The Crystal Structure of Phosphorus Heptabromide, PBr₇

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The crystal structure of phosphorus heptabromide, PBr₇, has been determined by single-crystal X-ray diffraction studies. The red compound crystallizes in the orthorhombic space group *Pnma* with $a=9.35 \pm 0.02$, $b=7.94 \pm 0.01$, and $c=14.69 \pm 0.02$ Å. The structure contains tetrahedral PBr₄⁺ ions with P-Br distances all about 2.17 Å and an almost linear unsymmetrical Br₃⁻ 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 PBr₅ was actually PBr₇. Bromine is easily absorbed by PBr₅ to form the red PBr₇ and, conversely, is easily lost by PBr₇ to form PBr₅. It seemed likely that the PBr₄⁺ ion of the PBr₅ (van Driel & MacGillavry, 1943) remained intact in PBr₇ and that a tribromide ion was formed, in a similar way to the formation of PCl₄⁺ and ICl₂⁻ on addition of ICl to PCl₅ (Zeelezny & Baenziger, 1952). Romers & Keulemans (1958) have reported the structure of a tribromide ion in [N(CH₃)₃H⁺]₂Br⁻Br₃⁻. It was symmetrical and slightly bent (171°) with the Br-Br distances both 2.54 Å. An X-ray diffraction study of PBr₇ was undertaken in order to determine if the tribromide ion existed in PBr₇ and its configuration if its existence was confirmed.

Preparation and experimental data

The compound PBr₇ was prepared in a manner similar to the preparation of PBr₆I (Fialkov & Kuzmenko, 1949) by saturating carbon disulfide with phosphorus pentabromide and slowly adding Br₂ 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 PBr₅ and Br₂ (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 PBr₇, determined from Mo $K\alpha$ precession camera photographs and Cu $K\alpha$ Weissenberg camera photographs, are $a=9.35\pm0.02$, $b=7.94\pm0.01$, and $c=14.69\pm0.02$ 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 $K\alpha$ 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 $K\alpha$ 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 PBr₇ 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 *.

