that the cations depart significantly from S_4 symmetry. Zaslow and Rundle[20] had commented that the versatility of form of the tetraphenylarsonium cation helps to account for its effectiveness as a precipitating agent. Our results serve to reinforce this statement and help to explain the effectiveness of this large cation in precipitating trinuclear halogeno anions of Re(III) which have fewer than 12 halogen atoms.[15]

Ionic Packing.—The anions are well shielded from one another by the bulky cations as can be seen from Figure 1 and there are no interionic Cl---Cl contacts within 4.5 A. The closest Cl---C contacts made by individual chlorine atoms range from 3.2 A for Cl(10) to 3.8 A for Cl(7), which, considering the large errors in carbon positions, are reasonable van der Waals distances.

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The Crystal Structure of Bis(cesium) Tri-μ-bromo-octabromotrirhenate(III), $Cs_2Re_3Br_{11}$

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A three-dimensional crystal structure analysis of the compound of composition $Cs_2Re_3Br_{11}$ establishes that it contains the trinuclear anion $(Re_3Br_{11})^{2-}$ which possesses the same general structural features as other rhenium(III) species of the general formula $(Re_3X_{9+n})^{n-}$ where X is Br or Cl. As with the $(Re_3Cl_{11})^{2-}$ anion, Re–Re bond lengths are unequal, those involving the deficient Re atom being 2.43 A and the remaining Re–Re bond 2.49 A. A new feature is that the bonds which the deficient Re atom makes to its off-plane bromine atoms are greatly shortened to 2.38 A and are bent toward one another to make an angle of 133°.

Introduction

The existence of trinuclear Re(III) bromide species analogous to the chloride compounds already known[1–4] was first reported by Fergusson and Robinson[5] and independently by Cotton and Lippard.[6] The preparative and spectral properties of some of these compounds have been discussed by Robinson and Fergusson[7] and by Cotton, Lippard, and Mague.[8] It is as a part of our systematic studies of the structures of trinuclear Re(III) species that we have determined in detail the crystal structure of $Cs_2Re_3Br_{11}$, a preliminary account of which has already been given.[9] The crystal structure of one other compound containing the neutral Re_3Br_9 species has been reported by Cotton and Lippard.[10]

Experimental Section

Small black needle-shaped crystals were prepared following the method of Fergusson and Robinson.[5] The crystals were completely stable in air.

Crystal Data.—$Cs_2Re_3Br_{11}$, formula weight 1704, orthorhombic, space group Pnma from systematic absences of X-ray reflections; $a = 9.53 \pm 0.01$ A, $b = 16.114 \pm 0.007$ A, $c = 13.744 \pm 0.007$ A ($\lambda = 1.5405, 1.5443$ for Cu $K\alpha_1,\alpha_2$ radiation), $U = 2109.5$ A^3, $D_x = 5.38$ g cm^{-3}, $Z = 4$, symmetry of anion C_s (=m). Linear absorption coefficients are 865 cm^{-1} for Cu $K\alpha$ and 459 cm^{-1} for Mo $K\alpha$ radiation.

Reciprocal lattice levels (0–$6kl$) were recorded by the equi-inclination Weissenberg method using Cu $K\alpha$ radiation, and levels ($hk0$–1), ($h0l$), and (hkk–$hk(k + 4)$) were recorded on the Buerger precession camera using Mo $K\alpha$ radiation. Intensities were estimated visually by comparison with a suitably calibrated scale. The Weissenberg data totalled 1713 independent reflections of which 323 were recorded as unobserved and given an estimated intensity one-third of the minimum observable intensity. These Weissenberg data were used for the structure refinement, supplemented by 178 precession reflections with $h > 6$, of which 30 were recorded as unobserved. The two crystals used were each mounted on a glass fiber and showed no signs of deterioration after prolonged exposure to the atmosphere and to X radiation. They were of a very similar size, needles of length about 0.5 mm and rectangular cross section 0.095 mm × 0.070 mm. Corrections for absorption were applied assuming a cylindrical crystal of radius 0.04 mm ($\mu R = 3.5$) for the Weissenberg data and assuming a spherical crystal of the same radius ($\mu R = 1.8$) for the precession data.

