Re(1)	44 (3)	18 (2)	36 (3)	0 (2)	18 (2)	0 (2)	1.04
Re(2)	38 (4)	22 (3)	55 (5)	0	21 (3)	0	1.23
I(1B)	124 (6)	52 (3)	145 (6)	−17 (4)	58 (5)	−6 (3)	3.36
I(2B)	63 (7)	47 (4)	99 (7)	0	39 (5)	0	2.26
I(1T)	101 (5)	36 (3)	40 (4)	5 (3)	24 (3)	0 (3)	2.01
I(2T)	89 (7)	73 (5)	70 (7)	0	−7 (5)	0	3.03
I(3T)	89 (5)	26 (3)	34 (4)	13 (3)	21 (3)	1 (3)	1.67
I(4T)	113 (8)	76 (5)	76 (7)	0	66 (6)	0	2.87

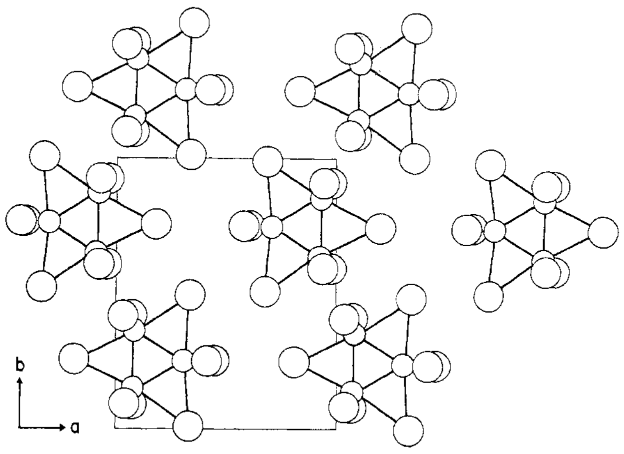

Figure 1.—The molecular packing as seen in projection down the c^* axis.

Figure 3 shows one Re_3I_9 unit, together with part of one of its neighboring Re_3I_9 units. Figure 3 also shows the numbering system employed, in which all atoms lying on 4f equipoints are given odd serial numbers, all atoms in 2e equipoints have even serial numbers, and T and B signify terminal and bridging iodine atoms, respectively. Bond lengths, angles, and nonbonded contacts[29] are given in Table IV. The two independent Re–Re separations are: Re(1)–Re(1)′, 2.507 (4) Å; Re(1)–Re(2), 2.440 (3) Å.

Discussion

The Re_3I_9 Structure.—Rhenium(III) iodide is composed of Re_3I_9 molecules similar in structure to the Re_3Cl_9 and Re_3Br_9 cluster groups which have already been characterized.[2–11] The Re_3I_9 units are linked

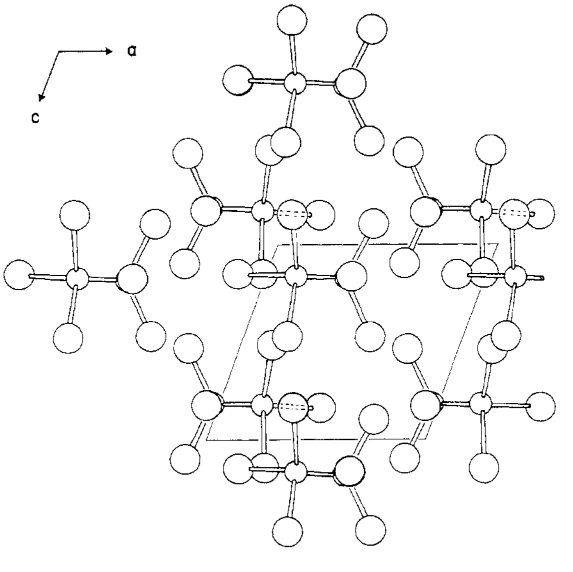

Figure 2.—The molecular packing as seen in projection down the b axis.