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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 $16 - 623$ H+ 2 L+ 1 1 $608 - 739$ 2 $-45 - 21$ 3 $1412 + 1889$ 4 $380 - 329$	a j41 400 9 258 - J47 He 2 Le 2 0 099 - 541 1 1288 1466 2 361 - 381 3 1179 - 1099 4 209 - 207 5 541 547 7 297 - 291 8 - 102 101 9 - 82 27 He 3 1 2 2	0 188 105 2 260 -225 3 729 -721 3 1557 1401 4 -08 108 5 705 723 6 211 -227 7 1110 1149 8 176 91 9 585 550 H-3 [-3] 0 150 74 1 1171 1050 0 150 149	6 226 -273 7 1030 1033 8 532 463 9 342 -362 H= 3 L= 4 0 357 -251 1 228 701 2 437 -252 1 3 -67 -12 3 -67 -223 5 -64 185 6 518 558 6 518 558 8 210 -200 9 -73 66	H= 3 L= 5 0 556 -441 1 337 -264 2 1326 1243 3 898 -908 4 330 -908 4 330 -908 4 330 -908 4 370 -908 4 370 -908 5 3102 -301 8 3102 -301 9 396 -457 H= 4 L= 5 0 -73 -88 1 -75 -55	 410 411 410 411 411	H= 4 L= 7 0 861 -767 1 -86 -74 2 721 -205 3 653 905 4 472 -458 5 512 610 6 -131 17 7 887 826 8 -93 -35 H= 5 L= 7 0 572 584 1 -77 584 2 428 -413
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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 3 4380 -739 4 4380 -390 5 256 226 6 194 199	6 541 400 9 258 -347 HF 2 LE 2 0 509 -541 1 1288 1466 2 361 -381 3 1179 -1099 4 209 -207 5 541 547 7 297 -291 8 -102 101 9 -82 27 HF 3 LE 2	0 188 105 2 729 -721 3 1557 1401 3 1557 1401 5 705 723 6 211 -227 7 110 1149 8 176 91 9 585 550 H= 3 [= 3 0 130 74 1 1171 1050 2 410 418 3 1401 -1443 4 -73 -25	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 3 -67 -12 5 -84 185 5 -110 87 8 210 -200 9 -73 66	H= 3 L= 5 0 556 -441 1 337 -264 2 1326 1243 3 893 -908 4 386 -306 6 487 -534 7 1118 -1056 8 302 -301 9 396 -457 H= 4 L= 5 0 -73 68 1 -75 -55 2 570 - 325	 410 410 410 417 4187 4187 4187 4187 4187 4184 418	H* 4 L 7 0 861 -767 1 -86 -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 -9
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 1 065 -739 3 1412 1489 3 1412 1489 4 380 -739 2 -45 276 2 76 276	a j41 400 9 258 - J47 He 2 Le 2 0 699 - 541 1 1288 1466 2 361 - 381 3 1179 - 1099 4 209 - 207 5 541 547 7 297 - 291 8 -102 101 9 -82 27 He 3 Le 2 0*2541 3212	0 188 105 2 200 -223 3 729 -721 3 1557 1401 4 -08 108 5 705 723 6 211 -227 7 1110 1149 8 176 91 9 585 550 H= 3 (± 3) 0 150 74 1 1171 1060 2 410 418 3 1401 -1443 5 4 299	6 226 -273 7 1030 1033 8 532 463 9 342 -362 H= 3 L+ 4 0 357 -251 1 225 701 2 1530 1543 3 467 -12 4 105 1543 5 -84 185 6 -110 87 8 210 -200 9 -73 66 H= 4 L+ 4	H 3 L 5 0 556 -441 137 -264 1 137 -264 1243 2 1226 1243 1280 3 893 -908 3804 -306 5 740 -308 -307 66 6 9396 -457 -457 -457 H= 4 L= 5 0 -73 68 1 -75 -55 2 570 -333	<pre>+ <10 <01 5 876 - 85% 6 987 -1018 7 187 742 8 334 340 9 203 -421 H* 4 1* 6 0 1013 -935 1 1482 -1330 3 937 -913 3 937 -913 3 937 -913 6 -108 -79 7 36% 361 8 -100 -128</pre>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
1 205 -249 2 447 479 3 998 -1003 4 241 -229 5 1002 -955 6 353 321 7 870 -919 8 290 -243 9 -2 L+1 1 008 -739 2 -45 21 3 1412 1489 4 380 -390 5 256 226 6 194 199	a 541 400 9 258 - 347 14 2 La 2 0 699 -541 1 1288 1466 2 361 -381 3 1179 - 1099 4 224 - 139 4 219 - 139 5 209 -164 7 297 - 291 8 -102 101 8 -102 27 H= 3 La 2 0 2545 3217	0 188 105 2 200 -253 2 729 -721 3 1557 1401 4 -08 108 5 705 723 6 211 -227 7 1110 1149 8 170 91 9 585 550 M-3 [4 3] 0 130 74 1 1571 1050 2 410 418 3 1401 -1443 4 -73 -25 5 204 249	6 226 -273 