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Structure Determination

A three-dimensional trial structure was based upon a self-consistent set of atomic positions obtained from solutions of the Patterson function projected down each of the principal axes. Because the rhenium triangle is nearly parallel to (101) there is good resolution of atoms in the projections on (001) and (100). The cesium atom, one rhenium atom, and four bromine atoms were located on general (8-fold) positions, and the one remaining rhenium atom and three remaining bromine atoms on mirror planes normal to *b*, positions of 4-fold multiplicity. Four successive three-dimensional difference maps and subsequent sets of structure factors were computed, in the course of which all atoms were more precisely located and the *R* index dropped from 0.40 to 0.27 for all Weissenberg data. Next, five cycles of least-squares refinement were performed using the same data and *R* was further reduced to 0.17. The block diagonal approximation was used with a two-parameter weighting scheme suggested by Mills and Rollett.[11] The weight is expressed as

$$w = 1/\left\{1 + \left(\frac{F_o - b}{a}\right)^2\right\}$$

with $a = 90$ and $b = 60$ in this case. Atomic scattering factors used were, for Cs and Re, from the Thomas–Fermi–Dirac statistical model and, for Br, from the self-consistent field model, all corrected for anomalous dispersion,[12] the actual values used being $f = \sqrt{\{(f_o + \Delta f')^2 + (\Delta f'')^2\}}$.

At this stage in the refinement all data were scaled to $\Sigma F_o = \Sigma|F_c|$ for individual layers. The precession data covering $h = 7$–11 were added, and all unobserved reflections were removed. The remaining 1538 reflections were used in the computation of a final difference map. This showed no evidence of anisotropy for any atoms, so all atoms were treated as isotropic in the final cycles of least squares. Three cycles were run and the *R* index fell from 0.18 to its final value of 0.145.

Final atomic coordinates and isotropic thermal parameters are listed in Table I. The *B* values have no absolute significance since absorption corrections calculated on the basis of a regular cylinder can only be approximate. Corresponding structure factors are given in Table II for all observed reflections. Interatomic distances and bond angles involving the anions are listed in Table III.

Appended to Table III are estimated mean standard deviations based on 1.5 times the indications of the least-squares refinement. Although somewhat arbitrary, this figure is reasonable on the basis of past experience with the block diagonal approximation in similar structure analyses and also because of the internal consistency of chemically equivalent bonds and angles, which will be expected to agree within $3\sqrt{2}\sigma$ ($=4.2\sigma$). The agreement is well within this figure for all sets except for the two pairs of angles Br(1)-Re(1)Br(3) and Br(2)Re(1)Br(3) (difference of 4.2σ), and Br(1)Re(1)Br(6) and Br(2)Re(1)Br(6) (difference of 7σ). Intermolecular forces could well influence these angles, Br(2) being involved in the closest of all intermolecular contacts.

TABLE I

ATOMIC PARAMETERS FOR THE ASYMMETRIC UNIT OF $Cs_2Re_3Br_{11}$[a]

	x	*y*	*z*	*B*, A^2
Re(1)	0.3020	0.1725	0.4669	2.3
Re(2)	0.4461	0.2500	0.5814	2.5
Cs	0.3368	0.0697	0.1202	4.2
Br(1)	0.0961	0.1478	0.5714	3.4
Br(2)	0.4869	0.1462	0.3427	2.8
Br(3)	0.2057	0.0304	0.3832	3.6
Br(4)	0.3354	0.2500	0.7355	4.2
Br(5)	0.6864	0.2500	0.5299	3.9
Br(6)	0.4572	0.0915	0.5863	3.9
Br(7)	0.1538	0.2500	0.3452	3.2

[a] Atom numbering corresponds to that of Figure 1.

Discussion

Crystal Structure.—The crystal structure consists of discrete $(Re_3Br_{11})^{2-}$ anions and Cs^+ cations. A view of the structure projected down the *c* axis is shown in Figure 1. The anions occur on mirror planes and are related by the two glide planes. The cesium atom has nine bromine neighbors at less than 4.0 A, five at 3.57–3.66 A, and a further four at 3.82–3.88 A. There is no discernible pattern in the arrangement of the bromine atoms around the cesium atom, but this is predictable since the anion packing must determine the structure. None of the distances is abnormally short compared with the value in CsBr (3.72 A), the shortest of 3.57 A being comparable with the shortest Cs---Cl distance of 3.3 A observed in $Cs_3Re_3Cl_{12}$.[1] The two shortest intermolecular Br---Br contacts are indicated in Table III. These values lie between the van der Waals distance of 3.9 A and those for the short intramolecular nonbonded contacts, of which the shortest is 3.29 A.

The $(Re_3Br_{11})^{-2}$ Anion.—The anion is based on the now familiar structural framework of the $(Re_3Cl_{9+n})^{n-}$ series[1–4] and the Re_3Br_9 species.[10] It closely resembles the $(Re_3Cl_{11})^{2-}$ anion,[2] possessing only two out of the three possible terminal bromine atoms in the plane of the Re_3 triangle. Thus, Re(2) is bonded to only four bromine atoms compared with the five for Re(1) and is termed "deficient."