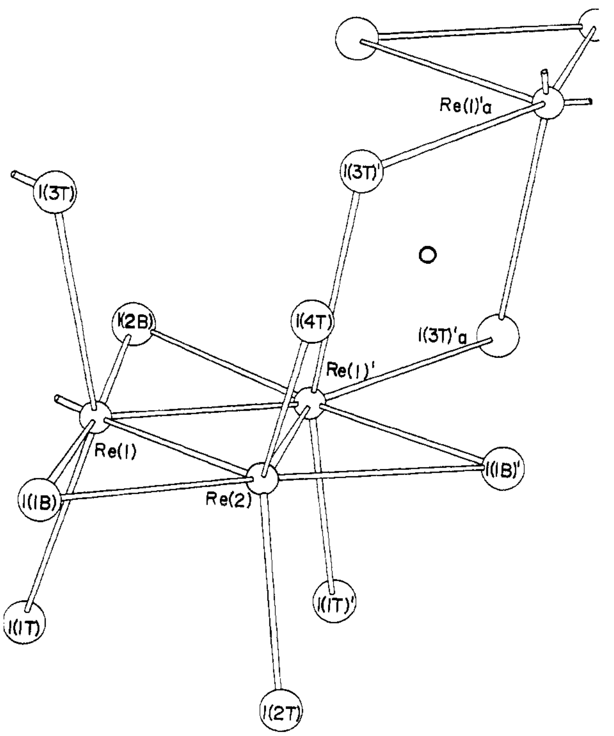

Figure 3.—The Re_3I_9 trinuclear cluster in rhenium(III) iodide, together with a portion of a centrosymmetrically related nearest neighbor to illustrate intercluster linking *via* iodine bridges.

together by bridging iodine atoms in the same way as are the Re_3Cl_9 units in rhenium(III) chloride,[11] except that in the iodide the bridge system is incomplete. Whereas each of the three Re atoms in each Re_3Cl_9 unit is involved in bridging so that four-layered infinite sheets are formed, in Re_3I_9 only two of each three Re atoms participate in the intermolecular linking. Thus, zigzag chains are formed. This feature can best be seen in Figure 1, where it is clear that the chains run parallel to the b axis. As a result of this incomplete bridging system, two of the rhenium atoms, Re(1) and

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(29) Bond distances and angles were calculated with local modifications of the Wood program MGEOM and Shoemaker program DISTAN.

TABLE IV

PRINCIPAL INTERATOMIC DISTANCES AND ANGLES

Bond distances, Å		Intramolecular nonbonded contacts, Å	
Re(1)–Re(2)	2.440 (3)	I(1T)–I(1T)′	3.623
Re(1)–Re(1)′	2.507 (4)	I(3T)–J(3T)′	3.593
Re(1)–I(1B)	2.743 (4)	I(1T)–I(2T)	3.917
Re(1)–I(2B)	2.745 (4)	I(3T)–1(4T)	3.834
Re(2)–I(1B)	2.729 (4)	I(1B)–I(2T)	3.717
Re(1)–I(1T)	2.635 (3)	I(1B)–I(4T)	3.677
Re(1)–I(3T)	2.744 (3)	I(1B)–I(1T)	3.804
Re(2)–I(2T)	2.580 (5)	I(1B)–I(3T)	3.766
Re(2)–I(4T)	2.596 (5)	I(2B)–I(1T)	3.840
Re(1)–I(3T)$_a$	2.944 (3)	I(2B)–I(3T)	3.878
		Re(2)–I(1T)	3.950
		Re(2)–I(3T)	3.961

