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The Crystal Structure of Phosphorus Heptabromide, PBr_7

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The crystal structure of phosphorus heptabromide, PBr_7, has been determined by single-crystal X-ray diffraction studies. The red compound crystallizes in the orthorhombic space group *Pnma* with $a=9{\cdot}35\pm0{\cdot}02$, $b=7{\cdot}94\pm0{\cdot}01$, and $c=14{\cdot}69\pm0{\cdot}02$ Å. The structure contains tetrahedral PBr_4^+ ions with P–Br distances all about 2·17 Å and an almost linear unsymmetrical Br_3^- ion with Br–Br distances of 2·91 and 2·39 Å. The bonding in the tribromide ion is discussed.

Introduction

Kastle & Beatty (1900) discovered that the supposed red form of PBr_5 was actually PBr_7. Bromine is easily absorbed by PBr_5 to form the red PBr_7 and, conversely, is easily lost by PBr_7 to form PBr_5. It seemed likely that the PBr_4^+ ion of the PBr_5 (van Driel & MacGillavry, 1943) remained intact in PBr_7 and that a tribromide ion was formed, in a similar way to the formation of PCl_4^+ and ICl_2^- on addition of ICl to PCl_5 (Zeelezny & Baenziger, 1952). Romers & Keulemans (1958) have reported the structure of a tribromide ion in $[N(CH_3)_3H^+]_2Br^-Br_3^-$. It was symmetrical and slightly bent (171°) with the Br–Br distances both 2·54 Å. An X-ray diffraction study of PBr_7 was undertaken in order to determine if the tribromide ion existed in PBr_7 and its configuration if its existence was confirmed.

Preparation and experimental data

The compound PBr_7 was prepared in a manner similar to the preparation of PBr_6I (Fialkov & Kuzmenko, 1949) by saturating carbon disulfide with phosphorus pentabromide and slowly adding Br_2 until crystals appeared. The crystals grew as red flat needles. They were very hygroscopic and lost bromine unless kept in solution or sealed in a glass tube. The crystals can also be prepared by sublimation of a mixture of PBr_5 and Br_2 (Kastle & Beatty, 1900). It was found that the 'wet' crystals from solution lasted longer in the air, making it possible to mount one in a Pyrex glass capillary.

The lattice constants for PBr_7, determined from Mo *Kα* precession camera photographs and Cu *Kα* Weissenberg camera photographs, are $a=9{\cdot}35\pm0{\cdot}02$, $b=7{\cdot}94\pm0{\cdot}01$, and $c=14{\cdot}69\pm0{\cdot}02$ Å. The systematic extinctions ($k+l=2n+1$ for $0kl$ reflections, $h=2n+1$ for $hk0$ reflections) implied the space group $Pn2_1a$ or *Pnma*.

Owing to the instability of the compound an experimental density was not obtained. However, the only choice for the number of molecules per unit cell that was consistent with the space group and gave a reasonable value for the calculated density (3·60 g.cm^{-3}) was 4.

Intensity data were collected on a Weissenberg camera with the multi-film technique using Cu *Kα* radiation. The size of the crystal used was approximately 0·6 mm × 0·15 mm × 0·12 mm. The zero through fifth layers were recorded while rotating around the [100] direction (needle axis). Of the 761 reflections within the limiting sphere of Cu *Kα* radiation for the layers recorded, 604 had an intensity greater than the minimum observable intensity. These intensities were measured visually with a set of standard spots made from the same crystal used to collect the intensity data.

Determination of the structure

It was assumed that the centrosymmetric space group *Pnma* was the correct one. This choice was confirmed by the solution of the phase problem, and subsequently by a statistical analysis by Wilson's (1949) method. With eightfold general positions and four molecules per unit cell, it was necessary to place some of the atoms of the PBr_7 unit in sets of fourfold special positions. Stereochemically, it was necessary to place the PBr_4^+ moieties on the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$ with the phosphorus atom and two of the bromine atoms [labeled Br(2) and Br(3)] located directly on the mirror plane and with the remaining two bromine atoms [labeled Br(1)] related to each other by the mirror plane. For the Br_3^- ions, three choices were possible. One choice would locate the central bromine on a center of symmetry, thus requiring the ion to be linear and symmetrical ($D_{\infty h}$). A second choice would locate each tribromide ion across one of the mirror planes with a symmetrical but possibly non-linear ion (C_{2v}) resulting. The third choice involved locating all three bromine atoms on a mirror plane. In this case, the ion would not be required to have any symmetry beyond C_s.

