$PFe_3(CO)_{11}$ (average Fe–C(bridging), 2.04 and 1.87 Å).[7] As Dahm and Jacobson pointed out,[7] this asymmetry need not be the result of crystal packing forces but could be inherent in the bonding of the parent $Fe_3(CO)_{12}$, in which there is some evidence for unsymmetrical bridging carbonyl groups.[5] The C–O bond lengths average 1.17 Å, and the distances in the bridging carbonyl groups are not significantly longer than the average.

All the other bond lengths and valency angles (Table IV) are quite similar to those in related molecules. The angles in the $Fe_3(CO)_{10}$ moiety are similar to those in $(C_6H_5)_3PFe_3(CO)_{11}$,[7] and the dimensions of the diarsine ligand are quite close to those in $LFe_2(CO)_6$,[8] apart from the differences caused by the nonplanarity of the ligand in the latter compound. The valency angles at arsenic show deviations from the exact tetrahedral value, the Fe–As–C angles (113–121°) being larger than the C–As–C angles (99–104°).

The magnitudes of the principal axes of the thermal vibration ellipsoids of the iron and arsenic atoms are given in Table V. The largest vibrations are approximately perpendicular to the plane of the iron triangle.

TABLE V

MAGNITUDES (Å, σ = 0.005–0.008 Å) OF THE PRINCIPAL AXES OF THE THERMAL VIBRATION ELLIPSOIDS OF THE IRON AND ARSENIC ATOMS

	Molecule 1			Molecule 2		
	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3
Fe(1)	0.186	0.233	0.235	0.179	0.249	0.292
Fe(2)	0.165	0.175	0.277	0.195	0.223	0.298
Fe(3)	0.190	0.192	0.261	0.190	0.222	0.273
As(4)	0.177	0.179	0.249	0.194	0.212	0.243
As(5)	0.166	0.218	0.260	0.193	0.232	0.240

All the intermolecular distances correspond to normal van der Waals interactions, the closest approaches being about 3.1 Å. The molecules are arranged (Figure 2) so that an oxygen atom of a bridging carbonyl group of each molecule in the asymmetric unit is approximately equidistant from three of the four terminal carbonyl groups of the unique iron atom of the other molecule. Another, simplified view of the molecular packing is shown in Figure 3.

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Some Reactions of the Octahalodirhenate(III) Ions. VIII. Definitive Structural Characterization of the Octabromodirhenate(III) Ion[1]

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The compound $Cs_2Re_2Br_8$ has been prepared and its structure investigated by single-crystal X-ray diffractometry. The existence of the $Re_2Br_8^{2-}$ ion with virtual D_{4h} symmetry is confirmed. The Re–Re bond has a length of 2.228 (4) Å, very similar to that found in related compounds. The Re–Br bonds have an average length of 2.478 ± 0.006 Å. The set of eight bromine atoms defines a right, square parallelepiped with mean basal edge 3.39 ± 0.02 Å and mean vertical edge 3.48 ± 0.04 Å. Each cesium ion is surrounded by 11 bromine atoms ($Cs\cdots Br$ distances in the range 3.63–4.17 Å), while each $Re_2Br_8^{2-}$ ion has a cesium ion in approximately symmetrical contact with each of its four vertical faces. The space group is Pbca with $a = 12.625 \pm 0.004$ Å, $b = 12.953 \pm 0.004$ Å, and $c = 10.141 \pm 0.003$ Å. For $Z = 4$, $d(\text{calcd}) = 5.11$ g cm^{-3} ($d(\text{measd}) = 5.10$ g cm^{-3}) and the $Re_2Br_8^{2-}$ units are required to have $\bar{1}$ symmetry. The structure was solved using 770 reflections within the sphere bounded by $2\theta = 40°$ (Mo Kα) collected with a counter diffractometer and refined by full-matrix least-squares methods with anisotropic temperature parameters to a conventional R factor of 7.1% and a weighted R of 5.4%.

Introduction

A number of molecules and ions containing a quadruple Re–Re bond are known[2] and several have been structurally characterized with high accuracy by X-ray crystallography. Among these are the $Re_2Cl_8^{2-}$ ion[3-5] in which the Re–Re distance is 2.241 (7) Å, the $Re_2Cl_6[P(C_2H_5)_3]_2$ molecule[6] in which Re–Re = 2.222 (3) Å, and the $(C_3H_7CO_2)_4Re_2(ReO_4)_2$ and $(C_6H_5CO_2)_4Re_2Cl_2$ molecules[7] in which the Re–Re distances are 2.251 (2) and 2.235 (2) Å, respectively. In $Re_2Cl_4(O_2CCH_3)_2(H_2O)_2$, where the four oxygen atoms of the bridging acetato groups lie on one vertical face of the Re_2X_8 parallelepiped and the four Cl atoms define the opposite, parallel vertical face, with approximately the same nonbonded distances as in the $Re_2Cl_8^{2-}$ ion itself, the Re–Re distance is reported[8] to be 2.224 (5) Å. In these species, then, the bond length is relatively in-

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[1] Supported in part by the U. S. Atomic Energy Commission.

[2] F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

[3] V. G. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1965).