The asymmetric unit includes one-half of the anion, which lies on a crystallographic mirror plane passing through the unique rhenium atom, Re(2), its two terminal bromine atoms, Br(4) and Br(5), and the bromine, Br(7), that bridges Re(1) and Re(1′). There are no significant deviations from the least-squares plane (calculated by the method of Schomaker, *et al.*[13]) for the atoms Re(1), Re(2), Br(3), Br(6), Br(7) of

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[11] O. S. Mills and J. S. Rollett, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, London, 1961, p 117.

[12] "International Tables for X-ray Crystallography," Vol. III, the Kynoch Press, Birmingham, England, 1962, pp 206–216.

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TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

K	L	|FO|	|FC|
H=0			
0	2	3525	4006
0	4	2533	2832
0	6	1220	1344
0	8	389	420
0	10	559	700
0	16	731	771
1	5	2307	1814
1	7	2010	2076
1	9	2384	2869
1	11	1141	1222
1	15	395	406
1	17	623	666
2	0	3416	2471
2	2	1279	1407
2	4	2775	2807
2	8	1173	1570
2	10	930	1252
2	12	708	742
2	16	850	843
3	1	2613	2086
3	3	1090	1085
3	5	452	722
3	7	1195	1306
3	9	679	729
3	11	613	722
3	15	269	294
3	17	184	151
4	2	1091	872
4	4	259	41
4	6	537	405
4	8	778	767
4	10	395	460
5	3	450	131
5	5	2875	2302
5	7	1958	2298
5	9	740	689
5	11	269	242
5	13	1061	969
5	15	772	747
6	0	971	1008
6	2	1590	1470
6	4	2152	1890
6	6	1914	1602
6	8	736	703
6	10	1230	1095
6	12	1075	886
6	14	784	625
6	16	419	408
7	1	1468	1941
7	3	2915	2654
7	5	2605	2286
7	7	389	233
7	9	1004	707
7	11	947	981
7	13	766	686
7	15	267	152
8	4	389	54
8	6	615	628
8	8	1009	897
8	12	1575	1476
8	14	834	850
9	1	388	31
9	3	829	837
9	5	2209	2252
9	11	423	292
10	0	2989	3261
10	2	475	420
10	4	680	683
10	10	1003	644
10	12	359	342
11	1	276	191
11	5	1185	1109
11	7	813	924
11	9	1461	1287
11	11	613	502
12	0	2346	3100
12	2	1482	1497
12	4	478	362
12	6	467	398
12	8	508	304
12	10	312	360
13	5	654	459
13	9	1175	1005
13	11	658	628
14	0	761	1062
14	2	967	997
14	4	826	979
15	5	470	515
15	9	247	120
16	4	315	201
17	5	672	822
17	7	414	295
18	0	492	675
18	2	178	289
18	4	832	794
18	6	445	444
19	3	758	931
19	5	854	1080
20	2	302	333
20	4	235	330
H=1			
0	2	189	33
0	3	532	503
0	5	440	518
0	6	1822	1915
0	7	703	508
0	8	2499	2867
0	9	641	702
0	10	1207	1446
0	11	468	504
0	12	843	918
0	13	782	661
0	14	221	217
0	15	685	674
0	16	323	260
0	17	670	673
1	1	1499	2710
1	2	743	740
1	3	982	987
1	4	686	755
1	5	587	778
1	6	688	717
1	7	651	593
1	8	1667	1610
1	9	679	763
1	10	273	223
1	11	413	425
1	14	313	168
1	15	681	576
1	16	308	215
1	17	511	473
2	1	1938	1812
2	2	640	727
2	4	866	624
2	5	571	220
2	6	864	887
2	8	1746	1912
2	9	441	371
2	10	776	845
2	12	452	442
2	13	107	112
2	15	243	159
2	17	121	114
3	1	715	599
3	3	1376	1321
3	4	204	24
3	5	628	421
3	6	914	945
3	7	380	453
3	8	494	430
3	9	443	341
3	10	742	764
3	11	378	333
3	12	718	572
3	13	195	86
3	14	649	504
3	16	253	244
3	17	115	54
4	1	399	279
4	2	875	1332
4	3	1305	946
4	4	207	187
4	5	844	547
4	6	1204	1132
4	7	1776	1346
4	8	218	106
4	9	445	294
4	10	156	83
4	11	342	284
4	13	235	194
4	14	239	250
4	15	412	402
4	17	104	76
5	1	2339	2193
5	2	3311	3541
5	3	1735	1862
5	4	1529	1303
5	5	690	498
5	7	442	244
5	8	219	132