Interbond angles	
Atoms	Deg
Re(1)–Re(1)′–Re(2)	59.09 (10)
Re(1)–Re(2)–Re(1)′	61.82 (11)
Re(1)–I(1B)–Re(2)	52.96 (9)
Re(1)–I(2B)–Re(1)′	54.33 (10)
Re(1)–Re(2)–I(1B)	63.80 (10)
Re(2)–Re(1)–I(1B)	63.24 (10)
Re(1)–Re(1)′–I(2B)	62.83 (14)
I(1T)–Re(1)–I(1B)	90.04 (11)
I(1T)–Re(1)–I(3T)$_a$	78.04 (9)
I(1T)–Re(1)–I(2B)	91.07 (10)
I(3T)–Re(1)–I(1B)	86.67 (11)
I(3T)–Re(1)–I(3T)$_a$	75.86 (13)
I(3T)–Re(1)–I(2B)	89.89 (10)
I(1B)–Re(2)–I(2T)	88.82 (15)
I(1B)–Re(2)–I(4T)	87.30 (13)
I(2T)–Re(2)–I(4T)	131.18 (14)
I(1T)–Re(1)–I(3T)	153.86 (11)
Re(1)–I(3T)$_a$–Re(1)$_a$	104.15 (15)
I(1B)–Re(2)–I(1B)′	170.45 (19)
I(1B)–Re(1)–I(2B)	174.31 (11)

Intermolecular contacts			
Atom A	Atom B	Vector from molecule containing A to molecule containing B	Distance, Å
I(3T)	I(3T)	$(-x, 1-y, -z)$	3.500
I(3T)	I(1T)	$(-x, 1-y, -z)$	3.521
I(1B)	1(4T)	$(1-x, 1-y, -z)$	3.716
I(1B)	I(3T)	$(-x, 1-y, -z)$	3.858
I(1T)	I(4T)	(0, 0, 1)	3.948
I(2B)	I(3T)	$(-x, 1-y, 1-z)$	4.005
I(2B)	I(4T)	(1, 0, 0)	4.121
I(1B)	I(2T)	$(1-x, 1-y, 1-z)$	4.196
I(1T)	I(2T)	$(1-x, 1-y, 1-z)$	4.369
Re(1)	Re(1)	$(-x, 1-y, -z)$	4.489

Re(1)′, which are crystallographically equivalent by virtue of the mirror planes at $y = {}^1/_4$ and ${}^3/_4$, have a fifth iodine neighbor lying in the plane of the Re_3 cluster whereas the other rhenium atom, Re(2), has only four intramolecular iodine neighbors. This is most clearly seen in Figure 3. In subsequent discussion we shall sometimes refer to the Re(2) atoms as *deficient*, using the nomenclature of Elder and Penfold.

The asymmetric unit consists of half of the Re_3I_9 molecule, which is divided by a crystallographic mirror plane passing through Re(2) and its two terminal iodine atoms, I(2T) and I(4T), and the iodine atom, I(2B), that forms a symmetrical bridge between Re(1) and Re(1)′.

Discussion of the Re_3I_9 structure and comparisons with other $Re_3X_{9+n}{}^{n-}$ structures will be facilitated by the summary of principal structural features of such structures which is presented in Table V. Some features of the Re_3I_9 structure specially deserving of attention follow.

(1) The Re–Re bond lengths are not equal. The longest bond (2.507 Å) occurs between the nondeficient rhenium atoms; the two short bonds associated with the deficient rhenium atom are 2.440 Å. Thus, there is an increase in Re–Re bond strength for a rhenium atom which is six-coordinate instead of seven-coordinate.

Although it might have been expected that the larger iodine atoms would cause a lengthening of the Re–Re bonds, there are no significant differences between these bonds in Re_3I_9 and the corresponding bonds in the $Re_3X_{11}{}^{2-}$ (X = Cl, Br) systems, which also contain one deficient and two nondeficient Re atoms.

(2) The set of out-of-plane iodine atoms on Re(1) is quite different structurally from the set on Re(2). One of the iodine atoms bonded to Re(1), namely I(3T), is involved in intermolecular bridging, while the other, I(1T), is terminal. Their bond distances, 2.744 (3) and 2.635 (3) Å, respectively, parallel those observed for similar environments in Re_3Cl_9. The shorter bond distances from Re(2), the deficient rhenium atom, to its two *terminal* iodine atoms, I(2T) and I(4T), are 2.580 (5) and 2.596 (5) Å, respectively. These are significantly shorter than the Re(1)–I(1T) distances, which parallels the shortening of bonds from deficient rhenium to out-of-plane bromine atoms in $Re_3Br_{11}{}^{2-}$.