A three-dimensional sharpened Patterson map was calculated with the Fourier summation program of Sly, Shoemaker & Van den Hende (1962) on an IBM 709 computer. The positions of the atoms in the PBr_4^+ ion were estimated from this map. There were no

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Patterson vectors consistent with the first two possible choices for the location of the tribromide ion. Since no vectors could be found that fit a symmetrical or slightly distorted linear tribromide ion, a Fourier synthesis was computed using only the positions of the atoms in the PBr_4^+ ion. Six extra peaks showed up on the first map and by trial and error it was found which of these were the three bromine atoms in the tribromide ion. The Busing, Martin & Levy (1962) 709-7090 FORTRAN crystallographic least-squares program was used for final refining. The atomic scattering factors used for P and Br were those in Table 3.3.1A in *International Tables for X-ray Crystallography* (1962). The refinement with isotropic temperature factors proceeded to a value of $R_1 = 0·134$ (see Table 1 for definition of R_1). On refinement of anisotropic temperature factors and utilizing a modified Hughes weighting scheme (Willett, Dwiggens, Kruh & Rundle, 1962), a value of $R_1 = 0·095$ was obtained. Unobserved reflections were assigned an intensity equal to one third of the lowest observable intensity. They were omitted from the refinement if the calculated structure factor was less than the 'observed' value. The values of the scale factors for the different layers of Weissenberg data obtained during the isotropic refinement were not varied during the anisotropic refinement.

After removing 10 reflections which appeared to be suffering from extinction, the value of R_1 reduced to 0·080. Final parameters are listed in Table 1. The tem-

Table 2. *Observed and calculated structure factors*

The columns contain k, $10|F_o|$ and $10\ F_c$. An unobserved reflection is denoted by a negative sign in front of $10|F_o|$. Reflections suffering from extinction are denoted by *.