7 1030 1033 8 532 463 9 342 -362 m-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 H-4 L+4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<pre>4 410 401 5 876 - 894 6 987 -1018 7 187 742 8 334 340 9 203 -421 H+ 4 1+ 6 0 1013 -935 1 482 -1330 2 609 -630 3 937 913 4 617 -600 5 886 -993 6 -108 -75 3 63 161 8 -100 -128 H+ 5 17 6</pre>	H** 4 1.2 7 0 861 -767 1 -86 -767 1 -86 -767 1 201 -205 1 -86 -767 1 201 -205 1 -78 -7405 4 5 -205 4 -512 610 -131 17 7 887 82-6 8 -93 -255 8 -93 -25 8 -93 1 17 0 572 586 -12 7 0 572 586 -413 3 2 -468 -413 3 77 567 5 -89 71 1 3 3 7 5 4 3 7 1 1 1 1 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	a 341 400 9 258 -347 H= 2 L= 2 0 099 -541 1 1281 1381 3 1170 -1099 4 209 -207 5 541 547 6 209 -207 5 541 547 6 209 -184 7 297 -291 8 -102 101 8 -102 27 H= 3 L= 2 0 -2543 3217 1 473 1395	0 188 105 2 200 -253 2 729 -721 3 1557 1401 4 -08 108 5 705 723 0 211 -227 1 110 191 9 385 550 H= 3 L= 3 0 190 74 1 1171 1060 2 4101 -418 3 101 -123 3 101 -125 5 204 209 6 248 179	6 226 -273 7 1030 1033 8 532 483 9 342 -382 m-3 L+ 4 0 357 -251 1 228 201 2 1530 1543 3 -67 -12 4 264 -223 5 558 7 -110 87 8 210 -200 9 -73 66 H- 4 L+ 4	H=3 L=5 0 556 -441 1327 -245 -241 1393 -906 1243 1393 -906 57 4 386 -396 5 799 -809 6 487 534 7 1118 -1056 8 302 -301 9 396 -457 9 -809 -301 9 396 -557 2 570 -575 2 3134 325 5 -106 75 5 -314 -75	<pre>+ <10 <01 5 876 - 894 6 987 -1018 7 187 727 8 333 340 203 -421 H* 4 1* 6 0 1013 -935 1 1482 -1330 2 6007 -030 3 017 -030 5 016 -75 7 364 361 # -90 128 H* 5 L* 6</pre>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	a 341 400 0 258 -347 H* 2 L* 2 0 099 -541 1 288 1466 2 361 -381 3 1170 -1099 4 209 -207 5 341 547 6 209 -104 4 -102 101 6 -102 101 6 -82 27 H* 3 L* 2 0*3543 3217 0*3543 3217 0*3555 3217 0*35555 3217 0*3555 3217 0*35555 3217 0*35555 3217 0*35555 3217 0*35555 3217 0*3555555555555555	0 188 105 1 280 -253 2 729 -721 3 1557 1401 4 -68 108 5 701 -227 7 (119 1149 8 176 91 9 585 550 H-3 (1-3) 0 150 74 1 (1171 1060 2 410 418 3 1401 -1443 5 2044 209 9 592 -1000	6 226 -273 7 1030 1033 6 532 463 9 342 -362 H 3 L 4 0 357 -251 1 228 701 2 1507 1251 3 257 -253 1 258 701 2 1507 1253 5 267 -223 5 -64 165 5 16 558 7 -110 87 8 210 -87 6 210 -87 7 -10 87 8 210 -87 8 21	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<pre>4 410 401 5 876 - 854 6 987 -1018 7 191 740 8 203 -421 N* 4 1* 6 0 1013 - 035 1 482 -1330 2 4097 -030 3 806 -937 4 617 -600 5 886 -993 7 36* 361 8 -100 -128 H* 5 1* 6</pre>	$\begin{array}{c} H=4\ \ L=7\\ 0\ \ 861\ \ -767\\ 1\ \ -886\ \ -74\\ 2\ \ 221\ \ -205\\ 8\ \ 532\ \ 615\\ 4\ \ 472\ \ -586\\ 8\ \ 532\ \ 615\\ 8\ \ 532\ \ 615\\ 8\ \ 532\ \ 615\\ 8\ \ 532\ \ 615\\ 8\ \ 532\ \ 615\\ 8\ \ -75\\ 8\ \ -75\\ 8\ \ -77\ \ 584\\ 1\ \ -77\ \$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6 341 400 9 258 - 367 H* 2 L* 2 0 699 -541 1 208 - 1646 2 361 - 381 5 1179 - 1089 4 209 - 207 5 309 - 1089 4 209 - 207 5 309 - 1089 6 -102 101 9 -82 27 H* 3 L* 2 0*254 3217 1 471 1355 2 0.58 747	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	6 226 -273 7 1030 1033 6 532 463 9 342 -362 m 3 L* 4 0 257 -251 2 1530 1543 3 -67 -12 5 -64 185 5 -74	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+ (10 401) 5 876 - 874 8 6 9 87 - 1015 7 334 140 9 203 - 421 H 34 140 9 203 - 421 H 4 1+6 1-635 1 1482 - 1330 2 609 - 630 3 097 913 5 609 - 630 5 097 913 6 010 - 178 H 100 - 128 H 5 L 6 6 0 1631 1721	He & Le 7 0 861 -767 2 221 -205 3 651 905 4 512 -66 5 -131 17 7 687 826 8 -93 -55 He 5 Le 7 0 572 584 1 -77 28 2 428 -413 3 -979 71 6 -164 -164 5 -89 71 6 -164 -164 5 -164 -164 -164 5 -164 -164 -164 -164 -164 -164 -164 -164