[4] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

[5] W. K. Bratton and F. A. Cotton, *ibid.*, **8**, 1299 (1969), where footnote 19 pertains to the $Re_2Cl_8^{2-}$ structure.

[6] F. A. Cotton and B. M. Foxman, *ibid.*, **7**, 2135 (1968).

[7] (a) C. Calvo, N. C. Jayadevan, C. J. L. Lock, and R. Restivo, *Can. J. Chem.*, **48**, 219 (1970); (b) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

[8] N. A. Porai-Koshits, presenting the paper of V. G. Kuznetsov, P. A. Koz'min, and M. D. Suraxskaya, Eighth Congress of the International Union of Crystallography, Stony Brook, N. Y., Aug 1969.

variant, as might be expected for a very strong bond under roughly similar sets of steric constraints. In the case of the $(C_6H_5CO_2)_2Re_2I_4$ molecule,[5] where the coordination about the rhenium atoms differs significantly from that in the other three molecules the Re–Re distance is appreciably shorter, *viz.*, 2.198 (1) Å.

In connection with studies of the vibrational spectra and other properties of species containing quadruply bonded rhenium atoms the structure of the $Re_2Br_8^{2-}$ ion took on special interest. While it was expected to be isostructural with the $Re_2Cl_8^{2-}$ ion, the exact dimensions, especially the length of the Re–Re bond, were required. Two previously reported structures[9] only served to increase the uncertainty concerning the exact value. The two substances studied were crystallographically different forms of $(C_5H_6N)_2Re_2Br_8$ (incorrectly formulated as $(C_5H_6N)_2H_2Re_2Br_8$). For one, where the structure was said to have been refined by least squares (to $R = 14.2\%$), the distance was reported as 2.207 ± 0.003 Å while for the other form, which was not refined, the distance was reported as 2.27 Å with no stated uncertainty interval. The first of these distances seemed unreasonably short; the second seemed unreasonably long though of such dubious accuracy that it could not in any case be taken seriously. A new, accurate investigation was considered necessary.

We report here the preparation of $Cs_2Re_2Br_8$, which is a new compound and the first one, to our knowledge, in which an $Re_2X_8^{2-}$ ion occurs in a crystal containing only a monatomic counterion and no additional molecules such as H_2O. The virtue of such a substance is that it makes possible the computation of a lattice energy which in turn may be introduced into a thermodynamic cycle involving the energy of the metal-to-metal bond. The results of an accurate single crystal study of the structure of this substance are reported here.

Experimental Section

Preparation.—Ten grams of $KReO_4$, 10 ml of 50% aqueous H_3PO_2, and 20 ml of 48% HBr were refluxed for 2 hr under prepurified nitrogen. Then 8.0 g of CsBr was added; the mixture was stirred for a few minutes and allowed to cool. The resulting brown precipitate was filtered off and washed with ethanol. This crude product was stirred with 6 *M* HBr at ~80°; the brownish green solution was filtered from the much less soluble yellow Cs_2ReBr_6 and slowly cooled to produce tabular black crystals of $Cs_2Re_2Br_8$. This recrystallization was repeated to give samples for elemental analysis and the crystallographic examination. *Anal.* Calcd for $Cs_2Re_2Br_8$: Re, 29.15; Br, 50.09. Found: Re, 29.2; Br, 49.9.

Collection of X-Ray Data.—A single crystal was examined by Weissenberg and precession photography. It was found to belong to the orthorhombic system with the following systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. The space group uniquely indicated is Pbca (D_{2h}^{15}, no. 61).[10] The unit cell dimensions were derived from values of 2θ for the $h00$, $0k0$, and $00l$ sets of reflections which were carefully measured on a manually operated General Electric XRD-5 quarter-circle diffractometer using Mo Kα radiation $\lambda(K\alpha_1)$ 0.70926; $\lambda(K\alpha_2)$ 0.71354 Å). The measurements extended to at least the 14th order on all three axes, and the α doublet was resolved at the higher angles. Measurements on two crystals were in good agreement giving $a = 12.625 \pm 0.004$ Å, $b = 12.953 \pm 0.004$ Å, and $c = 10.141 \pm 0.003$ Å, where the standard deviations are the authors' estimates and exceed the average deviations of the individual measurements. The density calculated with these dimensions and assuming $Z = 4$ with a formula weight of 1277.48 is 5.11 g cm^{-3}. The density measured pycnometrically was 5.10 g cm^{-3}. Since the general position in the space group Pbca has a multiplicity of 8, it is required that $Re_2Br_8^{2-}$ units lie on centers of symmetry.

The crystal, glued to the end of a glass fiber, was so aligned that the b axis was coincident with the ϕ axis of the goniometer. This crystal was a rhombic tablet 0.018 mm thick (between principal (100) and ($\bar{1}00$) faces) whose periphery was bounded by approximately equally developed {111} faces and smaller {010} faces. The two greatest thicknesses of the crystal, parallel to the b and c axes and to the diagonals of the rhombus, were both 0.06 mm. This morphology is typical of the crystals obtained.

