*Acta Cryst.* (1969). B25, 1073

# The Crystal Structure of Cesium Tribromide and a Comparison of the $Br_3^-$ and $I_3^-$ Systems

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(*Received* 31 *January* 1967 *and in revised form* 22 *April* 1968)

The crystal structure of $CsBr_3$ has been determined by X-ray diffraction techniques. The unit cell is orthorhombic with $a=6{\cdot}52$, $b=10{\cdot}04$ and $c=9{\cdot}54$ Å. The space group is *Pmnb*. The tribromide ion is nearly linear, but unsymmetrical, with Br–Br distances of 2·440 and 2·698 Å. The $Br_3^-$ ions in this compound, in $PBr_7$, and in $[(CH_3)_3NH^+]_2Br^-Br_3^-$ form a system analogous to that of $I_3^-$ in which the configuration of the trihalide ion depends on the cation present in the crystal. A qualitative discussion comparing the two systems is given.

## Introduction

Structural studies of the tribromide ion previously done have shown that $Br_3^-$ in $[(CH_3)_3NH^+]_2Br^-Br_3^-$ (Romers & Keulemans, 1958) is an essentially symmetrical ion with the two bond lengths almost equal while $Br_3^-$ in $PBr_7$ (Breneman & Willett, 1967) is extremely distorted from the symmetrical configuration with the two bond lengths differing by more than 0·5 Å. Both of these $Br_3^-$ ions are essentially linear. It was observed that $PBr_7$ lost bromine very rapidly when taken out of a bromine environment while $[(CH_3)_3NH^+]_2Br^-Br_3^-$ was much more stable under the same conditions. Since the stability of $CsBr_3$ was observed to be intermediate to these other two compounds it was hoped that the configuration of $Br_3^-$ in $CsBr_3$ would also be intermediate to the other two compounds thus forming a system of tribromide ions analogous to that found for triiodide ions whose configurations vary with the cation present in the crystal.

## Experimental

The compound was prepared by adding a large amount of $Br_2$ to a concentrated solution of CsBr in water. The $CsBr_3$ was recrystallized from bromine water to obtain crystals suitable for diffraction study. A single crystal $0{\cdot}10\times0{\cdot}13\times0{\cdot}22$ mm was mounted in a Lindemann glass capillary.

Lattice constants were measured and intensity data collected on a Picker diffractometer equipped with a General Electric single crystal orienter using Mo $K\alpha$ radiation. The lattice constants of the orthorhombic unit cell were found to be $a=6{\cdot}522\pm0{\cdot}005$, $b=10{\cdot}037\pm0{\cdot}003$, and $c=9{\cdot}539\pm0{\cdot}009$ Å. The $\theta$–$2\theta$ scan method was used for measuring intensities with background measured at the beginning and end of each scan. 425 unique non-zero intensities were measured. Weissenberg photographs with Cu $K\alpha$ radiation showed systematic absences for $h0l$, $h+l=2n+1$, and for $hk0$, $k=2n+1$ indicating the space group to be *Pmnb* or $P2_1nb$. Solution of the structure within the space group *Pmnb* proved this to be the correct choice.

## Determination of the structure

Since the choice of space groups for $CsBr_3$ was the same as for $CsI_3$ (Tasman & Boswijk, 1955) and the lattice constants of $CsBr_3$ were only slightly smaller than for $CsI_3$, it was assumed that the two structures were isomorphic. Structure factors calculated using the $CsI_3$ parameters resulted in $R=0{\cdot}382$ and $R_W=0{\cdot}357$

* Work performed while an NSF predoctoral Fellow.

Table 1. *Final parameters for* $CsBr_3$[a,b,c]

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{12}$ | $\beta_{33}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|
| Cs | 0·25 | 0·8175 | 0·4534 | 0·0224 | 0·0108 | 0·0138 | −0·0010 |
| | | (0·0003) | (0·0003) | (0·0008) | (0·0004) | (0·0004) | (0·0003) |
| Br(1) | 0·25 | 0·1740 | 0·3833 | 0·0257 | 0·0099 | 0·0124 | −0·0005 |
| | | (0·0004) | (0·0005) | (0·0013) | (0·0005) | (0·0006) | (0·0004) |
| Br(2) | 0·25 | 0·3805 | 0·5644 | 0·0205 | 0·0086 | 0·0116 | 0·0017 |
| | | (0·0004) | (0·0004) | (0·0011) | (0·0005) | (0·0006) | (0·0004) |
| Br(3) | 0·25 | 0·5603 | 0·7366 | 0·0315 | 0·0101 | 0·0133 | −0·0007 |
| | | (0·0004) | (0·0005) | (0·0014) | (0·0006) | (0·0006) | (0·0004) |

$$R=\sum_{hkl}||F_{obs}|-|F_{calc}||/\sum_{hkl}|F_{obs}|=0{\cdot}068$$

$$R_w=\sqrt{\sum_{hkl}w(|F_{obs}|-|F_{calc}|)^2}\Big/\sqrt{\sum_{hkl}w(F_{obs})^2}=0{\cdot}090$$

[a] Standard deviations are given in parentheses.
[b] The $\beta_{ij}$ are defined by: $T=\exp(-\beta_{11}h^2-\beta_{22}h^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$.
[c] $\beta_{12}=\beta_{13}=0$ by symmetry.