H= 0 L= 0		
2*	2884	-4123
4*	4683	5743
6*	1858	-2320
8	1675	1724
H= 2 L= 0		
1	1189	-1709
2*	2389	-3414
3	992	1003
4	273	-295
5	1006	-1090
6	1096	-1099
7	289	325
8	356	313
9	516	-477
H= 4 L= 0		
1*	1597	-2576
2*	2872	4035
3	2411	2623
4	758	-789
5	1244	-1214
6	1528	1665
7	1725	1476
8	760	-713
9	380	-414
H= 0 L= 1		
1	290	-349
3	690	-741
5	851	-842
7	640	-722
9	415	-530
H= 1 L= 1		
1	265	-249
2	447	479
3	998	-1003
4	241	-229
5	1002	-955
6	353	321
7	876	-919
8	290	-249
9	561	-623
H= 2 L= 1		
1	608	-739
2	-45	21
3	1412	1489
4	380	-390
5	256	226
6	194	199
7	1073	1057
8	179	-200
9	298	284
H= 3 L= 1		
1*	1748	2343
2	583	-663
3	836	-882
4	-70	-18
5	2123	2091
6	267	-241
7	-91	25
8	-103	127
9	989	1037
H= 4 L= 1		
0	1323	1174
1	136	-127
2	227	-251
3	582	-647
4	714	725
5	588	-546
6	319	-241
7	817	-704
8	268	178
9	341	-332
H= 5 L= 1		
0	223	-179
1	793	1009
2	1082	1224
3	1504	-1644
4	-78	-177
5	-86	88
6	455	417
7	1348	-1204
8	-88	-173
H= 0 L= 2		
0	327	248
2	680	632
4	200	250
6	-86	-10
8	189	165
H= 1 L= 2		
0	721	-495
1	949	-873
2*	2643	-3802
3	555	556
4	-68	-24
5	625	-644
6	1240	-1263
7	323	289
8	341	400
9	258	-347
H= 2 L= 2		
0	699	-541
1	1288	1466
2	361	-381
3	1179	-1099
4	209	-207
5	541	547
6	209	-184
7	297	-291
8	-102	101
9	-82	27
H= 3 L= 2		
0*	2543	3217
1	1473	1395
2	658	747
3	737	-760
4	1686	1729
5	1132	1120
6	206	164
7	159	-247
8	-102	93
9	461	539
H= 4 L= 2		
0	695	568
1	812	826
2	152	172
3	504	-503
4	225	274
5	388	377
6	-108	92
7	-131	-6
8	-116	-39
9	-84	9
H= 5 L= 2		
0	1338	-1394
1	500	-462
2	1206	-1411
3	-70	-152
4	841	-817
5	666	-610
6	485	-397
7	412	-356
8	-87	-37
H= 0 L= 3		
1	548	-457
3	1048	-1017
5	992	-1020
7	962	-1126
9	473	-574
H= 1 L= 3		
0	1145	-997
1	2006	1945
2	769	692
3	848	-883
4	663	-648
5	1594	1559
6	423	432
7	189	-173
8	343	-324
9	723	788
H= 2 L= 3		
0	188	105
1	280	-253
2	729	-721
3	1557	1401
4	-68	108
5	705	723
6	211	-227
7	1119	1149
8	176	91
9	585	550
H= 3 L= 3		
0	150	74
1	1171	1060
2	410	418
3	1401	-1443
4	-73	-25
5	264	269
6	248	179
7	952	-1000
8	-100	-98
9	-77	48
H= 4 L= 3		
0	2512	2386
1	474	449
2	1061	-1113
3	1243	-1319
4	1446	1567
5	485	-511
6	670	-746
7	1104	-1013
8	510	495
9	424	-476
H= 5 L= 3		
0	1225	1148
1	99	-67
2	1417	-1693
3	458	474
4	959	938
5	336	302
6	915	-906
7	488	407
8	669	585
H= 0 L= 4		
0	1824	-2024
2	1743	-1836
4	1112	-1047
6	389	-447
8	-105	-32
H= 1 L= 4		
0	1525	-1360
1	2583	-2774
2	394	-363
3	1869	2084
4	728	-723
5	1379	-1431
7	700	754
8	-107	-54
9	370	-419
H= 2 L= 4		
0*	2609	3393
1	2247	-2315
2	357	303
3	2103	2105
4	2097	2031
5	1078	-1143
6	226	-273
7	1030	1033
8	532	463
9	342	-362
H= 3 L= 4		
0	357	-251
1	228	201
2	1530	1543
3	-67	-12
4	267	-223
5	-84	185
6	518	558
7	-110	87
8	210	-200
9	-73	66
H= 4 L= 4		
0	1646	-1613
1	770	-733
2	1160	-1224
3	170	190
4	829	-906
5	641	-699
6	338	-361
7	-129	-119
8	-110	-10
9	297	-324
H= 5 L= 4		
0	1184	-1210
1	1825	1879
2	-67	74
3	1465	-1714
4	775	-790
5	935	892
6	-89	173
7	922	-758
8	263	-205
H= 0 L= 5		
1	624	-457
3	762	676
5	-82	59
7	243	356
9	163	198
H= 1 L= 5		
0	1570	-1447
1	1166	1048
2	1076	986
3	331	325
4	953	-974
5	1474	1586
6	574	594
7	505	585
8	393	-395
9	835	958
H= 2 L= 5		
0	1917	1878
1	276	245
2	1516	-1507
3	536	-537
4	1314	1300
5	-81	-25
6	825	-864
7	471	-455
8	730	579
9	-72	-35
H= 3 L= 5		
0	556	-441
1	337	-264
2	1326	1243
3	893	-908
4	386	-396
5	799	-809
6	487	534
7	1118	-1056
8	302	-301
9	396	-457
H= 4 L= 5		
0	-73	68
1	-75	-55
2	570	-375
3	334	325
4	-98	78
5	-106	92
6	-109	-162
7	402	352
8	-106	88
H= 5 L= 5		
0	864	809
1	700	642
2	1775	-1907
3	288	287
4	752	766
5	993	1030
6	1184	-951
7	686	536
8	649	583
H= 0 L= 6		
0	924	-796
2	1384	-1248
4	267	-298
6	514	-531
8	217	255
H= 1 L= 6		
0	1743	1607
1	1757	1526
2	1302	1258
3	1088	-1099
4	744	797
5	766	855
6	436	454
7	416	-357
8	-101	-102
9	192	260
H= 2 L= 6		
0	1310	1270
1	2093	-1937
2	664	652
3	1698	1736
4	816	770
5	1035	-1093
6	-88	62
7	927	899
8	-92	134
9	367	-425
H= 3 L= 6		
0	524	470
1	1277	-1108
2	2716	-2718
3	701	678
4	410	401
5	876	-894
6	987	-1018
7	187	242
8	334	340
9	203	-421
H= 4 L= 6		
0	1013	-935
1	1482	-1330
2	609	-630
3	937	913
4	617	-600
5	886	-993
6	-108	-75
7	364	361
8	-100	-128
H= 5 L= 6		
0	1631	1721
1	193	-189
2	231	246
3	441	470
4	1007	1074
5	270	261
6	-107	-21
7	277	274
8	194	170
H= 0 L= 7		
1	540	382
3	838	783
5	1021	1001
7	962	891
9	512	628
H= 1 L= 7		
0	1238	-1074
1	904	-806
2	1016	1001
3	621	620
4	711	-737
5	504	-543
6	443	500
7	271	272
8	282	-291
9	191	-231
H= 2 L= 7		
0	1311	1073
1	492	415
2	477	-458
3	1448	-1383
4	726	736
5	463	-466
6	350	-366
7	1164	-1167
8	294	269
9	304	-395
H= 3 L= 7		
0	683	594
1	397	-336
2	642	-614
3	352	312
4	404	406
5	-90	-126
6	275	-285
7	-104	125
8	-85	145
H= 4 L= 7		
0	861	-767
1	-88	-74
2	221	-205
3	853	905
4	472	-458
5	532	610
6	-131	17
7	887	826
8	-93	-35
H= 5 L= 7		
0	572	584
1	-77	28
2	428	-413
3	-84	-90
4	377	364
5	-89	71
6	-104	-164
7	-90	-150
8	-65	79
H= 0 L= 8		
0	1276	1024
2	990	866
4	714	742
6	-91	22
8	220	271
H= 1 L= 8		
0	435	-348
1	1335	-1190