The intensities of 770 reflections within one octant of the sphere bounded by $2\theta = 40°$ were measured by a coupled θ–2θ scan technique. The diffractometer was operated with a zirconium foil filter between the crystal and scintillation detector, a pulse height discriminator set to accept ~95% of the Mo Kα peak, and a takeoff angle of ~2° to the molybdenum X-ray tube anode. Each reflection was measured by performing a 1.33° (2θ) scan, centered on the peak, at a rate of 2°/min, accumulating P counts in 40 sec. Twenty-second background counts, B_1 and B_2, were taken at each end of the scan range. Four strong reflections which were remeasured at regular intervals showed only random fluctuations in the range ±2%. All of the systematic absences in the region of the data set were also measured and found to confirm the extinction rules previously observed on films.

Values for the magnitudes of the observed structure factors, $|F_o|$, and their standard deviations, $\sigma(|F_o|)$, were calculated from the experimental data as $|F_o| = (I/Lp)^{1/2}$ and $\sigma(|F_o|) = (P + B_1 + B_2 + (0.04I)^2)^{1/2}/2Lp|F_o|$, where $I = P - B_1 - B_2$ (if $P - B_1 - B_2 \leq 0$, $I = 0.5(P + B_1 + B_2)^{1/2}$) and Lp is the Lorentz–polarization factor.

Solution and Refinement.[11]—A three-dimensional Patterson function was calculated. From it and the assumption of 4/mmm (D_{4h}) symmetry in the $Re_2Br_8^{2-}$ ion, the positions of all atoms were found. After four cycles of least-squares refinement[12] with all atoms assigned isotropic temperature factors, the residuals $R_1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 0.14 and 0.12, respectively. Scattering factors employed in these and all subsequent cycles were those of Cromer and Waber[13] for neutral Cs, Re, and Br atoms and included anomalous dispersion corrections as given by Cromer.[14]

Before proceeding with the refinement, an absorption correction was applied to the data using the measured dimensions of the crystal and the absorption coefficient of 402 cm^{-1}. Calculated transmission factors ranged from 0.271 to 0.542. The ratio of $|F_o|_{max}^2$ to $|F_o|_{min}^2$ for the 020 and 040 reflections over $0° \leq \phi \leq 360°$ at $\chi = 90°$ was 2.6; the absorption correction reduced this to 1.3. No attempt was made to modify the calculation in order to reduce the ratio further. Four more cycles of least-squares refinement on the corrected data in which all atoms were allowed anisotropic temperature factors converged to $R_1 = 0.071$ and $R_2 = 0.054$. In the last cycle, no parameter shifted by more than 3% of its estimated standard deviation. The standard deviation of an observation of unit weight was 1.13, average $w(F_o -$

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[9] P. A. Koz'min, V. G. Kuznetzov, and Z. V. Popova, *Zh. Strukt. Khim.*, **6**, 651 (1965).

[10] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962.

[11] Local, modified versions of the following programs were used: (1) MIXG2, D. P. Shoemaker, diffractometer settings; (2) FORDAP, A. Zalkin, Fourier syntheses; (3) GONO9, W. C. Hamilton, absorption corrections; (4) SFLS5, C. T. Prewitt, least-squares refinements; (5) MGEOM, J. S. Wood, and DISTAN, D. P. Shoemaker, interatomic distances and angles; (6) ORTEP, C. Johnson, thermal ellipsoid drawings.

[12] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights, w, were the reciprocals of $\sigma^2(|F_o|)$.

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

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

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Cs_2Re_2Br_8$ (IN UNITS OF 0.1 ELECTRON)