Table 2. *Observed and calculated structure factors for* $CsBr_3$

The columns contain $k$, $l$, $10|F_{obs}|$, and $10F_{calc}$. Reflections suffering from extinction are denoted by an asterisk. Unobserved reflections are denoted by negative $10|F_{lim}|$ in the $|F_{obs}|$ column.

H = 0

| | | | |
|---|---|---|---|
| 0 | 2 | 614 | 679 |
| 0 | 4 | 225 | 228 |
| 0 | 6 | 623 | -663 |
| 0 | 8 | 109 | -76 |
| 0 | 10 | 220 | -220 |
| 1 | 1 | 194 | -131 |
| 1 | 2 | 196 | -195 |
| 1 | 3 | 106 | -58 |
| 1 | 4 | 763 | -854 |
| 1 | 5 | 127 | 137 |
| 1 | 6 | 684 | -737 |
| 1 | 7 | 273 | -258 |
| 1 | 8 | 256 | -271 |
| 1 | 9 | -66 | 0 |
| 1 | 10 | 128 | 133 |
| 2 | 0 | 498 | -504 |
| 2 | 1 | 78 | 51 |
| 2 | 2 | 852 | -887 |
| 2 | 3 | 671 | -660 |
| 2 | 4 | 322 | 331 |
| 2 | 5 | 427 | 429 |
| 2 | 6 | 134 | -105 |
| 2 | 7 | 189 | 194 |
| 2 | 8 | 118 | 103 |
| 2 | 9 | 127 | 159 |
| 2 | 10 | -71 | 16 |
| 3 | 1 | 800 | 865 |
| 3 | 2 | 176 | -159 |
| 3 | 3 | -41 | 11 |
| 3 | 4 | 308 | -268 |
| 3 | 5 | 101 | -102 |
| 3 | 6 | 146 | 134 |
| 3 | 7 | -58 | 30 |
| 3 | 8 | -63 | -4 |
| 3 | 9 | -67 | 77 |
| 4 | 0 | 677 | -704 |
| 4 | 1 | 515 | 512 |
| 4 | 2 | 420 | -413 |
| 4 | 3 | 641 | -596 |
| 4 | 4 | 125 | 132 |
| 4 | 5 | 350 | -342 |
| 4 | 6 | 229 | 223 |
| 4 | 7 | 558 | -549 |
| 4 | 8 | 146 | 153 |
| 4 | 9 | -70 | 53 |
| 5 | 1 | 943 | -1017 |
| 5 | 2 | 125 | 115 |
| 5 | 3 | 225 | -207 |
| 5 | 4 | 276 | 265 |
| 5 | 5 | 183 | 169 |
| 5 | 6 | 452 | 487 |
| 5 | 7 | 206 | 217 |
| 5 | 8 | -65 | 41 |
| 5 | 9 | 130 | 89 |
| 6 | 0 | 441 | 464 |
| 6 | 1 | 399 | 396 |
| 6 | 2 | 517 | 516 |
| 6 | 3 | 190 | 186 |
| 6 | 4 | 259 | -246 |
| 6 | 5 | 566 | 567 |
| 6 | 6 | 109 | 33 |
| 6 | 7 | 138 | 105 |
| 6 | 8 | -66 | -26 |
| 7 | 1 | 125 | 145 |
| 7 | 2 | 246 | 226 |
| 7 | 3 | 196 | 188 |
| 7 | 4 | 96 | -74 |
| 7 | 5 | -59 | -35 |
| 7 | 6 | 231 | -241 |
| 7 | 7 | -65 | -5 |
| 8 | 0 | 447 | -482 |
| 8 | 1 | -59 | -6 |
| 8 | 2 | -59 | 86 |
| 8 | 3 | -61 | 0 |
| 8 | 4 | 142 | -125 |
| 8 | 5 | 156 | 146 |
| 8 | 6 | -65 | 58 |
| 9 | 1 | 396 | 413 |
| 9 | 2 | 96 | -30 |
| 9 | 3 | -66 | 82 |
| 9 | 4 | -68 | 78 |
| 9 | 5 | 178 | -198 |
| 10 | 0 | -69 | 26 |
| 10 | 1 | 108 | -95 |
| 10 | 2 | 192 | 196 |
| 10 | 3 | -70 | -77 |