1 205 -240 2 447 479 3 998 -1003 4 241 -229 5 1002 -955 1002 -955 1002 -955 1002 -956 3 200 -249 8 200 -249 8 200 -249 8 200 -249 14 10 1 608 -739 2 -45 21 3 1410 1689 4 306 -390 4 306 -390 5 164 169 4 306 -739 2 -45 21 3 1410 1689 4 306 -739 2 -45 21 5 169 5 169	8 141 100 9 238 -347 11 228 146 0 699 -541 1 1288 1466 1 1288 1466 1 1288 1466 1 1288 1466 1 1288 1466 1 1299 -201 5 541 547 5 541 547 5 541 547 6 209 -181 7 297 -291 8 -102 101 9 -82 27 14 3 14 2 14 471 1395 2 658 747 3 737 -760	0 186 103 1 200 -253 2 729 -721 3 1557 120 5 705 723 6 211 -227 6 211 -227 6 211 -227 6 3 105 7 110 110 9 365 550 m-3 1c 3 0 150 7c 1 10 -10 2 410 418 3 100 418 5 704 208 6 246 109 7 932 -1000 9 -985 -098 -208 -988 -208 -	6 226 -271 7 1030 1031 8 532 461 9 342 -552 H* 3 1* 4 0 357 -251 1 228 201 2 1530 1541 3 -67 -12 4 267 -221 8 -71 105 7 -10 -570 9 -73 66 H* 4 1* 4 0 1646 -1613 1 170 -725 6 100 -725 7 10 -	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	 4 (10 40) 5 876 - 86% 6 987 - 1018 7 187 72-7 8 315 3-16 9 203 - 421 M* 4 1* 6 0 (011 - 913) 0 20 - 621 1 482 - 1330 2 609 - 6310 2 636 - 693 5 846 - 693 6 -108 - 75 7 156 361 8 -100 - 128 H* 5 1* 6 0 1631 1721 	$\begin{array}{c} \begin{array}{c} \begin{array}{c} H=4 \\ c\\ \end{array} \left[\begin{array}{c} c\\ $
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8 141 100 9 238 -147 14 2 14 2 1 1288 1466 3 1319 -108 3 1319 -108 3 1319 -108 3 1319 -108 5 341 547 8 -107 101 8 -107 101 8 -107 101 8 -107 101 8 -107 101 8 -107 101 8 -107 101 9 -82 21 14 3 14 2 10 224 1321 10 29 - 10 9 - 10	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6 226 -271 7 1030 1033 9 332 -357 M 3 1 4 4 0 357 -251 1 228 201 2 1530 1543 3 -24 185 6 318 559 7 -10 -200 8 -71 -251 1 228 201 1 257 -251 1 258 201 2 1597 1543 3 -24 185 6 318 559 7 -10 -200 8 -71 -20 1 2 120 -200 1 2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	 c.10 ACI BTD-AEGA BTD-AEGA BTD-AEGA BTD-AEGA BTD-AEGA BTD-AEGA BTD-AEGA ACD ACD	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 5.41 1.00 9 2.38 -1.67 MI 2 1.62 0 9.78 -1.61 1 1.79 -1.04 1 1.79	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0 220 -271 10327 0033 9 342 -362 0 354 -351 1 2 1330 124 0 354 -351 1 2 1330 124 1 -27 -13 1 -27 -13 2 -27 -273 2 -27 -273	He 3 1, 5 5 0 556 -<61	10 - 401 10 - 401 10 - 101	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 141 100 9 238 -167 H 2 L 2 1 1988 166 2 388 166 2 381 -181 3 1179 -1009 2 381 -181 3 1179 -1009 3 1179 -1009 9 -282 221 0 204 122 0 204 122	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0 220 -271 10327 0033 0 342 -587 10337 -271 1 2130 1033 0 342 -587 1 2130 1033 1 -07 -271 1 2130 15-3 3 -07 -273 3 -	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 110 - 401 - 810 - 110 - 817 - 110 - 917 - 917 - 91 - 917 -	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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Table 1. Parameters for PBr₇ Standard deviations are given in parentheses. The β_{ij} are defined by: $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl).$