Table 1. *Parameters for* PBr_7

Standard deviations are given in parentheses.
The β_{ij} are defined by:
$T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}	β_{12}	β_{23}
P	0·1133 (0·0016)	0·25	0·1477 (0·0005)	0·0010 (0·0020)	0·0053 (0·0010)	0·0018 (0·0003)	0·0008 (0·0005)	0·0	0·0
Br(1)	0·2352 (0·0003)	0·0311 (0·0003)	0·1085 (0·0001)	0·0047 (0·0006)	0·0057 (0·0003)	0·0040 (0·0001)	−0·0003 (0·0001)	−0·0007 (0·0003)	−0·0001 (0·0001)
Br(2)	0·0761 (0·0005)	0·25	0·2934 (0·0003)	0·0060 (0·0010)	0·0168 (0·0005)	0·0026 (0·0002)	0·0004 (0·0003)	0·0	0·0
Br(3)	−0·0916 (0·0006)	0·25	0·0773 (0·0003)	0·0043 (0·0010)	0·0164 (0·0006)	0·0038 (0·0002)	−0·0016 (0·0003)	0·0	0·0
Br(4)	0·1818 (0·0005)	0·75	0·3778 (0·0002)	0·0076 (0·0008)	0·0101 (0·0005)	0·0029 (0·0001)	−0·0007 (0·0002)	0·0	0·0
Br(5)	−0·0804 (0·0005)	0·75	0·4848 (0·0002)	0·0039 (0·0009)	0·0075 (0·0005)	0·0031 (0·0001)	−0·0000 (0·0002)	0·0	0·0
Br(6)	0·4031 (0·0006)	0·75	0·2966 (0·0003)	0·0059 (0·0011)	0·0204 (0·0007)	0·0050 (0·0002)	0·0005 (0·0003)	0·0	0·0

$$R_1 = \frac{\sum_{hkl} ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum_{hkl} |F_{\text{obs}}|} = 0·080$$

$$R_3 = \frac{\sqrt{\sum_{hkl} w\,(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}}{\sqrt{\sum_{hkl} w|F_{\text{obs}}|^2}} = 0·102$$

Table 2 (*cont.*)