H	K	FOBS	FCAL
L = 0**			
2	0	3563	3551
4	0	6254	6475
6	0	6478	6634
8	0	614	584
10	0	2572	2567
12	0	303	522
2	1	1255	1217
4	1	2303	2487
6	1	3006	3088
8	1	1750	1711
10	1	342	522
12	1	1178	1099
0	2	4337	4183
2	2	2577	2574
4	2	1144	929
6	2	229	130
8	2	623	476
10	2	342	61
2	3	2048	2093
4	3	505	396
6	3	5453	5637
8	3	764	678
10	3	2992	2941
0	4	4840	4648
2	4	6484	6724
4	4	661	454
6	4	3410	3434
8	4	1268	1186
10	4	1286	1400
2	5	260	456
4	5	2962	3047
6	5	543	689
8	5	2272	2320
10	5	1545	1350
0	6	3706	3698
2	6	2762	2796
4	6	3425	3635
6	6	3832	4072
8	6	2870	2903
10	6	1630	1628
2	7	222	182
4	7	1132	1189
6	7	1377	1511
8	7	1587	1655
10	7	272	263
0	8	1681	1704
2	8	4486	4707
4	8	3070	3147
6	8	1018	1107
8	8	3385	3474
2	9	359	490
4	9	1563	1612
6	9	379	86
8	9	1245	1193
0	10	1070	1144
2	10	303	135
4	10	550	594
6	10	686	521
2	11	658	826
4	11	1080	1112
0	12	413	103
2	12	1751	1864
L = 1**			
1	1	5537	5316
2	1	606	491
3	1	3128	3167
4	1	5111	5201
5	1	4287	4491
6	1	1235	1355
7	1	2412	2453
8	1	310	79
9	1	2117	2183
10	1	765	739
11	1	947	657
12	1	249	33
0	2	374	349
1	2	470	467
2	2	2361	2261
3	2	392	76
4	2	501	495
5	2	2875	2913
6	2	732	912
7	2	420	446
8	2	1463	1542
9	2	984	921
10	2	1086	975
11	2	2181	2277
1	3	542	424
2	3	4062	3959
3	3	425	68
4	3	825	771
5	3	452	496
6	3	1944	1910
7	3	429	139
8	3	451	96
9	3	257	263
10	3	1162	1046
11	3	363	468
0	4	4258	4252
1	4	1851	1684
2	4	1593	1628
3	4	519	618
4	4	2102	2120
5	4	2495	2584
5	5	2134	2126
6	4	1876	1913
7	4	2560	2585
8	4	730	585
9	4	1673	1756
10	4	871	803
11	4	2617	2631
1	5	2221	2236
2	5	3170	3124
3	5	254	274
4	5	470	56
6	5	592	710
7	5	326	25
8	5	676	761
9	5	856	858
10	5	1256	1291
11	5	537	60
0	6	657	552
1	6	867	905
2	6	367	819
3	6	273	515
4	6	922	779
5	6	1069	990
6	6	325	248
7	6	1073	1025
8	6	860	890
9	6	724	626
10	6	987	986
1	7	5531	5503
2	7	889	1018
3	7	3872	3837
4	7	2107	2256
5	7	4392	4477
6	7	1326	1284
7	7	1836	1844
8	7	961	921
9	7	1802	1796
0	8	1229	1246
1	8	1319	1286
2	8	1460	1536
3	8	1039	1021
4	8	330	136
5	8	598	578
6	8	359	588
7	8	522	331
8	8	378	491
9	8	774	628
1	9	292	558
2	9	431	305
3	9	2107	2080
4	9	1496	1526
5	9	517	258
6	9	378	743
7	9	1093	972
8	9	964	1034
0	10	1623	1718
1	10	1103	1058
2	10	860	1060
3	10	997	1014
4	10	1934	1765
5	10	771	792
6	10	1194	1151
7	10	1980	2038
1	11	442	139
2	11	1195	1243
3	11	1177	1213
4	11	390	487
5	11	704	770
0	12	1032	1028
1	12	664	708
2	12	1149	1168
3	12	1034	1155
L = 2**			
0	0	2595	2471
1	0	2270	2184
2	0	2926	2840
3	0	1281	1315
4	0	5013	5136
5	0	2530	2595
6	0	3123	3169
7	0	2772	2799
8	0	2903	2996
9	0	572	430
10	0	2321	2457
11	0	3504	3492
1	1	1305	1230
2	1	667	619
3	1	3970	3981
4	1	363	229
5	1	2001	2108
6	1	369	460
7	1	638	367
8	1	436	312
9	1	662	494
10	1	695	631
11	1	279	459
0	2	148	50
1	2	794	750
2	2	788	651
3	2	640	504
4	2	1802	1707
5	2	419	165
6	2	2040	1998
7	2	289	103
8	2	1592	1535
9	2	578	563
10	2	1298	1265
11	2	627	682
1	3	6930	6597
2	3	1948	1953
3	3	986	1069
4	3	232	53
5	3	5478	5434
6	3	2403	2485
7	3	2532	2503
8	3	1421	1362
9	3	1018	945
10	3	1972	2009
11	3	1379	1252
0	4	1528	1591
1	4	1768	1722
2	4	1150	1091
3	4	1189	1198
4	4	1026	881
5	4	1319	1197
6	4	1604	1575
7	4	746	653
8	4	1031	895
9	4	1925	1814
10	4	624	253
11	4	838	936
1	5	354	214
2	5	537	565
3	5	3981	3890
4	5	242	111
5	5	620	639
6	5	1630	1470
7	5	1305	1350
8	5	581	715
9	5	796	994
10	5	1047	984
0	6	5862	5903
1	6	440	468
2	6	2719	2622
3	6	1486	1453
4	6	3243	3223
5	6	1989	2001
6	6	1122	1085
7	6	988	919
8	6	494	81