H = 1

| | | | |
|---|---|---|---|
| 0 | 1 | 161 | 167 |
| 0 | 3 | *836 | -1021 |
| 0 | 5 | 280 | 272 |
| 0 | 7 | 175 | -202 |
| 0 | 9 | 111 | -113 |
| 1 | 1 | -29 | -64 |
| 1 | 2 | 766 | 848 |
| 1 | 3 | 526 | -541 |
| 1 | 4 | 465 | 480 |
| 1 | 5 | 478 | -477 |
| 1 | 6 | 315 | 310 |
| 1 | 7 | 159 | 116 |
| 1 | 8 | 107 | -71 |
| 1 | 9 | 144 | 143 |
| 1 | 10 | -72 | 46 |
| 2 | 0 | 413 | 402 |
| 2 | 1 | 779 | 816 |
| 2 | 2 | 1057 | 1186 |
| 2 | 3 | 308 | 294 |
| 2 | 4 | 236 | 222 |
| 2 | 5 | 462 | 470 |
| 2 | 6 | 90 | -50 |
| 2 | 7 | 112 | -52 |
| 2 | 8 | 498 | -519 |
| 2 | 9 | 143 | 138 |
| 3 | 1 | 519 | 504 |
| 3 | 2 | 997 | -1045 |
| 3 | 3 | 402 | 376 |
| 3 | 4 | 834 | -860 |
| 3 | 5 | -51 | -168 |
| 3 | 6 | 228 | -195 |
| 3 | 7 | 114 | -108 |
| 3 | 8 | 96 | -126 |
| 3 | 9 | 210 | -209 |
| 4 | 0 | 651 | -664 |
| 4 | 1 | 63 | -23 |
| 4 | 2 | 87 | -64 |
| 4 | 3 | 240 | -210 |
| 4 | 4 | 798 | -817 |
| 4 | 5 | 239 | -229 |
| 4 | 6 | 154 | 150 |
| 4 | 7 | 144 | -108 |
| 4 | 8 | 143 | 142 |
| 4 | 9 | -71 | 70 |
| 5 | 1 | 127 | -148 |
| 5 | 2 | 269 | 251 |
| 5 | 3 | 302 | 284 |
| 5 | 4 | 203 | 167 |
| 5 | 5 | 125 | 120 |
| 5 | 6 | -57 | -22 |
| 5 | 7 | -61 | 56 |
| 5 | 8 | 164 | 135 |
| 6 | 0 | 381 | -381 |
| 6 | 1 | 558 | -556 |
| 6 | 2 | 225 | 222 |
| 6 | 3 | 388 | -382 |
| 6 | 4 | -56 | -5 |
| 6 | 5 | 329 | -306 |
| 6 | 6 | 226 | 246 |
| 6 | 7 | -63 | 57 |
| 6 | 8 | -67 | -25 |
| 7 | 1 | 397 | -412 |
| 7 | 2 | 127 | 75 |
| 7 | 3 | 390 | -390 |
| 7 | 4 | 138 | 148 |
| 7 | 5 | 128 | -113 |
| 7 | 6 | -63 | -57 |
| 7 | 7 | 247 | 263 |
| 8 | 0 | 143 | -141 |
| 8 | 1 | 88 | 79 |
| 8 | 2 | -60 | 31 |
| 8 | 3 | 653 | 672 |
| 8 | 4 | 144 | 112 |
| 8 | 5 | 161 | 158 |
| 8 | 6 | 94 | 61 |
| 9 | 1 | 233 | 223 |
| 9 | 2 | 167 | -137 |
| 9 | 3 | 170 | 175 |
| 9 | 4 | -69 | 29 |
| 9 | 5 | -68 | 67 |
| 10 | 0 | 167 | 179 |
| 10 | 1 | 103 | -93 |
| 10 | 2 | -69 | -95 |
| 10 | 3 | -70 | 88 |