(3) The Re–I intramolecular bridge bonds are 2.743 (4), 2.745 (4), and 2.729 (4) Å. The shortest distance occurs for an iodine atom bonded to the deficient rhenium atom; however, it is not significantly different from the others. The iodine atoms I(1B) and I(2B) are shifted slightly out of the plane of the three rhenium atoms by 0.04 and 0.08 Å, respectively. The shift moves I(2B) toward I(3T) which is farther from the plane of rhenium atoms and away from I(1T) which is closer to the plane of rhenium atoms; a similar effect, of expected smaller magnitude, is observed for I(1B). The net result is that the contacts from I(1B) to I(1T) and I(3T) are nearly equal, and the contacts from I(2B) to I(1T) and I(3T) are nearly equal.

(4) The Re(1)–I(3T)$_a$ bonds (where I(3T)$_a$ is an I(3T) atom of an adjacent Re_3I_9 unit) are 2.944 (3) Å, about 0.2 Å longer than the longest Re–I bond within the molecular unit. A similar effect is observed in Re_3Cl_9.

(5) The intermolecular Re–Re distance, 4.489 Å, precludes any major direct interaction.

(6) The absence of an iodine intercluster bridge from another unit to Re(2), the deficient rhenium atom, relieves some of the steric strain and there is a concomitant contraction of the I(2T)–Re(2)–I(4T) angle to 131.18 (14)°. The analogous angle subtended by a pair of out-of-plane iodine atoms at the nondeficient rhenium atom is 153.86 (11)°. In $Re_3Br_{11}{}^{2-}$, the analogous angles at deficient and nondeficient rhenium atoms are 134 and 159°, respectively.

Table V

Structural Features of Trinuclear Rhenium(III) Halo Complexes

Formula	Ref	Description and general characteristics
$Re_3X_{12}^{3-}$ (X = Cl or Br)	2, 3, 8	Three types of halogen atoms: (1) three bridging chlorine atoms, (2) six terminal out-of-plane chlorine atoms, and (3) three terminal in-plane chlorine atoms. Short Re–Re bonds (~2.48 Å) are all equivalent; each rhenium atom has five halogen atoms coordinated to it. Virtual symmetry is D_{3h}
$Re_3X_{11}^{2-}$ (X = Cl or Br)	4, 8	Again, three types of halogen atoms; however, there are only *two* terminal in-plane halogen atoms. Thus, there are two rhenium atoms with fivefold halogen coordination, while the third rhenium atom, having only four halogens bonded to it, is termed "deficient." Two independent Re–Re distances (2.483 and 2.435 Å for X = Cl; 2.496 and 2.433 Å for X = Br). Removal of one terminal in-plane bromine atom relieves steric strain and out-of-plane bromine atoms bend so that in $Re_3Br_{11}^{2-}$ the Br–Re–Br angle at the deficient Re decreases from the normal range of 155–160° to 134°. Angular contraction does not occur for $Re_3Cl_{11}^{2-}$ probably owing to the water molecule coordinated to the halogen-deficient rhenium atom
$Re_3Br_{10}^{-}$	9	Probably similar to the $Re_3X_{11}^{2-}$ system with only *one* terminal in-plane bromine atom. There would be two "deficient" rhenium atoms
Re_3Cl_9	11	Three types of halogen atoms: (1) three intramolecular bridging atoms, (2) three terminal, out-of-plane chlorine atoms, similar to those in all of the above cases, and (3) three out-of-plane chlorine atoms involved in intercluster bridging so that each rhenium has five chlorines bonded to it as in $Re_3Cl_{12}^{3-}$. Re–Re bonds are equivalent (2.489 Å). Considerable lengthening of bonds from Re to chlorine involved in intermolecular bridging occurs. Virtual symmetry is C_{3v}
Re_3I_9	This work	Four types of halogen atoms: (1) three intramolecular bridging atoms, (2) two terminal out-of-plane atoms attached to nondeficient Re atoms, (3) *two* out-of-plane iodine atoms involved in intercluster bridging so that *two* rhenium atoms are nondeficient, and (4) two iodine atoms, which do *not* bridge to other clusters, bonded to a halogen-deficient rhenium atom. Two independent Re–Re distances (2.440, 2.507 Å). The angle subtended by out-of-plane iodine atoms at deficient rhenium is 131°; that subtended by out-of-plane halogens at nondeficient rhenium is 154°. Considerable lengthening of bonds from Re to the iodine atom involved in intercluster bridging occurs