5	9	525	401
5	10	586	441
5	11	821	643
5	12	525	356
5	13	1130	877
5	14	718	587
5	15	294	311
5	16	292	233
5	17	283	295
6	1	860	403
6	2	1910	1988
6	3	898	889
6	4	1503	1323
6	5	1738	1312
6	6	382	266
6	7	2487	2312
6	8	271	269
6	9	316	241
6	10	1721	1462
6	11	1158	999
6	12	738	700
6	13	940	735
6	15	426	347
6	16	319	233
7	1	2079	2170
7	2	1748	1618
7	3	1545	1721
7	4	1489	1279
7	5	605	506
7	6	898	780
7	7	607	562
7	10	701	476
7	11	796	743
7	12	135	62
7	13	1519	1257
7	14	825	625
7	15	610	532
7	16	253	283
8	1	699	519
8	2	533	564
8	3	744	780
8	4	1095	1030
8	5	870	789
8	6	1667	1777
8	8	316	255
8	9	534	330
8	10	149	18
8	11	247	245
8	12	184	86
8	13	351	307
8	14	420	323
9	1	826	718
9	2	717	714
9	3	1419	1709
9	5	1391	1400
9	6	499	490
9	9	730	559
9	10	415	283
9	12	175	202
9	13	307	254
10	4	155	204
10	5	548	519
10	7	348	304
10	8	764	789
10	9	296	237
10	10	372	326
10	12	348	261
10	13	243	229
11	1	220	250
11	2	272	337
11	3	742	869
11	4	157	234
11	5	907	882
11	6	348	345
11	7	717	616
11	8	577	627
11	9	1059	870
11	13	416	382
12	1	882	1083
12	2	222	238
12	3	471	515
12	4	348	443
12	5	343	366
12	6	1301	1331
12	7	698	696
12	8	1715	1472
12	10	494	470
12	11	219	243
12	12	231	294
12	13	170	132
13	1	1321	1561
13	2	803	1047
13	4	373	340
13	6	206	179
13	7	316	194
13	8	652	545
13	10	818	794
13	11	489	428
13	12	268	317
13	13	287	423
14	1	742	944
14	2	1056	1266
14	3	598	707
14	4	792	792
14	5	607	580
14	7	704	826
14	8	682	785
14	9	294	201
14	10	720	846
14	12	309	398
15	1	287	337
15	2	495	682
15	5	294	218
15	7	167	125
15	10	375	496
15	11	115	203
15	12	202	344
16	2	348	336
16	3	407	400
16	6	503	472
16	7	344	477
16	8	280	356
16	10	186	218
17	1	338	455
17	2	391	500
17	3	197	258
17	4	268	311
17	9	137	105
18	4	480	479
18	5	191	232
18	6	527	582
18	7	189	188
19	3	604	738
19	4	331	445
19	5	469	592
19	6	196	258
20	2	193	227
20	3	212	317
20	4	324	499
H=2			
0	2	1125	1202
0	3	1749	1807
0	4	1465	1463
0	5	902	864
0	6	923	942
0	7	1222	1303
0	8	1588	1742
0	9	1155	1319
0	10	358	327
0	11	1060	1031
0	12	1774	2168
0	13	275	196
0	14	1382	1310
0	15	492	362
0	16	95	24
1	1	409	688
1	2	453	520
1	3	2376	2350
1	4	441	392
1	5	1825	1303
1	6	654	492
1	8	438	470
1	11	611	562
1	12	317	307
1	13	295	238
1	14	575	495
1	15	208	149
1	16	371	304
1	17	171	153
2	0	718	448
2	1	1105	1099
2	2	502	619
2	3	469	347
2	4	2121	2189
2	5	931	1078
2	6	887	727
2	7	1092	1202
2	8	308	330
2	9	333	394
2	10	597	671
2	11	766	634
2	12	413	352
2	13	220	130
2	14	604	445
2	15	204	129
2	16	536	421
2	17	154	119
3	0	1268	984
3	1	832	726
3	2	348	157
3	3	829	413
3	4	1466	1600
3	5	240	238
3	6	932	885
3	7	890	1025
3	8	726	830
3	9	335	273
3	10	126	02
3	11	835	764
3	12	606	488
3	13	108	54
3	14	257	202
3	15	478	396
4	0	1764	1326
4	1	2068	1845
4	2	852	879
4	3	1319	1139
4	4	1068	1046
4	5	519	294
4	6	582	336
4	7	357	307
4	8	532	432
4	10	473	327
4	11	613	503
4	12	233	231
4	15	176	177
5	0	910	632
5	1	1735	1039
5	2	392	558
5	3	938	1029
5	4	1252	1121
5	5	2329	2557
5	6	2298	2057
5	7	1609	1604
5	8	177	170
5	9	971	862
5	10	721	605
5	11	980	718
5	12	781	625
5	13	103	81
5	14	809	636
5	15	338	207
5	16	577	546
6	0	1384	1246
6	1	1127	902
6	1	1133	902
6	2	1874	2083
6	3	903	758
6	4	791	764
6	5	2052	1855
6	6	1196	1093
6	8	762	644
6	9	336	301
6	10	551	423