H = 2

| | | | |
|---|---|---|---|
| 0 | 0 | *1652 | -2483 |
| 0 | 2 | 544 | -579 |
| 0 | 4 | 181 | -186 |
| 0 | 6 | 524 | 570 |
| 0 | 8 | -64 | 75 |
| 1 | 1 | 164 | 108 |
| 1 | 2 | 166 | 173 |
| 1 | 3 | 69 | 47 |
| 1 | 4 | 670 | 727 |
| 1 | 5 | 118 | -112 |
| 1 | 6 | 603 | 642 |
| 1 | 7 | 217 | 223 |
| 1 | 8 | 220 | 237 |
| 1 | 9 | -68 | 2 |
| 2 | 0 | 442 | 424 |
| 2 | 1 | -38 | -34 |
| 2 | 2 | 738 | 721 |
| 2 | 3 | 563 | 540 |
| 2 | 4 | 278 | -271 |
| 2 | 5 | 365 | -361 |
| 2 | 6 | 115 | 87 |
| 2 | 7 | 173 | -172 |
| 2 | 8 | 143 | -89 |
| 2 | 9 | 153 | -139 |
| 3 | 1 | 717 | -714 |
| 3 | 2 | 136 | 136 |
| 3 | 3 | -45 | -14 |
| 3 | 4 | 231 | 229 |
| 3 | 5 | 137 | 86 |
| 3 | 6 | 117 | -112 |
| 3 | 7 | -61 | -27 |
| 3 | 8 | -65 | 1 |
| 3 | 9 | 125 | -66 |
| 4 | 0 | 594 | 596 |
| 4 | 1 | 434 | -414 |
| 4 | 2 | 368 | 353 |
| 4 | 3 | 550 | 504 |
| 4 | 4 | 125 | -113 |
| 4 | 5 | 319 | 305 |
| 4 | 6 | 192 | -198 |
| 4 | 7 | 502 | 478 |
| 4 | 8 | 152 | -137 |
| 4 | 9 | -72 | -44 |
| 5 | 1 | 839 | 874 |
| 5 | 2 | 113 | -101 |
| 5 | 3 | 215 | 183 |
| 5 | 4 | 227 | -235 |
| 5 | 5 | 132 | -149 |
| 5 | 6 | 428 | -425 |
| 5 | 7 | 180 | -193 |
| 5 | 8 | -67 | -38 |
| 6 | 0 | 372 | -406 |
| 6 | 1 | 319 | -338 |
| 6 | 2 | 450 | -443 |
| 6 | 3 | 169 | -171 |
| 6 | 4 | 214 | 209 |
| 6 | 5 | 494 | -495 |
| 6 | 6 | -61 | -27 |
| 6 | 7 | -64 | -96 |
| 6 | 8 | -68 | 22 |
| 7 | 1 | 155 | -129 |
| 7 | 2 | 197 | -196 |
| 7 | 3 | 160 | -163 |
| 7 | 4 | 106 | 64 |
| 7 | 5 | -62 | 30 |
| 7 | 6 | 197 | 212 |
| 7 | 7 | -67 | 6 |
| 8 | 0 | 395 | 414 |
| 8 | 1 | -61 | 5 |
| 8 | 2 | -62 | -70 |
| 8 | 3 | -64 | -2 |
| 8 | 4 | 108 | 107 |
| 8 | 5 | 144 | -128 |
| 8 | 6 | -67 | -47 |
| 9 | 1 | 346 | -366 |
| 9 | 2 | 98 | 26 |
| 9 | 3 | -68 | -72 |
| 9 | 4 | -70 | -68 |
| 10 | 0 | -71 | -27 |
| 10 | 1 | -70 | 84 |
| 10 | 2 | 173 | -171 |

H = 3

| | | | |
|---|---|---|---|
| 0 | 1 | -43 | -87 |
| 0 | 3 | 625 | 693 |
| 0 | 5 | 179 | -188 |
| 0 | 7 | 127 | 150 |
| 0 | 9 | -71 | 94 |
| 1 | 1 | 104 | 59 |
| 1 | 2 | 573 | -584 |
| 1 | 3 | 366 | 385 |
| 1 | 4 | 362 | -363 |
| 1 | 5 | 341 | 353 |
| 1 | 6 | 228 | -235 |
| 1 | 7 | -61 | -84 |
| 1 | 8 | -65 | 50 |
| 1 | 9 | 154 | -111 |
| 2 | 0 | 344 | -318 |
| 2 | 1 | 560 | -542 |
| 2 | 2 | 829 | -828 |
| 2 | 3 | 231 | -227 |
| 2 | 4 | 169 | -172 |
| 2 | 5 | 344 | -346 |
| 2 | 6 | -57 | 51 |
| 2 | 7 | -61 | 31 |
| 2 | 8 | 393 | 401 |
| 2 | 9 | -70 | -105 |
| 3 | 1 | 373 | -367 |
| 3 | 2 | 775 | 752 |
| 3 | 3 | 279 | -272 |
| 3 | 4 | 639 | 644 |
| 3 | 5 | 122 | 124 |
| 3 | 6 | 159 | 158 |
| 3 | 7 | -63 | 91 |
| 3 | 8 | 99 | 98 |
| 4 | 0 | 456 | 471 |
| 4 | 1 | -49 | 22 |
| 4 | 2 | 103 | 69 |
| 4 | 3 | 180 | 162 |
| 4 | 4 | 587 | 599 |
| 4 | 5 | 184 | 179 |
| 4 | 6 | 114 | -106 |
| 4 | 7 | 118 | 83 |
| 4 | 8 | 120 | -114 |
| 5 | 1 | 75 | 108 |
| 5 | 2 | 178 | -183 |
| 5 | 3 | 209 | -209 |
| 5 | 4 | 91 | -122 |
| 5 | 5 | 128 | -95 |
| 5 | 6 | -61 | 14 |
| 5 | 7 | -65 | -41 |
| 6 | 0 | 261 | 280 |
| 6 | 1 | 404 | 410 |
| 6 | 2 | 172 | -156 |
| 6 | 3 | 311 | 300 |
| 6 | 4 | -60 | -3 |
| 6 | 5 | 238 | 234 |
| 6 | 6 | 180 | -187 |
| 6 | 7 | -66 | -38 |
| 7 | 1 | 324 | 324 |
| 7 | 2 | 88 | -60 |
| 7 | 3 | 300 | 302 |
| 7 | 4 | 124 | -113 |
| 7 | 5 | 127 | 83 |
| 7 | 6 | 103 | 40 |
| 8 | 0 | 127 | 107 |
| 8 | 1 | -63 | -71 |
| 8 | 2 | -64 | -23 |
| 8 | 3 | 502 | -516 |
| 8 | 4 | -68 | -87 |
| 8 | 5 | 125 | -135 |
| 9 | 1 | 164 | -177 |
| 9 | 2 | -68 | 102 |
| 9 | 3 | 114 | -138 |