2	2293	2293
3	1090	1071
4	379	-402
5	680	-690
6	858	966
7	594	557
8	390	-433
H= 2 L= 8		
0	1889	-1826
1	385	261
2	-72	-77
3	344	-318
4	1067	-1133
5	-87	-6
6	154	111
7	-99	-131
8	213	-202
H= 3 L= 8		
0	3182	-3227
1	-75	-115
2	1279	1194
3	-83	-92
4	2036	-2160
5	211	-198
6	959	845
7	-99	-140
8	659	-663
H= 4 L= 8		
0	1186	1127
1	812	-809
2	455	433
3	896	966
4	550	640
5	389	-441
6	-128	164
7	000	678
H= 5 L= 8		
0	318	277
1	957	1031
2	980	1151
3	573	-627
4	-89	106
5	1049	873
6	605	439
7	268	-220
H= 0 L= 9		
1	1519	1437
3	1191	-1088
5	979	1013
7	474	-474
H= 1 L= 9		
0	1194	-1032
1	551	-533
2	1210	1183
3	454	-421
4	726	-806
5	853	-955
6	699	662
7	629	-640
8	303	-427
H= 2 L= 9		
0	783	-685
1	349	291
2	615	655
3	368	-375
4	423	-463
5	-88	82
6	276	300
7	261	-233
8	204	-166
H= 3 L= 9		
0	-79	66
1	950	848
2	660	-679
3	-86	15
4	-90	144
5	1010	1183
6	387	-326
7	350	306
8	122	202
H= 4 L= 9		
0	463	423
1	255	-194
2	515	-474
3	266	281
4	332	375
5	-132	-33
6	337	-321
7	207	179
H= 5 L= 9		
0	753	713
1	431	361
2	-87	186
3	846	-925
4	417	462
5	-105	-219
6	-95	-57
7	852	-777
H= 0 L=10		
5	269	-231
0	2312	2526
2	465	-438
4	1637	1611
6	377	-382
8	316	343
H= 1 L=10		
0	509	-421
1	-83	57
2	750	-707
3	-89	-43
4	234	-220
5	-94	-100
6	301	-259
7	-96	73
H= 2 L=10		
0	369	-358
1	800	-848
2	1442	-1425
3	509	560
4	-88	-137
5	501	-544
6	618	-527
7	-88	127
H= 3 L=10		
0	429	-370
1	558	507
2	1312	1328
3	375	-328
4	389	-385
5	530	439
6	738	677
7	150	-134
8	174	-344
H= 4 L=10		
1	972	-1010
2	1167	1252
3	982	1071
4	-109	117
5	475	-446
6	466	431
7	659	588
H= 5 L=10		
0	878	-925
1	666	-756
2	-89	96
3	445	460
4	717	-658
5	649	-550
6	250	180
7	-65	80
H= 0 L=11		
1	1346	1266
3	1678	-1759
5	435	365
7	1275	-1243
H= 1 L=11		
0	153	140
1	681	610
2	-90	-66
3	732	-783
4	-94	54
5	309	240
6	-104	16
7	452	-535
H= 2 L=11		
0	404	-400
1	164	160
2	-86	36
3	448	478
4	218	-227
5	644	575
6	97	15
7	566	530
H= 3 L=11		
0	344	-348
1	480	542
2	174	189
3	239	-255
4	238	-241
5	592	547
6	-95	129
7	-76	-55
H= 4 L=11		
0	598	621
1	875	-917
2	-109	-19
3	234	272
4	544	462
5	1015	-995
6	186	-183
7	-79	-114
H= 5 L=11		
0	317	346
1	-89	-152
2	-89	-144
3	-108	-54
4	302	286
6	237	-189
H= 0 L=12		
0	1103	-1090
2	408	454
4	648	-728
6	261	261
H= 1 L=12		
0	778	-825
1	-92	45
2	749	-794
3	-94	-75
4	439	-480
5	-108	-52
6	-96	-238
H= 2 L=12		
0	439	447
1	533	562
2	-88	86
3	347	-385
4	438	332
5	303	278
6	89	-58
H= 3 L=12		
0	495	514
1	-91	-0
2	812	934
3	-91	159
4	299	248
5	-100	102
6	402	367
7	-62	163
H= 4 L=12		
0	-109	-161
1	1088	1136
2	209	-267
3	1112	-1032
4	-125	-115
5	635	619
6	-94	-72
H= 5 L=12		
0	1085	-1070
1	190	-293
2	-107	-141
3	-103	24
4	836	-731
5	348	-329
6	-65	100
H= 0 L=13		
1	336	383
3	630	-637
5	-100	73
7	265	-502
H= 1 L=13		
0	434	461
1	671	676
2	509	-546
3	-93	-136
4	385	359
5	768	759
6	325	-293
H= 2 L=13		
0	636	713
1	624	689
2	661	-792
3	361	-329
4	595	588
5	713	674
6	504	-487
H= 3 L=13		
0	264	-293
1	-91	164
2	535	607
3	589	-517
4	315	-276
5	246	-234
6	347	328
H= 4 L=13		
0	559	495
1	245	-212
2	252	-254
3	-125	-34
4	386	362
5	364	-358
6	191	-205
H= 5 L=13		
0	327	-345
1	-104	83
2	-101	-142
3	-96	240
4	234	-206
5	361	302
H= 0 L=14		
0	243	309
2	1683	-1514
4	364	313
6	656	-667
H= 1 L=14		
0	656	-690
1	719	-788
2	820	800
3	660	684
4	735	-541
5	502	-493
6	486	470
H= 2 L=14		
0	1116	1164
1	494	-458
2	-105	95
3	535	489
4	738	760
5	269	-249
H= 3 L=14		
0	741	-694
1	264	-243
2	627	516
3	197	196
4	526	-518
5	220	-194
6	201	313
H= 4 L=14		
0	1180	-1073
1	278	-231
2	-121	-9
3	-114	46
4	714	-719
5	264	-261
H= 5 L=14		
0	-97	-110
1	1022	1091
2	163	195
3	908	-916
4	152	-79
5	453	747
H= 0 L=15		
1	431	-473
3	674	679
5	-77	-82
H= 1 L=15		
1	-109	13
2	-106	13
3	350	263
4	-91	-59
5	247	207
H= 2 L=15		
0	598	567
1	-100	78
2	418	-379
3	346	-341
4	495	415
5	-68	-117
H= 3 L=15		
0	-101	166
1	272	251
2	-97	10
3	490	-462
4	-80	116
H= 4 L=15		
0	-115	-184
1	260	305
2	-109	-90
3	-100	-45
4	-86	-108
H= 5 L=15		
0	343	-371
1	398	358
2	-81	104
3	-72	-104
H= 0 L=16		
0	-99	76
2	-95	-145
4	-77	75
H= 1 L=16		
0	595	575
1	-99	-77
2	355	355
3	-88	124
4	318	319
H= 2 L=16		
1	423	417
2	316	261
3	309	-368
4	180	-167
H= 3 L=16		
0	-91	-114
1	-89	-37
2	707	-666
3	-77	-57
H= 4 L=16		
0	-100	76
1	-98	-111
2	206	-142
3	-81	104
H= 5 L=16		
0	564	546
1	262	262
2	113	147
H= 0 L=17		
1	344	337
H= 1 L=17		
0	-87	-93
1	284	-285
2	-81	138
3	-72	99
H= 2 L=17		
0	459	420
1	-77	-72
2	286	-289
3	193	-159
H= 3 L=17		
0	367	346
1	-74	-18
2	437	-447
H= 4 L=17		
0	483	412
1	-77	35
2	369	-567
H= 0 L=18		
0	-70	44
2	279	549
H= 1 L=18		
0	167	147
1	626	-607
H= 2 L=18		
0	-328	-476