It is unlikely that intermolecular forces are the cause of this reduction. Table III shows that there are no intermolecular contacts of less than ~4 Å involving I(2T) or I(4T). The important contacts, then, are the intramolecular contacts I(1T)–I(2T) and I(3T)–I(4T), which are 0.2–0.3 Å longer than the I–I contacts of the terminal iodine atoms attached to the nondeficient rhenium atoms.

The structure of Re_3I_9 thus represents an independent confirmation of the result obtained by Penfold and coworkers,[8] namely, that there is a significant reduction in the off-plane X–Re–X angle when the rhenium atom is deficient.

Reexamination of the Re_3Br_9 Structure.—In view of the evidence obtained here supporting the idea that the X–Re–X angle at a deficient rhenium atom tends to contract significantly, we were led to reconsider the contrary indication previously obtained for the Re_3Br_9 molecule.[6]

The crystal structure[6] of $(C_9H_7NH)_2Re_4Br_{15}$ is built up of quinolinium cations, $ReBr_6^{2-}$ anions, and, according to the analytical and X-ray structural evidence then available, Re_3Br_9 units with off-plane Br–Re–Br angles of ~155°. The report of this structure antedates the first report of an angle reduction at a deficient rhenium atom, and, at the time it was done, the large angles were not considered to be an unusual feature. However, in light of current results, there are indeed unusual features. In spite of the supposed deficiency of the rhenium atoms in the Re_3Br_9 unit, the terminal out-of-plane bonds (2.45 Å) are not significantly shorter than the normal range (2.48–2.49 Å), and the angle subtended by two out-of-plane bromines (~155°) is in the normal range expected for that at nondeficient rhenium atoms. A reexamination of the structure was therefore undertaken.

Assuming the space group to be the centrosymmetric Cmcm (no. 63), the published data were used, along with the positional and thermal parameters of only the rhenium and bromine atoms, in four cycles of full-matrix least-squares refinement.[22] The values of R_1 and R_2 (unit weights) at this stage were 0.154 and 0.145, respectively; the reported value of R_1 for *all* atoms was 0.15. A difference Fourier map was then computed;[28] it revealed many peaks with electron density $\sim 2e^-/\text{Å}^3$ in the vicinity of the reported position of the quinolinium cation and in the vicinity of the rhenium atoms ($\sim 4e^-/\text{Å}^3$), near the position where one might expect to find an in-plane terminal ligand atom, *i.e.*, at a distance of ~2.4 Å. Since many of the peaks in the region assigned to the quinolinium ion reach their maximum values at coordinates with $x \neq 0$, the exact mirror plane reported for the structure and hence the chosen space group would appear to be in serious doubt. The low accuracy and poor resolution in the *a* direction of the data preclude any meaningful refinement in an alternate space group (C2cm) and indeed all attempts to refine either the published coordinates or alternate solutions failed. In general, the addition of light-atom parameters gave no significant improvement in R_1 and R_2. This was consistent with the observation that the noise level of the difference Fourier (even away from the heavy-atom positions) was of the order expected for the light-atom peaks. Clearly a proper solution would require the collection of a more accurate and complete data set.