H = 4

| | | | |
|---|---|---|---|
| 0 | 0 | *1297 | 1467 |
| 0 | 2 | 375 | 396 |
| 0 | 4 | 116 | 108 |
| 0 | 6 | 363 | -374 |
| 0 | 8 | 127 | -67 |
| 1 | 1 | -51 | -61 |
| 1 | 2 | 122 | -125 |
| 1 | 3 | -51 | -25 |
| 1 | 4 | 460 | -479 |
| 1 | 5 | -57 | 62 |
| 1 | 6 | 408 | -436 |
| 1 | 7 | 107 | -148 |
| 1 | 8 | 136 | -161 |
| 2 | 0 | 302 | -280 |
| 2 | 1 | -50 | 4 |
| 2 | 2 | 457 | -436 |
| 2 | 3 | 353 | -332 |
| 2 | 4 | 140 | 158 |
| 2 | 5 | 216 | 222 |
| 2 | 6 | -61 | -50 |
| 2 | 7 | 113 | 121 |
| 2 | 8 | -68 | 58 |
| 3 | 1 | 450 | 443 |
| 3 | 2 | 107 | -94 |
| 3 | 3 | -54 | 15 |
| 3 | 4 | 132 | -150 |
| 3 | 5 | -60 | -54 |
| 3 | 6 | 103 | 67 |
| 3 | 7 | -66 | 21 |
| 4 | 0 | 399 | -392 |
| 4 | 1 | 247 | 239 |
| 4 | 2 | 221 | -234 |
| 4 | 3 | 352 | -322 |
| 4 | 4 | 109 | 73 |
| 4 | 5 | 196 | -220 |
| 4 | 6 | 95 | 139 |
| 4 | 7 | 337 | -319 |
| 5 | 1 | 568 | -581 |
| 5 | 2 | -57 | 72 |
| 5 | 3 | 152 | -129 |
| 5 | 4 | 164 | 169 |
| 5 | 5 | -62 | 103 |
| 5 | 6 | 274 | 287 |
| 6 | 0 | 260 | 278 |
| 6 | 1 | 222 | 217 |
| 6 | 2 | 303 | 288 |
| 6 | 3 | 129 | 134 |
| 6 | 4 | 128 | -129 |
| 6 | 5 | 315 | 336 |
| 6 | 6 | -66 | 15 |
| 7 | 1 | -63 | 93 |
| 7 | 2 | 176 | 130 |
| 7 | 3 | -65 | 110 |
| 7 | 4 | -67 | -41 |
| 7 | 5 | -67 | -17 |
| 8 | 0 | 255 | -266 |
| 8 | 1 | -66 | -2 |
| 8 | 2 | -67 | 39 |
| 8 | 3 | -69 | 6 |