6	12	249	178
6	13	552	397
6	14	419	396
6	15	704	610
6	16	417	414
7	0	117	218
7	1	265	281
7	2	785	916
7	3	408	296
7	4	1085	954
7	5	867	828
7	6	1883	1743
7	7	1125	1049
7	9	1877	1785
7	10	914	728
7	10	914	728
7	11	1350	1263
7	12	926	713
7	14	485	499
7	15	448	477
7	16	308	401
8	0	1809	1860
8	1	1343	1387
8	2	952	1078
8	3	901	1006
8	4	566	487
8	6	177	157
8	7	381	346
8	9	739	611
8	10	267	140
8	11	391	329
8	12	229	111
8	13	257	129
8	14	186	156
8	16	250	280
9	0	1759	1846
9	1	356	430
9	2	931	968
9	3	218	203
9	4	852	943
9	7	803	771
9	8	276	288
9	9	796	794
9	11	214	82
9	12	524	477
9	13	291	213
9	14	248	182
9	15	99	52
10	2	249	212
10	3	591	778
10	4	358	464
10	5	381	368
10	6	178	116
10	7	329	273
10	8	656	523
10	10	292	213
10	11	202	183
10	12	591	537
10	13	170	80
10	14	378	372
11	0	1023	1340
11	2	283	203
11	3	663	919
11	4	402	437
11	5	867	822
11	6	480	439
11	7	343	194
11	8	648	652
11	9	111	160
11	10	231	214
11	11	162	107
11	12	441	372
11	14	271	317
12	0	219	330
12	1	126	121
12	2	358	412
12	3	356	471
12	4	984	1133
12	5	347	251
12	6	706	953
12	7	485	566
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0	1	1218	1240
0	3	859	1027
0	6	980	1123
0	8	1169	1572
1	4	332	353
2	1	1254	1056
2	2	489	509
2	3	386	378
2	4	299	292
3	1	490	380
3	3	424	363
3	4	546	603
3	5	422	380
4	2	422	358
4	3	472	452
4	4	298	350
4	5	903	124
4	6	1034	469
5	2	332	251
5	4	1637	1538
5	5	782	748
6	1	355	450
6	2	2112	1666
6	3	1400	1290
6	4	1303	1177
6	5	1241	1112
7	3	934	701
7	4	1160	1118
7	5	840	778
7	6	1100	998
7	7	627	609
7	8	370	308
7	11	352	522
8	1	353	512
8	4	500	423
8	5	235	265
8	6	590	682
8	7	261	314
8	11	394	430
9	6	235	254
9	10	229	237
11	8	229	247
11	9	385	277
12	1	1034	1082
12	10	343	375
13	1	898	943
14	1	571	651
15	1	314	355
H=8			
0	2	1303	1484
0	3	416	403
0	5	1273	1525
0	6	472	646
0	7	462	634
1	1	421	385
1	4	680	694
2	0	786	710
2	1	953	873
2	2	987	803
2	3	865	740
2	4	797	753
3	0	1197	1143
3	1	357	349
3	3	510	475
3	4	979	990
4	0	804	685
4	3	607	546
4	4	502	459
4	5	535	542
5	0	705	632
5	2	339	333
5	3	735	622
5	5	1359	1350
5	6	373	399
5	7	415	510
5	8	471	548
6	2	508	428
6	3	238	366
6	4	987	819
6	5	459	418
6	6	613	558
6	7	258	322
6	9	329	389
7	0	436	398
7	1	704	628
7	3	1434	1131
7	4	629	609
7	5	934	929
7	6	367	301
7	7	257	361
7	9	280	311
8	0	428	307
8	1	494	474
8	5	235	243
8	6	504	540
8	7	561	589
8	9	228	212
8	10	265	292
9	0	419	453
9	7	402	347
10	0	286	306
11	9	348	347
12	0	996	982
12		1025	179
H=9			
0	2	461	433
0	3	465	475
0	4	1312	968
0	5	451	519
0	6	438	592
0	7	841	1043
1	0	268	00
1	1	709	606
1	2	1367	1197
1	4	537	509
2	4	515	409
2	5	338	356
2	6	810	775
3	6	335	368
4	1	497	437
5	1	927	769
5	2	238	295
5	3	1028	901
5	5	450	322
5	8	327	440
6	3	338	294
6	6	339	510
6	7	417	412
6	8	478	636
6	9	224	196
6	10	595	588
7	1	1293	1196
7	3	723	504
7	4	235	247
7	8	439	408
7	10	214	225
8	1	682	636
8	5	405	425
8	6	395	203
9	6	322	287
9	7	460	307
10	7	540	482
H=10			
0	0	743	551
0	2	600	686
0	4	702	659
0	6	500	591
1	3	504	511
1	5	724	613
2	2	570	426
2	4	500	470
4	0	761	773
5	0	583	465
5	4	480	336
5	7	751	783
5	9	1014	869
6	2	956	765
6	5	227	283
9	7	389	404
H=11			
0	2	885	818
0	4	615	450
1	1	637	517
1	2	602	575
1	4	454	431
2	6	690	581
3	1	627	484
5	1	677	521
6	1	509	442
7	1	935	787