Intermolecular geometry calculations show that the presence of coordinated molecules at the terminal in-plane positions of the trinuclear unit leads to no unusually short contacts. Hence in the light of the general structural features observed for the trinuclear rhenium halide species, the compound should probably be reformulated as $[C_9H_7NH]_2[ReBr_6][Re_3Br_9(H_2O)_3]$. The presence of water molecules is thus probably the reason for the "opening up" of the out-of-plane X–Re–X angles in this case and in $[(C_6H_5)_4As]_2Re_3Cl_{11}$ (in which the formulation $[(C_6H_5)_4As]_2Re_3Cl_{11}H_2O$ was considered[4]). However, in neither case could the presence of water molecules be demonstrated with certainty from the available X-ray data.

Chemical Relationships.—Rhenium(III) iodide appears to form very few compounds; this is probably due to its insolubility in most solvents, which may arise from the strength of the Re–I–Re intermolecular bridge bonds and the relative inaccessibility of the sterically crowded molecule to solvation. The compound is appreciably soluble in dimethylformamide; however, decomposition is so rapid that neither solution spectra nor isolable products could be obtained. Observations in this laboratory indicate that Re_3I_9 reacts with diethylphenylphosphine and undergoes halogen-replacement reactions similar to those observed by other workers.[9,10] The current literature contains only one example of what appears to be a genuine complex of an intact trinuclear iodorhenium species.[17a] This compound is formed by reaction of ReI_3 and *p*-tolyl isocyanide; it has been formulated as $Re(p\text{-}CH_3C_6H_4NC)I_3$, and is nonconducting and diamagnetic. It would appear that there are no deficient rhenium atoms in this molecule.

TABLE VI

INTERPLANAR SPACINGS FOR "ReI_2" AND Re_3I_9 OBTAINED FROM X-RAY POWDER DATA

Re_3I_9 (this work)	ReI_2 (Fergusson, *et al.*[32])
8.27 vw	
7.38 s	
6.91 s	
6.69 s	
4.70 w	
3.46 m	3.43 m
3.24 vw	
3.10 vw	
2.96 m	2.95 w
2.84 m	2.81 w
2.77 s	2.73 m
2.68 m	
2.40 m	2.38 m
2.17 w	2.16 m
2.03 m	
2.01 s	2.02 s
1.96 w	
1.83 m	1.81 s
1.72 m	1.72 m
	1.28 s

Since the chemistry of rhenium was first investigated in the early 1930's by the Noddacks,[30] four iodides—ReI_4, ReI_3, ReI_2, and ReI—have been reported. The manner in which they are prepared and interconverted[31] might well raise questions about the structural and chemical distinctness of these precise stoichiometries. The structural study described here does establish the existence of a phase with ideal composition ReI_3, although, as we have already noted, this substance readily loses iodine. The extent to which iodine may be lost while the structure of the phase is retained has not been ascertained. It is, however, pertinent to record here some observations bearing on the possible relationship of "ReI_3" to "ReI_2."

The compound "ReI_2" was first reported in 1962;[32] it was prepared in a manner similar to either method A or B outlined above for the preparation of "ReI_3." Some interplanar spacings obtained from X-ray powder data for ReI_2 were given. We find that all but one reported value also occurs in the powder pattern of ReI_3 as shown in Table VI, although the intensities are slightly different, and there are many *d* values in the ReI_3 powder series which were not reported for ReI_2. It seems possible that ReI_2 may be an iodine-deficient form of the "ReI_3" (*i.e.*, Re_3I_9) phase.

Acknowledgments.—Fellowship support to B. M. F. from the National Institutes of Health, 1965–1966, is gratefully acknowledged. We thank Dr. L. N. Becka for helpful discussions.

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[30] I. Noddack and W. Noddack, "Das Rhenium," J. A. Barth Verlag, Leipzig, 1933.

[31] For a summary, see R. Colton, "The Chemistry of Rhenium and Technetium," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965, p 78.

[32] J. E. Fergusson, B. H. Robinson, and W. R. Roper, *J. Chem. Soc.*, 2113 (1962).