H = 5

| | | | |
|---|---|---|---|
| 0 | 1 | -56 | 30 |
| 0 | 3 | 344 | -363 |
| 0 | 5 | 102 | 96 |
| 0 | 7 | -70 | -86 |
| 1 | 1 | -58 | -35 |
| 1 | 2 | 318 | 329 |
| 1 | 3 | 200 | -219 |
| 1 | 4 | 255 | 225 |
| 1 | 5 | 189 | -204 |
| 1 | 6 | 117 | 141 |
| 1 | 7 | -68 | 45 |
| 2 | 0 | 214 | 218 |
| 2 | 1 | 282 | 286 |
| 2 | 2 | 486 | 467 |
| 2 | 3 | 152 | 146 |
| 2 | 4 | 120 | 109 |
| 2 | 5 | 202 | 199 |
| 2 | 6 | -66 | -45 |
| 3 | 1 | 241 | 221 |
| 3 | 2 | 446 | -435 |
| 3 | 3 | 150 | 156 |
| 3 | 4 | 391 | -385 |
| 3 | 5 | -65 | -71 |
| 3 | 6 | 120 | -107 |
| 4 | 0 | 252 | -261 |
| 4 | 1 | -59 | -19 |
| 4 | 2 | -60 | -63 |
| 4 | 3 | -63 | -103 |
| 4 | 4 | 345 | -338 |
| 4 | 5 | -65 | -113 |
| 4 | 6 | -68 | 55 |
| 5 | 1 | -62 | -61 |
| 5 | 2 | 109 | 102 |
| 5 | 3 | 142 | 117 |
| 5 | 4 | -64 | 68 |
| 5 | 5 | -66 | 60 |
| 6 | 0 | 164 | -158 |
| 6 | 1 | 197 | -233 |
| 6 | 2 | -65 | 78 |
| 6 | 3 | 182 | -189 |
| 6 | 4 | -67 | 11 |
| 7 | 1 | 183 | -206 |
| 7 | 2 | -68 | 39 |

H = 6

| | | | |
|---|---|---|---|
| 0 | 0 | 722 | -736 |
| 0 | 2 | 220 | -234 |
| 0 | 4 | -67 | -47 |
| 1 | 1 | -64 | 25 |
| 1 | 2 | -62 | 78 |
| 1 | 3 | -63 | 9 |
| 1 | 4 | 242 | 259 |
| 1 | 5 | -68 | -23 |
| 2 | 0 | 155 | 157 |
| 2 | 1 | -62 | 10 |
| 2 | 2 | 253 | 214 |
| 2 | 3 | 200 | 163 |
| 2 | 4 | -66 | -68 |
| 3 | 1 | 239 | -224 |
| 3 | 2 | 106 | 55 |
| 3 | 3 | -66 | -13 |
| 3 | 4 | -68 | 79 |
| 4 | 0 | 200 | 214 |
| 4 | 1 | 110 | -102 |
| 4 | 2 | 147 | 128 |
| 4 | 3 | 172 | 164 |
| 5 | 1 | 320 | 313 |
| 5 | 2 | -68 | -44 |

H = 7

| | | | |
|---|---|---|---|
| 0 | 1 | -74 | -4 |

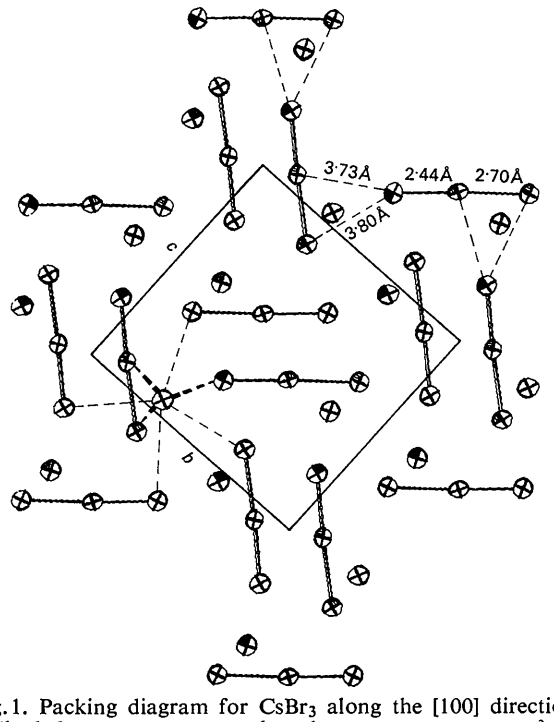


Fig. 1. Packing diagram for $CsBr_3$ along the [100] direction. Shaded atoms are at $x=\frac{1}{4}$; other atoms are at $x=\frac{3}{4}$.