9	6	1156	1297
10	6	1197	1275
1	7	627	793
2	7	1129	1121
3	7	2362	2436
4	7	1134	1254
5	7	622	781
6	7	928	813
7	7	27	27
8	7	626	614
9	7	849	855
0	8	3577	3768
1	8	218	365
2	8	2815	2827
3	8	1929	1890
4	8	1352	1386
5	8	805	821
6	8	1268	1321
7	8	886	739
8	8	377	358
1	9	715	794
2	9	905	935
3	9	2552	2621
4	9	270	198
5	9	146	86
6	9	1544	1574
7	9	1195	1123
8	9	278	312
0	10	220	97
1	10	1073	1069
2	10	2079	2041
3	10	249	54
4	10	279	330
5	10	270	189
6	10	270	55
1	11	1744	1747
2	11	320	190
3	11	3128	3108
4	11	1592	1678
5	11	1335	1255
0	12	625	574
1	12	320	320
2	12	339	198
L = 3**			
1	1	3238	3200
2	1	623	588
3	1	761	817
4	1	217	161
5	1	3236	3295
6	1	1548	1538
7	1	1926	1950
8	1	1186	1365
9	1	1271	1223
10	1	2667	2667
11	1	525	511
0	2	3536	3545
1	2	6461	6526
2	2	1696	1709
3	2	1660	1623
4	2	2517	2506
5	2	942	964
6	2	1736	1810
7	2	3215	3213
8	2	1072	1099
9	2	739	685
10	2	929	1098
11	2	1235	1179
1	3	1126	1176
2	3	1029	965
3	3	2507	2478
4	3	1564	1487
5	3	1938	1977
6	3	939	950
7	3	1553	1546
8	3	544	609
9	3	822	890
10	3	356	334
11	3	649	451
0	4	5603	5529
1	4	668	619
2	4	4705	4615
3	4	594	480
4	4	4395	4320
5	4	261	496
6	4	3312	3339
7	4	904	865
8	4	2223	2107
9	4	837	797
10	4	1538	1513
1	5	529	491
2	5	1078	1019
3	5	239	337
4	5	1273	1329
5	5	2796	2791
6	5	1487	1479
7	5	764	696
8	5	331	196
9	5	2026	1845
10	5	371	435
0	6	459	384
1	6	3845	3892
2	6	536	539
3	6	1670	1626
4	6	220	144
5	6	1788	1792
6	6	610	323
7	6	1334	1336
8	6	596	411
9	6	1397	1343
1	7	490	295
2	7	1923	1917
3	7	2121	2051
4	7	2277	2231
5	7	231	154
6	7	2447	2480
7	7	2273	2064
8	7	2197	2091
9	7	749	745
0	8	440	423
1	8	451	502
2	8	384	400
3	8	235	92
4	8	301	55
5	8	247	85
6	8	257	52
7	8	272	437
8	8	370	179
1	9	617	647
2	9	988	826
3	9	423	588
4	9	1102	996
5	9	334	189
6	9	497	515
7	9	1995	1975
0	10	3331	3407
1	10	1702	1747
2	10	3340	3302
3	10	634	607
4	10	2649	2779
5	10	1269	1234
6	10	2251	2106
1	11	531	303
2	11	318	243
3	11	1104	1012
4	11	1057	938
L = 4**			
0	0	1028	1070
1	0	1194	1180
2	0	660	584
3	0	3259	3294
4	0	718	591
5	0	2378	2533
6	0	2768	2899
7	0	2524	2658
8	0	687	542
9	0	2817	2907
10	0	273	215
11	0	1237	1227
1	1	193	294
2	1	723	644
3	1	2054	2115
4	1	457	191
5	1	247	344
6	1	265	417
7	1	286	213
8	1	436	491
9	1	874	804
10	1	786	627
11	1	372	39
0	2	3001	2932
1	2	1361	1380
2	2	1698	1673
3	2	1212	1167
4	2	1014	1079
5	2	1418	1494
6	2	381	149
7	2	1394	1322
8	2	538	440
9	2	574	416
10	2	271	183
1	3	4635	4622
2	3	771	784
3	3	5780	5817
4	3	1019	969
5	3	3609	3570
6	3	242	199
7	3	1982	1983
8	3	448	311
9	3	2700	2569
10	3	357	118
0	4	1913	1915
1	4	576	413
2	4	225	467
3	4	667	468
4	4	1817	1782
5	4	1435	1365
6	4	492	336
7	4	606	414
8	4	1445	1379
9	4	1030	837
10	4	1027	963
1	5	3163	3184
2	5	211	399
3	5	699	663
4	5	231	226
5	5	2911	2886
6	5	831	821
7	5	934	940
8	5	245	33
9	5	789	783
0	6	415	293
1	6	1577	1572
2	6	1390	1386
3	6	451	551
4	6	611	603
5	6	645	529
6	6	431	367
7	6	1970	1886
8	6	343	174
9	6	1301	1281
1	7	893	937
2	7	876	763
3	7	475	164
4	7	1035	954
5	7	236	27
6	7	537	420
7	7	1114	1044
8	7	500	91
0	8	279	494
1	8	271	74
2	8	964	979
3	8	287	160
4	8	504	509
5	8	998	937
6	8	1551	1434
7	9	1261	1297
1	9	2385	2375
2	9	506	543
3	9	857	761
4	9	709	700
5	9	2610	2625
6	9	919	904
0	10	826	882
1	10	1651	1610
2	10	614	565
3	10	551	355
4	10	331	266
5	10	257	51
1	11	2550	2620
2	11	559	655
L = 5**			
1	1	2466	2429
2	1	3701	3796
3	1	2162	2235
4	1	597	595
5	1	259	325
6	1	2961	3042
7	1	509	99
8	1	1599	1605
9	1	256	181
10	1	713	777