Table 3. *Bond lengths and angles in* PBr_7

Bond lengths	
P–Br(1)	2·16 ± 0·01 Å
P–Br(2)	2·17 ± 0·01
P–Br(3)	2·18 ± 0·01
Br(4)–Br(5)	2·91 ± 0·01
Br(4)–Br(6)	2·39 ± 0·01
Bond angles	
Br(1)–P–Br(2)	110·4 ± 0·3°
Br(1)–P–Br(3)	109·8 ± 0·3
Br(2)–P–Br(3)	109·1 ± 0·5
Br(1)–P–Br(1)	107·3 ± 0·5
Br(5)–Br(4)–Br(6)	177·3 ± 0·2

perature factors cannot be considered physically meaningful since no absorption corrections were made on the intensity data. The observed and calculated structure factors are listed in Table 2.

Bond lengths and angles with standard deviations are listed in Table 3. One half of the unit cell is shown in Fig. 1.

Discussion and conclusion

Phosphorus heptabromide exists in the crystalline state as discrete PBr_4^+ and Br_3^- ions. The overall structure is essentially the same as in NH_4I_3 (Mooney, 1935), CsI_3 (Tasman & Boswijk, 1955), and CsI_2Br (Carpenter, 1966). All of the compounds have the same space group

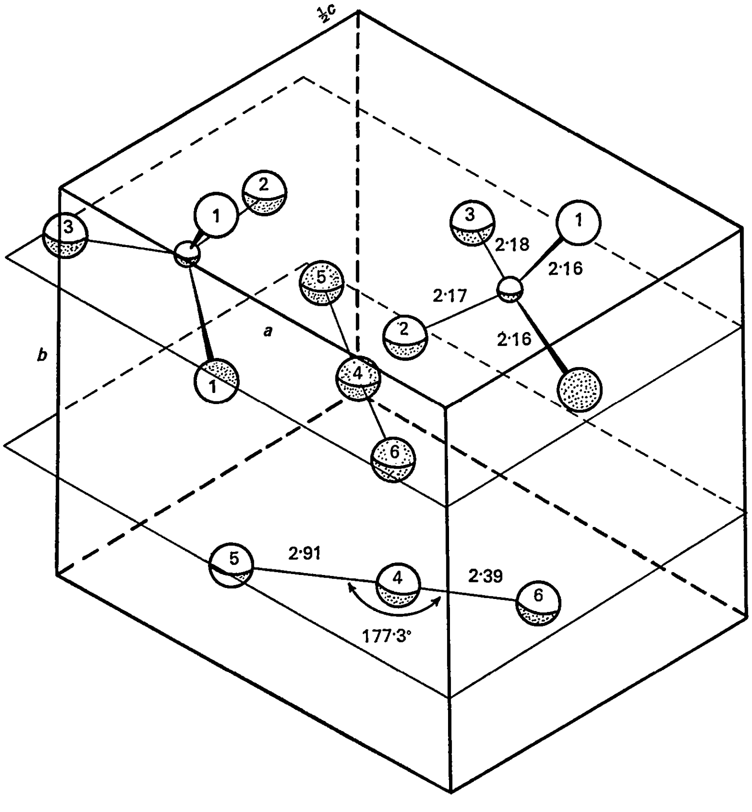

Fig. 1. Illustration of the structure of PBr_7.

if the axes are chosen similarly. The larger cations in PBr_7 expand the unit cell mainly in the **c** direction (for *Pnma*).