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[a] There is a scale factor of 5, making $F(000) = 14{,}400$.

TABLE III

INTERATOMIC DISTANCES AND BOND ANGLES INVOLVING THE $(Re_3Br_{11})^{2-}$ ANIONS[a]

Bond	Length, A	Angle	Value, deg
Re(1)-Re(1′)	2.496	Re(1)Br(6)Re(2)	56.7
Re(1)-Re(2)	2.433	Re(1)Re(2)Br(6)	61.8
Re(1)-Br(1)	2.46	Re(2)Re(1)Br(6)	61.5
Re(1)-Br(2)	2.49	Re(1)Re(2)Re(1′)	61.7
Re(1)-Br(3)	2.72	Re(1)Re(1′)Re(2)	59.1
Re(2)-Br(4)	2.37	Re(1)Br(7)Re(1′)	59.4
Re(2)-Br(5)	2.40	Re(1)Re(1′)Br(7)	60.3
Re(1)-Br(6)	2.57	Br(1)Re(1)Br(7)	91.2
Re(1)-Br(7)	2.52	Br(1)Re(1)Br(3)	80.9
Re(2)-Br(6)	2.56	Br(1)Re(1)Br(6)	90.2
Br(1)---Br(1′)	3.29	Br(2)Re(1)Br(7)	91.5
Br(2)---Br(2′)	3.34	Br(2)Re(1)Br(3)	78.8
Br(1)---Br(4)	3.73	Br(2)Re(1)Br(6)	86.8
Br(2)---Br(5)	3.76	Br(4)Re(2)Br(5)	133.7
Br(1)---Br(3)	3.37	Br(4)Re(2)Br(6)	89.7
Br(2)---Br(3)	3.31	Br(5)Re(2)Br(6)	88.2
Br(5)---Br(6)	3.45		
Br(4)---Br(6)	3.47		
Br(2)---Br(6)	3.48		
Br(2)---Br(7)	3.59		
Br(1)---Br(6)	3.56		
Br(1)---Br(7)	3.56		
Br(2)---Br(7)[b]	3.46		
Br(4)---Br(5)[b]	3.52		

[a] Estimated standard deviations based upon 1.5 times the indication of the least squares refinement are: Re(1)-Re(2), $\sigma = 0.008$ A; Re(1)-Re(1′), $\sigma = 0.011$ A; Re-Br, $\sigma = 0.012$ A; Br---Br, $\sigma = 0.016$ A; all angles, $\sigma \leqslant 0.5°$. [b] Denotes intermolecular contact between bromines of adjacent anions lying on the same mirror plane.

one anion. The equation of the plane is $-0.7579X - 0.0118Y + 0.6523Z + 0.0019 = 0$, where coordinates are expressed in angstrom units. Within limits of error this plane is a plane of symmetry for the anion, which thus has effective C_{2v} symmetry.