0	2	4390	4405
1	2	220	45
2	2	937	975
3	2	407	432
4	2	3646	3717
5	2	370	133
6	2	1550	1659
7	2	243	177
8	2	447	86
9	2	584	454
10	2	2419	2431
1	3	717	716
2	3	1229	1206
3	3	212	134
4	3	3161	3237
5	3	987	877
6	3	402	325
7	3	799	651
8	3	247	136
9	3	661	697
10	3	361	382
0	4	3288	3358
1	4	471	469
2	4	3555	3624
3	4	1252	1195
4	4	3305	3267
5	4	617	628
6	4	2042	1982
7	4	817	739
8	4	1640	1769
9	4	1154	1149
1	5	1754	1794
2	5	1793	1783
3	5	179	36
4	5	2255	2242
5	5	570	551
6	5	1276	1248
7	5	1004	864
8	5	1115	1150
9	5	503	236
0	6	213	207
1	6	211	35
2	6	2290	2230
3	6	271	222
4	6	398	23
5	6	418	30
6	6	694	790
7	6	256	155
8	6	1507	1468
1	7	1112	1017
2	7	454	1015
3	7	1945	1990
4	7	1913	1875
5	7	1269	1161
6	7	557	532
7	7	2063	1576
0	8	229	187
1	8	1024	958
2	8	957	899
3	8	420	367
4	8	1152	1004
5	8	555	633
6	8	476	94
1	9	247	542
2	9	1386	1336
3	9	1162	1125
4	9	1403	1331
5	9	579	633
0	10	1959	2012
1	10	230	69
2	10	2764	2800
3	10	240	181
L = 6**			
0	0	528	322
1	0	821	825
2	0	6072	6192
3	0	1145	1113
4	0	2998	2923
5	0	272	114
6	0	242	329
7	0	1054	1003
8	0	2398	2366
9	0	1020	1128
1	1	1327	1280
2	1	344	390
3	1	1462	1503
4	1	738	913
5	1	1224	1314
6	1	1353	1419
7	1	235	169
8	1	1029	960
9	1	1023	1153
0	2	871	819
1	2	210	74
2	2	696	701
3	2	622	678
4	2	457	296
5	2	229	153
6	2	292	140
7	2	531	672
8	2	270	97
9	2	1143	1018
1	3	2081	2124
2	3	417	542
3	3	2152	2182
4	3	1806	1635
5	3	2048	2149
6	3	243	44
7	3	496	623
8	3	2334	2324
9	3	1707	1637
0	4	4052	4168
1	4	1298	1317
2	4	1714	1273
3	4	441	684
4	4	220	53
5	4	1190	1157
6	4	1049	1192
7	4	450	674
8	4	1257	1152
1	5	1920	2021
2	5	598	704
3	5	1402	1369
4	5	755	584
5	5	1455	1571
6	5	1552	1531
7	5	1422	1442
8	5	94	54
0	6	1472	1413
1	6	1130	1056
2	6	1734	1703
3	6	1176	1092
4	6	2045	1960
5	6	1522	1515
6	6	1538	1510
7	6	1345	1395
1	7	230	130
2	7	290	171
3	7	296	42
4	7	306	54
5	7	317	104
6	7	976	883
0	8	2910	2972
1	8	420	158
2	8	426	92
3	8	1235	1214
4	8	1148	1051
5	8	1145	1236
1	9	1862	1858
2	9	832	584
3	9	1014	1038
L = 7**			
1	1	1193	1245
2	1	528	434
3	1	2231	2206
4	1	559	390
5	1	2270	2309
6	1	678	752
7	1	1912	1995
8	1	580	244
0	2	1994	1934
1	2	1462	1395
2	2	1194	1247
3	2	547	525
4	2	937	898
5	2	414	472
6	2	1186	1140
7	2	1725	1788
9	2	752	809
1	3	655	676
2	3	384	505
3	3	221	35
4	3	572	567
5	3	297	355
6	3	310	465
7	3	1169	1196
0	4	1802	1767
1	4	221	97
2	4	480	109
3	4	499	889
4	4	926	877
5	4	959	901
6	4	772	781
7	4	1319	1280
1	5	1497	1555
2	5	230	284
3	5	1572	1678
4	5	672	540
5	5	439	275
6	5	1206	1262
0	6	861	861
1	6	1093	1032
2	6	1288	1323
3	6	426	74
4	6	1218	1149
5	6	1152	1053
6	6	664	531
1	7	3253	3192
2	7	314	818
3	7	2982	2972
4	7	452	303
5	7	1310	1250
0	8	2311	2239
1	8	231	125
2	8	235	60
3	8	557	434
L = 8**			
0	0	2934	2712
1	0	1254	1355
2	0	2680	2690
3	0	739	272
4	0	2387	2487
5	0	1340	1247
6	0	1807	1835
1	1	1735	1677
2	1	236	194
3	1	920	724
4	1	237	261
5	1	1772	1773
6	1	578	594
0	2	1280	1266
1	2	492	445
2	2	1551	1563
3	2	927	1050
4	2	1165	1234
5	2	1076	1233
6	2	1162	1105
1	3	242	527
2	3	504	345
3	3	1730	1860
4	3	914	1027
5	3	995	927
6	3	1220	1126
0	4	292	306
1	4	509	514
2	4	593	344
3	4	1482	1519
4	4	245	255
5	4	320	68
1	5	301	126
2	5	234	216
3	5	1550	1589
4	5	779	866
0	6	1594	1784
1	6	310	397
2	6	2257	2367
3	6	897	771
1	7	715	680
L = 9**			
1	1	2589	2732
2	1	235	343
3	1	2043	2048
4	1	319	273
0	2	682	501
1	2	1181	1103
2	2	815	762
3	2	327	848
4	2	237	27
1	3	1452	1436
2	3	442	220
3	3	635	592
0	4	701	642
1	4	313	237
2	4	1053	1075