The PBr_4^+ ion in PBr_7 is very similar in configuration to the PBr_4^+ ion in PBr_5. It is nearly tetrahedral with all angles in the range 107–110° and all bond distances in the range 2·16–2·18 Å.

The tribromide ion in PBr_7 differs, however, from that found in $[N(CH_3)_3H^+]_2Br^-Br_3^-$ in that the two bond lengths are significantly different and the angle between the bonds is more nearly 180°. The Br(4)–Br(6) distance of 2·39 Å is only slightly greater than the single-bond distance of 2·28 Å in Br_2, while the Br(4)–Br(5) distance is lengthened to 2·91 Å. This is analogous to the triiodide ion, which is symmetrical in $(C_6H_5)_4AsI_3$ (Mooney-Slater, 1959) but unsymmetrical in NH_4I_3 (Mooney, 1935) and CsI_3 (Tasman & Boswijk, 1955), except that the distortion is considerably greater in the tribromide case.

Havinga & Wiebenga (1959) have pointed out that in both cases of the unsymmetrical I_3^-, one iodine atom is more closely surrounded by the cation than the other two iodine atoms, whereas the surroundings of the symmetrical I_3^- are more nearly symmetrical. This is also found in the Br_3^- ion of PBr_7, where Br(5) is much closer to the bromine atoms of various PBr_4^+ ions than is either Br(4) or Br(6). In fact, Br(5) has four bromine neighbors in the 3·1–3·4 Å range while the nearest approaches to Br(4) and Br(6) are all greater than 3·8 Å. Since the van der Waals radius of bromine is 1·95 Å, it would appear that there are significant interactions (presumably mainly ionic) between the positive PBr_4^+ ion and the elongated end of the tribromide ion. It is interesting to note that each bromine atom on the PBr_4^+ ion is involved in one and only one short contact with Br(5), thus explaining why the PBr_4^+ ion is so close to tetrahedral despite these interactions. These distances are shown in Table 4 and Fig. 2.

Table 4. *Nearest neighbors of atoms in* Br_3^-

Br(5)–Br(1)	3·14Å
Br(5)–Br(2)	3·26
Br(5)–Br(3)	3·36
Br(6)–Br(1)	3·88
Br(4)–Br(1)	3·89

All other distances are above 4·00 Å.

Havinga & Wiebenga (1959) have discussed the structure of polyhalogen compounds and ions, in particular I_3^-, in terms of the LCAO molecular orbital method. The molecular orbitals were represented as linear combinations of the outer *p*-orbitals of the halogen atoms in the normal *3c–4e* approximation. The Coulomb integrals were considered as a function of the electronegativity and the formal charge of the atoms, and the overlap integrals were assumed equal to zero. In the case of the unsymmetrical I_3^- ion, the Coulomb integral of the atom closest to the cations was increased by $0{\cdot}1\beta$ to take into account the effect of these cations. The most stable configurations and bond orders were qualitatively correct for the numerous cases to which this method was applied. It was therefore used in considering the configuration of Br_3^- in PBr_7. In this case, however, the modification for the effect of the cation was greater since the distortion in Br_3^- is greater than in I_3^-. Hence, the Coulomb integral on Br(5) was increased by $0{\cdot}3\beta$. The resultant bond orders and atomic charges are shown in Fig. 3. The calculated bond orders agree