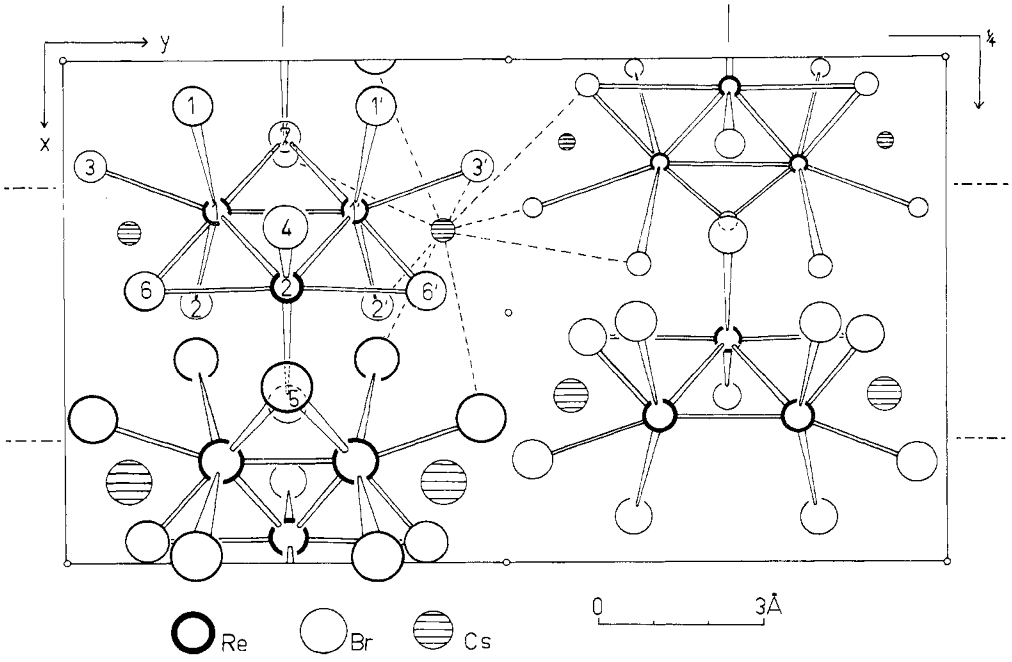

Figure 1.—The $Cs_2Re_3Br_{11}$ structure as viewed down the c axis. Broken lines indicate Cs- - -Br contacts, some of which are directed to anions related by translations $\pm c$ to those shown.

The most interesting dimensional features are the nonequality of the Re–Re bond lengths and the length and angular relation of the terminal Re–Br bonds to the deficient rhenium. The Re–Re bond lengths parallel those in $(Re_3Cl_{11})^{2-}$. The two short bonds, associated with the deficient rhenium atom, are 2.433 A (2.435 A in $(Re_3Cl_{11})^{2-}$). The bond between the nondeficient rhenium atoms is 2.496 A (2.483 A in $(Re_3Cl_{11})^{2-}$). (In $(Re_3Br_{12})^{3-}$[14] and Re_3Br_9, where the Re_3 triangles are equilateral, the corresponding mean lengths are 2.49 and 2.465 A, respectively.) The observation in $(Re_3Cl_{11})^{2-}$ of an increase in Re–Re bond strength associated with a rhenium atom that forms only six σ bonds instead of seven is thus strikingly confirmed. This increased bond strength has been accounted for in terms of greater directional character of the changed σ-bond framework.[15]

In all the trimeric rhenium compounds studied so far, the angle subtended by a pair of off-plane halogen atoms at a nondeficient rhenium atom has been within the range 155–160°. Representative values are 158° for $(Re_3Cl_{12})^{3-}$, 155° for $(Re_3Br_{12})^{3-}$, and 159° for $(Re_3Br_{11})^{2-}$ and $(Re_3Cl_{11})^{2-}$. When the same angle is considered for halogen atoms bonded to a deficient rhenium atom, it is found that in $(Re_3Cl_{11})^{2-}$ and in Re_3Br_9 the values (153 and 155°, respectively) are close to the above figures. (In $(Re_3Cl_{11})^{2-}$ the deficient Re atom is probably associated with an in-plane water molecule.[2]) In $(Re_3Br_{11})^{2-}$, however, the angle Br(4)Re(2)Br(5) is only 133°. This reduction does not appear to have been brought about by intermolecular forces. The only intermolecular distance less than 4.0

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(14) G. J. Gainsford, B. R. Penfold, and M. Elder, to be published.

(15) J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965).