$F_o)^2$ values were essentially invariant with respect to $|F_o|$ and $\lambda^{-1} \sin \theta$, and the largest peak on a final difference Fourier synthesis was 1.85 e$^-$ Å^{-3}. A list of the observed and final calculated structure factors was examined for evidence of secondary extinction effects (*i.e.*, (F_o/F_c) *vs.* I). None was found. The list is presented as Table I.

Results

The fractional atomic coordinates and isotropic temperature parameters are listed in Table II. Anisotropic temperature parameters are given in Table III. The thermal vibration ellipsoids are displayed in Figure 1. The dimensions of the $Re_2Br_8^{2-}$ ion are given in Table IV. The shorter Cs to Br and intermolecular Br to Br distances are given in Table V, and the crystal packing is shown in Figure 2.

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS[a]

Atom	x	y	z	B,[b] Å^2
Re	0.0154 (1)	0.0704 (1)	0.0600 (1)	2.38
Cs	−0.3072 (2)	0.1359 (2)	−0.1608 (2)	4.91
Br(1)	0.0640 (3)	0.0029 (3)	0.2801 (3)	3.84
Br(2)	−0.1585 (3)	0.1146 (3)	0.1558 (4)	3.64
Br(3)	−0.0155 (3)	0.2189 (3)	−0.0899 (3)	3.99
Br(4)	0.2068 (3)	0.1052 (3)	0.0247 (4)	3.52

[a] Estimated standard deviations occurring in the least significant figure are given in parentheses. [b] B's are isotropic thermal parameters equivalent to the anisotropic tensors of Table III.

TABLE III

ANISOTROPIC TEMPERATURE PARAMETERS[a,b] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	40 (1)	29 (1)	63 (2)	−2 (1)	−2 (1)	−3 (1)
Cs	88 (2)	53 (2)	135 (3)	21 (2)	−34 (3)	−26 (2)
Br(1)	66 (3)	63 (3)	74 (1)	2 (3)	−14 (3)	5 (3)
Br(2)	59 (3)	48 (3)	96 (4)	6 (3)	14 (3)	8 (3)
Br(3)	76 (4)	36 (3)	115 (5)	8 (3)	2 (3)	18 (3)
Br(4)	43 (3)	47 (3)	112 (4)	−5 (2)	−3 (3)	0 (3)

[a] Estimated standard deviations occurring in the least significant figure appear in parentheses. [b] Anisotropic temperature factors were defined as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN THE $Re_2Br_8^{2-}$ ION[a]

Bond Distances		Nonbond Distances	
Re–Re	2.228 (4)	Br(1)–Br(2)	3.402 (5)
Re–Br(1)	2.474 (4)	Br(2)–Br(3)	3.361 (5)
Re–Br(2)	2.469 (4)	Br(3)–Br(4)	3.377 (5)
Re–Br(3)	2.483 (4)	Br(4)–Br(1)	3.423 (5)
Re–Br(4)	2.484 (4)	Br(1)–Br(3)′	3.51 (1)
		Br(2)–Br(4)′	3.44 (1)
Bond Angles			
Re′–Re–Br(1)	104.3 (1)	Br(2)–Re–Br(3)	85.5 (2)
Re′–Re–Br(2)	104.4 (1)	Br(3)–Re–Br(4)	85.7 (2)
Re′–Re–Br(3)	105.8 (1)	Br(4)–Re–Br(1)	87.3 (2)
Re′–Re–Br(4)	103.8 (1)	Br(1)–Re–Br(3)	149.9 (2)
Br(1)–Re–Br(2)	87.0 (2)	Br(2)–Re–Br(4)	151.7 (2)

[a] Estimated standard deviations occurring in the least significant figure appear in parentheses.

TABLE V

INTERIONIC DISTANCES[a] (Å)

Anion at (0, 0, 0)		Anion at (0, 0.5, −0.5)	
Cs–Br(4)′	3.64	Cs–Br(2)	4.17
Cs–Br(2)	3.73	**Between anions**	
Cs–Br(1)′	3.76	Br(2)–Br(4)	3.66
Cs–Br(3)	3.90	Br(2)–Br(3)	3.81
Anion at (−0.5, 0, −0.5)		Br(1)–Br(2)	3.85
Cs–Br(4)	3.71	Br(1)–Br(3)	3.97
Cs–Br(1)′	3.76	Br(1)–Br(4)	4.06
Cs–Br(2)	3.77	Br(3)–Br(4)	4.23
Cs–Br(3)′	3.80	Bı(2)–Br(4)	4.41
Anion at (−0.5, 0.5, 0)			
Cs–Br(4)	3.63		
Cs–Br(3)	4.11		

[a] The estimated standard deviations of these distances are all 0.005 Å or less. All other Cs–Br and Br–Br distances are greater than 4.5 Å.