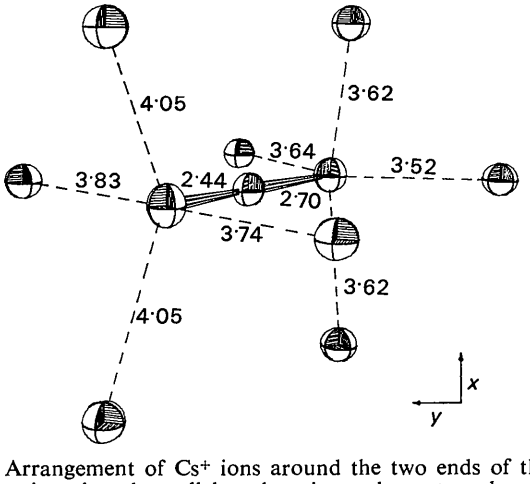


Fig. 2. Arrangement of $Cs^+$ ions around the two ends of the $Br_3^-$ ion viewed parallel to the mirror plane at $x=\frac{1}{4}$.

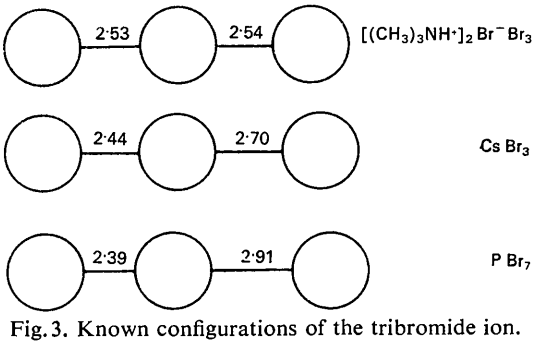


Fig. 3. Known configurations of the tribromide ion.

(see Table 1 for definition of $R$ and $R_W$). After refining the positions and isotropic temperature factors for several cycles using a FORTRAN least-squares program (Busing, Martin & Levy, 1962) on an IBM 709 computer, values of $R=0{\cdot}149$ and $R_W=0{\cdot}158$ were obtained. On conversion to anisotropic temperature factors and introduction of individual weights the refinement proceeded until values of $R=0{\cdot}108$ and $R_W=0{\cdot}099$ were obtained. A difference Fourier synthesis showed nothing of significance, indicating that the refinement had converged.

At this point absorption corrections were made on the data. All reflections which had a total count minus background less than 200 were called unobserved and removed from the refinement. This left 326 observed reflections. The unobserved reflections were set equal to one half of the minimum observed intensity for comparison purposes in the final structure factor calculation. Three of the observed reflections that appeared to be suffering from extinction were also removed from the refinement at this point. The refinement then proceeded until values of $R=0{\cdot}068$ and $R_W=0{\cdot}090$ were obtained. The weighting scheme used was as follows:

$$\text{weight}=1/\sigma^2$$
$$\sigma^2=F^2/4AI^2[E+2B+(0{\cdot}1I)^2]\,,$$

where $F$ is the structure factor, $A$ is the absorption correction, $I$ is the intensity, $E$ is total counts, and $B$ is the average background.

Table 1 lists the final atomic parameters and standard deviations. The atomic scattering factors for bromine were taken from Table 3.3.1A of *International Tables for X-ray Crystallography*, 1962). The atomic scattering factors used for $Cs^+$ were those of Thomas & Umeda (1959). The atomic scattering factors for $Cs^+$ were corrected for the real part of anomalous dispersion. Table 2 lists the observed and calculated structure factors.

## Discussion of the structure

$CsBr_3$ is isostructural with $CsI_3$ (Tasman & Boswijk 1955) and $CsI_2Br$ (Carpenter, 1966) as predicted by Wells & Penfield (1892). The structure consists of $Cs^+$ ions and linear asymmetrical $Br_3^-$ ions all lying on mirror planes at $x=\frac{1}{4}$ and $\frac{3}{4}$. Four tribromide ions in the same plane form a box for the $Cs^+$ ion to sit in, while bromine atoms in the plane above and below the $Cs^+$ form triangles. This results in the coordination around the $Cs^+$ ion being a trigonal prism with four bromine atoms around the middle of the prism. This can be seen in Fig. 1 which shows the packing of the ions. Figs. 1 and 2 were both drawn with a program furnished by Johnson (1965). Fig. 1, also shows a zigzag chain formed by the tribromide ions similar to that found in $PBr_7$ (Breneman & Willett, 1967).

Fig. 2 shows the arrangement of Cs atoms around the two ends of the tribromide ion. Note that the cations are arranged more closely around the end of

the tribromide ion with the longer bond. This case is typical of all the asymmetrical trihalides found so far. Table 3 lists the bond lengths and bond angle found in the tribromide ion. The elongation of $Br_3^-$ in $CsBr_3$ is about midway between the symmetrical $Br_3^-$ in $[(CH_3)_3NH^+]_2Br^-Br_3^-$ and the highly elongated $Br_3^-$ in $PBr_7$. Fig. 3 compares these ions.