A involving Br(4) or Br(5) is the Br(4)---Br(5) distance of 3.52 A between ions related by the *a* glide plane. This contact and the other short intermolecular distance are dependent upon the inclination of the Re_3 triangle to the (001) plane, but are not necessarily related to the size of the Br(4)Re(2)Br(5) angle. When the short intramolecular contacts are considered it is clear that a marked reduction in repulsive forces has been achieved by the closing of this angle. First we note that the distances Br(4)---Br(6) and Br(5)---Br(6) are virtually independent of the angle under consideration. This leaves the contacts Br(1)---Br(4) and Br(2)---Br(5) as the important factors. These two independent distances average 3.74 A, which, when compared with the Br(1)---Br(1′) distance of 3.31 A and the corresponding 3.38 A in Re_3Br_9, indicates a considerable decrease in bromine–bromine repulsive forces across the face of the anion.

Accompanying the decrease in the Br(4)Re(2)Br(5) angle is a corresponding shortening of the two off-plane terminal bonds to a mean value of 2.38 A, compared with the mean value of 2.47 A for the bonds to Re(1). This difference of 0.09 A is about 7σ and therefore highly significant. It may be accounted for by postulating some π bonding between filled 3d orbitals of the terminal bromines and the rhenium 5p or 5s5p hybrid lying in the plane of the Re_3 triangle and unused in the absence of an in-plane terminal bromine. It is significant that shortening of the terminal off-plane bonds has not occurred in the isolated Re_3Br_9[10] species where *all* rhenium atoms are "deficient." Neither has the angle subtended by the pair of off-plane bromine atoms decreased. Additional π bonding cannot therefore be postulated in this case. It is hard to believe that intermolecular packing forces (which appear to be quite weak in the complex in which Re_3Br_9 occurs) could cause such wide variations as exist between the dimensions of $(Re_3Br_{11})^{2-}$ and neutral Re_3Br_9. For a full understanding of these variations we must await a quantitative bonding theory which considers the trinuclear cluster as a whole.

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of Chlorothiodiazyl Chloride, $S_3N_2Cl_2$[1]

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$S_3N_2Cl_2$ crystallizes in the monoclinic space group $P2_1$ with cell dimensions $a = 6.546$ A, $b = 8.600$ A, $c = 5.508$ A, and $\beta = 102.37°$; there are two formula units per unit cell. The material is a salt consisting of a chloride anion and a $\underline{S{-}N{-}S{-}N{-}S}{-}Cl^+$ cation. The sulfur and nitrogen atoms form a puckered five-membered ring.

Introduction

$S_3N_2Cl_2$ was first identified by Demarcay,[2] who prepared it by allowing SCl_2 or S_2Cl_2 to react with S_4N_4. Meuwsen[3] prepared $S_3N_2Cl_2$ by allowing $(NSCl)_3$ to react with S_2Cl_2. More recently Jolly, Maguire, and Rabinovich[4] produced the material by refluxing a suspension of ammonium chloride in S_2Cl_2. An X-ray crystal structure analysis on a crystal prepared by Jolly's method was undertaken to determine the molecular structure of this compound.

Experimental Section

$S_3N_2Cl_2$ is a yellow crystalline salt which decomposes in the air. The salt was removed from its container in a nitrogen-filled drybox, crushed, and sieved. Several crystal fragments of about 0.3 mm were introduced into tapered quartz capillaries of about the same size and sealed. With patient use of a microscope and a file, a single crystal fragment was isolated and wedged in the capillary; the capillary was fire sealed to a final length of about 1 cm. The crystal fragment was an irregular plate with dimensions approximately 0.3 × 0.4 × 0.2 mm. Some decomposition of the crystal surface did occur as the crystal lost its yellow color and took on a blackish tinge; however, the crystal diffracted X-rays well and no further decomposition was encountered. The crystal was oriented with the monoclinic *b* axis parallel to the length of the capillary.

A General Electric XRD-5 apparatus equipped with a quarter-circle Eulerian cradle type goniostat, a scintillation counter, a pulse height discriminator, and a molybdenum X-ray tube was used to measure the cell dimensions and the intensities. The X-ray tube was operated at 20 ma and 40 kv. The primary X-ray beam was filtered with a Zr filter.

The measured monoclinic cell dimensions based on $\lambda_{K\alpha_1} = 0.70926$ A are: $a = 6.546 \pm 0.007$ A, $b = 8.600 \pm 0.004$ A, $c = 5.508 \pm 0.005$ A, and $\beta = 102.37 \pm 0.03°$. The observed density was 2.0 g/ml, suggesting two formula units per unit cell;

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) E. Demarcay, *Compt. Rend.*, **92**, 726 (1881).

(3) A. Meuwsen, *Ber.*, **65**, 1731 (1932).

(4) W. L. Jolly, K. D. Maguire, and D. Rabinovich, *Inorg. Chem.*, **2**, 1304 (1963).