Discussion

The geometric configuration of the $Re_2Br_8^{2-}$ ion is, as expected, that of a nearly cubic, right square parallelepiped. Figure 1 shows the structure with mean di-

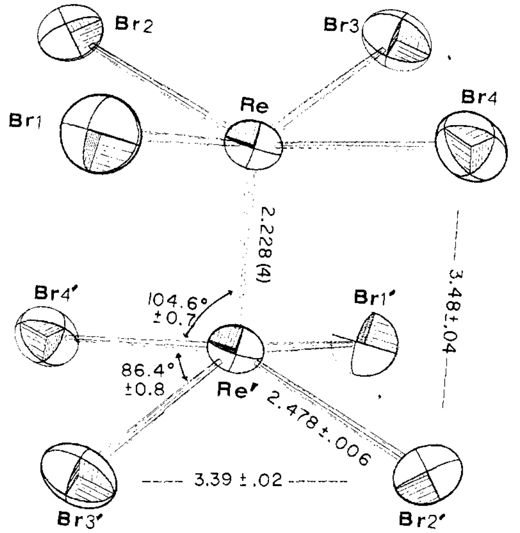

Figure 1.—The $Re_2Br_8^{2-}$ ion showing the atom numbering scheme and mean dimensions. Intervals indicated with ± are root-mean-square deviations from the mean and exceed the standard deviations of individual values used to compute the mean. Primed atoms are related by the center of symmetry to unprimed atoms with the same number.

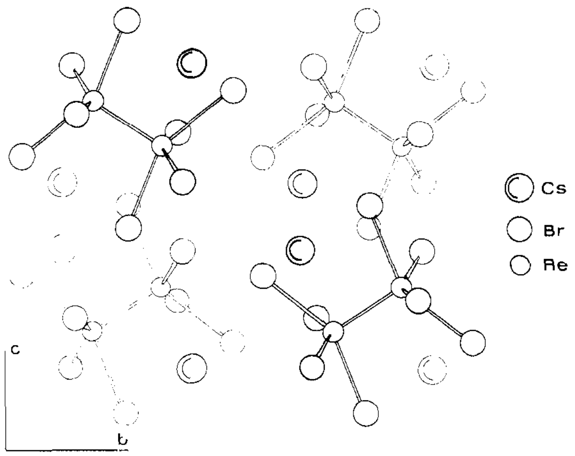

Figure 2.—The $Cs_2Re_2Br_8$ structure projected down *a*.

mensions and the atom numbering scheme. The individual dimensions are given in Table IV. The $Re_2Br_8^{2-}$ ion lies at a crystallographic center of symmetry. Its dimensions are such, however, that it is more chemically meaningful to think of it as having virtual D_{4h} symmetry. The eclipsed configuration and short Re–Re distance are diagnostic[2] of the quadruple Re–Re bond.

The Re–Re bond length, 2.228 (4) Å, is near the middle of the range, roughly 2.22–2.25 Å, covered by other Re–Re quadruple bonds. This is significant since it shows that the quadruple bond distance is relatively constant, 2.235 ± 0.015 Å, provided general stereochemistry remains essentially the same. The increase to 2.29 Å in the case of $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$ becomes meaningful and supports the view that the latter compound contains only a triple bond.[15]

The crystal packing, shown in Figure 2, is not particularly remarkable. Each $Re_2Br_8^{2-}$ ion is surrounded by four Cs^+ ions, each in approximately symmetrical contact with one of the vertical faces of the right square parallelepiped which it forms. Each Cs^+ ion is surrounded by 11 bromine atoms, four from each of two anions, two from a basal edge of another, and one corner of a fourth. This array of bromine atoms does not approximate to any particular symmetric polyhedron. Eight of the Cs–Br distances are in the range 3.63–3.80 Å, while the other three are appreciably longer, *viz.*, 3.90, 4.11, and 4.17 Å.

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[15] M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc., Ser. A*, **303**, 175 (1968).

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Synthesis of Sodium Cyanotrihydroborate and Sodium Isocyanotrihydroborate

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A convenient synthetic procedure for sodium cyanotrihydroborate ($NaBH_3CN$) is reported. Sodium isocyanotrihydroborate has also been isolated in mixtures with the normal salt and characterized. The isomerization of $NaBH_3NC$ to $NaBH_3CN$ has been investigated and is found to be H^- and CN^- catalyzed. Boron nmr data are reported for BH_3CN^-, BH_3NC^-, and $BH_3CNBH_3^-$. The infrared spectra of $NaBH_3NC$, $NaBD_3NC$, and $NaBH_3CNBH_3$ have been recorded and the fundamental vibrations assigned and compared with those reported earlier for $NaBH_3CN$ and $NaBD_3CN$.

Introduction

Wittig and Raff reported the first synthesis of a cyanotrihydroborate in 1951.[2] They prepared the lithium salt by allowing lithium borohydride to react with excess HCN in diethyl ether at 100° under pressure. These authors noted the unusual hydrolytic stability of the product toward acids. Thereafter, only one brief publication appeared on the reducing power of $LiBH_3CN$, and that report indicates limited applicability.[3]

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[1] (a) PRF Graduate Fellowship 1969–1970; abstracted in part from the Ph.D. thesis of J. R. Berschied, Kansas State University, 1970. (b) To whom inquiries should be addressed. (c) Kansas State University. (d) Ventron Corp.

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[3] G. Drefahl and E. Keil, *J. Prakt. Chem.*, **6**, 80 (1958).