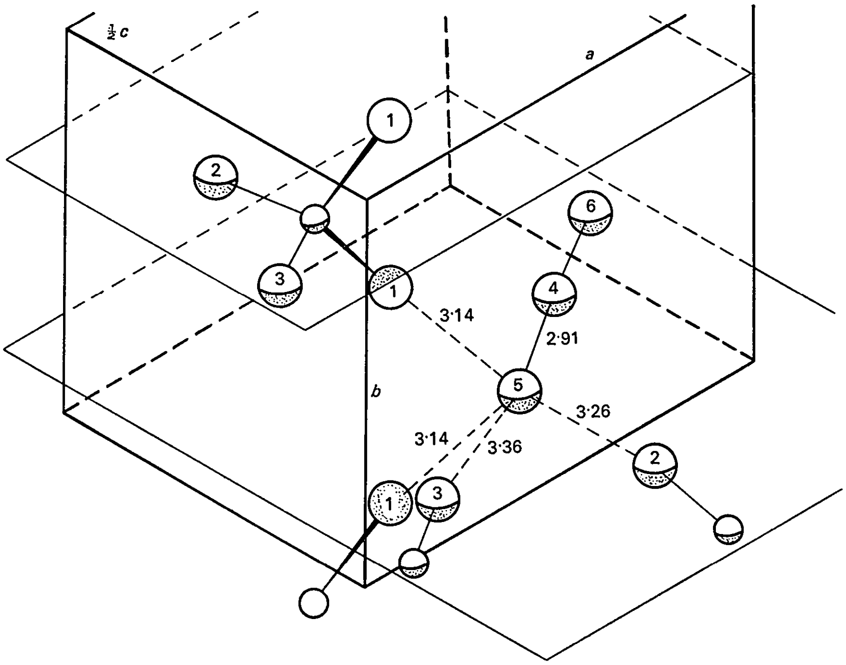

Fig. 2. Nearest neighbors of Br(5).

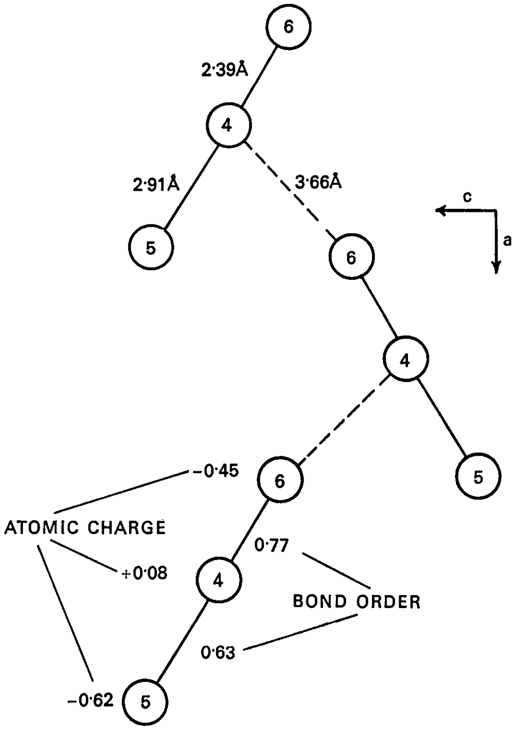

Fig. 3. Bond distances and bond orders in Br_3^-.

qualitatively with the observed bond lengths. In addition, the calculated atomic charges agree qualitatively with the preliminary results of a nuclear quadrupole resonance study of PBr_7. These results will be published when completed. The positive charge on Br(4) might explain the slight bending of the Br_3^- ion. As Fig. 3 shows, the tribromide ions form a zigzag chain through the crystal. It appears that electrostatic interaction between the positively charged Br(4) and the negatively charged Br(6) slightly bends the Br_3^- ion. The fact that the needle axis of the crystal is along the direction of the tribromide ion chain gives support to this proposed interaction between the tribromide ions.

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Die Kristallstruktur von Sn_2S_3

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The existence of a new sulphide of tin, Sn_2S_3, besides the well known compounds SnS_2 and SnS was confirmed, and its crystal structure determined, by a three-dimensional single-crystal X-ray diffraction analysis. The space group is *Pnam* with $a = 8{\cdot}864$, $b = 14{\cdot}020$, $c = 3{\cdot}747$ Å, and four formula units Sn_2S_3 in the unit cell. All atoms lie in mirror planes with $z = \frac{1}{4}, \frac{3}{4}$ [special position 4(*c*)]. Sn_2S_3 is almost isotypic with $MCdCl_3$ with $M = NH_4, K, Rb$. The crystal structure consists of infinite double rutile strings of $Sn^{IV}S_6$ octahedra parallel to the *c* axis, with the Sn^{II} atoms attached laterally. The geometric relationship to the crystal structure of SnS_2 is discussed.

Einleitung

Die Beobachtung von weiteren Phasen im System Zinn/Schwefel neben den bekannten Verbindungen SnS_2 und SnS wird wiederholt in der Literatur erwähnt (z.B. Albers & Schol, 1961; hier finden sich auch Hinweise auf andere Arbeiten). Die Zusammensetzungen dieser Phasen werden mit Sn_2S_3 und Sn_3S_4 angegeben. Die Pulverdiagramme, soweit sie mitgeteilt sind, vermitteln kein klares Bild von der Anzahl und Identität der beschriebenen Phasen, so dass die Erforschung des Systems Zinn/Schwefel noch nicht als abgeschlossen gelten kann.