Table 3. *Bond lengths and angle for tribromide ion in* $CsBr_3$

| | |
|---|---|
| Bond lengths | |
| Br(1)–Br(2) | 2·698 ± 0·006 Å |
| Br(2)–Br(3) | 2·440 ± 0·006 |
| Bond angle | |
| Br(1)–Br(2)–Br(3) | 177·5 ± 0·2° |

## Comparison of $Br_3^-$ and $I_3^-$ systems

An empirical approach to the existence of symmetrical and asymmetrical $I_3^-$ ions has been proposed by Mooney-Slater (1959) and Slater (1959). In this approach to the problem no specific type of bonding is assumed. Rather the $I_2$–$I^-$ system is compared with the simple triatomic system $H_2$–H in which it has been shown that the equilibrium position of the central hydrogen atom is a function of the total distance between the end atoms. In the $H_2$–H system when the total length, $D$, of the molecule is above a critical value, $D_c$, the energy of the $H_3$ molecule shows two minima between the end atoms. As $D$ decreases these minima approach each other and when $D = D_c$ the two minima merge into a single minimum, thus giving two possible configurations to the $H_3$ molecule depending on its total length.

The configurations which have been found for the tribromide ion also show a dependence on the total length of the ion. The $Br_3^-$ ion in $PBr_7$ is the most elongated of the three and is 5·30 Å long. The $Br_3^-$ ion in $CsBr_3$ has an intermediate configuration and is 5·14 Å long while the $Br_3^-$ ion in $[(CH_3)_3NH^+]_2Br^-Br_3^-$ is nearly symmetrical and is only 5·07 Å long.

The structure data for $Br_3^-$ are plotted in Fig. 4 in the same manner as the $I_3^-$ data were treated by Mooney-Slater (1959). The total ion length, $D$, is taken as the sum of the short bond length, $d_1$, and the long bond length, $d_2$, ignoring the small deviations from linearity of the ions. The curve exhibited by the $Br_3^-$ system is very similar to that of the $I_3^-$ system. In the tribromide case the critical ion length, $D_c$, where the ion becomes symmetrical appears to be about 5·07 Å.

To better compare the tribromide system with the triiodide system, $D/D_c$ was plotted against $d/(\frac{1}{2}D_c)$ in Fig. 5 using the data for both $Br_3^-$ and $I_3^-$. The two systems are very similar. Relative to the symmetric ions the tribromide ion distorts more rapidly with increasing ion length than the triiodide ion. This difference is probably due mainly to differences in electronegativity and polarizability.

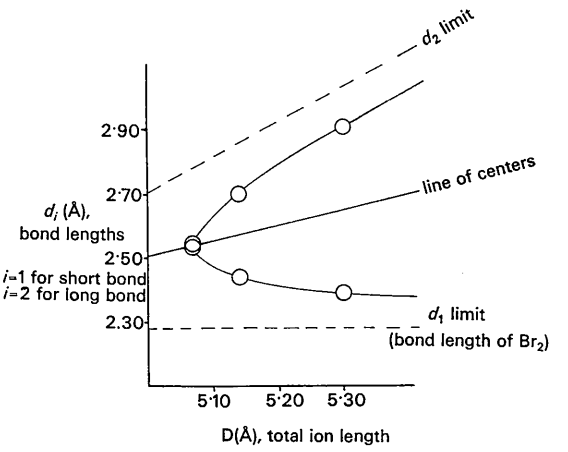


Fig. 4. Comparison of bond lengths and total ion lengths of the known tribromide ions.

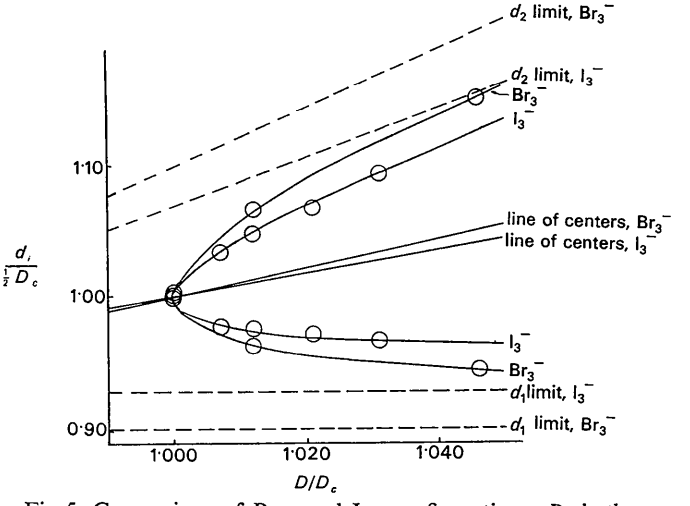


Fig. 5. Comparison of $Br_3^-$ and $I_3^-$ configurations. $D_c$ is the critical ion length where the ion becomes symmetrical.

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