P	x 0·1133 (0·0016)	<i>y</i> 0·25	<i>z</i> 0·1477 (0·0005)	β ₁₁ 0·0010 (0·0020)	β_{22} 0.0053 (0.0010)	β_{33} 0.0018 (0.0003)	β_{13} 0.0008 (0.0005)	$\beta_{12} \\ 0.0$	β ₂₃ 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

$$R_{1} = \frac{\sum ||F_{obs}| - |F_{calc}||}{\sum |F_{obs}|} = 0.080$$

$$\frac{\sqrt{\sum w (|F_{obs}| - |F_{calc}|)^{2}}}{\frac{hkl}{\sqrt{\sum w (|F_{obs}|^{2} - |F_{calc}|)^{2}}}} = 0.102$$

Table 2 (cont.)

2 2293 2293	2 615 655	2 1312 1328	6 166 -163	H= 1 L+13	0 741 -694	He 1 1-16
3 1090 1071	3 308 -375	3 375 -328	7 -79 -114		1 264 -243	
4 379 -402	4 423 -463	4 389 -385		0 434 461	2 627 516	0 595 575
5 680 -690	5 -88 82	5 530 439	H= 5 L=11	1 671 676	3 197 196	1 -99 -77
6 858 966	6 276 300	6 738 677		2 509 -546	526 -518	2 355 355
7 594 557	7 261 -233	150 -134	0 317 346	3 - 43 - 136	5 220 -194	3 -88 124
8 390 -433	8 204 -166	8 1/4 -344	1 -89 -152	385 354	6 201 313	 318 318
		No. 6 1.10		A 125 - 101	No. 6 1	No. 2
N= 2 L= 0	N= 3 L= 4		3 -108 -34	0 34 9 - 24 3		
0 1880 -1834	0 -70 -44	1 972 -1010	4 237 -149	He 2 (413	0 1180 -1073	1 623 617
1 385 261	1 950 865	2 1167 1252	0 157 -167		1 278 -231	2 316 261
2 -12 -11	2 660 -679	3 982 1071	H= 0 L=12	0 636 713	2 -121 -9	3 309 -368
3 144 -118	3 -86 15	4 -109 117		1 624 689	3 -114 46	4 180 -167
4 1067 -1133	4 -90 144	5 475 -446	0 1103 -1090	2 661 -792	4 714 -719	
5 -87 -6	5 1010 1183	6 406 431	2 408 454	3 361 -329	5 204 -261	H# 3 L=16
6 154 111	6 387 -326	7 659 588	4 648 -728	4 595 588	-	
7 -99 -131	7 350 305		8 261 261	5 713 674	H= 5 L-14	0 -91 -114
8 213 -202	8 122 202	H= 5 (=10		0 304 -487		1 -89 -37
			H- 1 L-12		0 -47 -110	2 707 -666
H= 3 L= 8	H* 4 (* V				1 1022 1091	3 -11 -51
		2 -89 96	0 778 -825	0 244 -202	1 103 193	Ma. 4. 1. 14
0 3182 -3221	1 165 -104	1 445 440	2 749 -704	1 -91 144	4 152 -79	No. 4 1018
3 1330 1104		4 717 -458	3 -94 -75	2 535 607	5 653 767	0 -100 - 74
1 - 81 - 92	3 266 281	5 649 -550	4 439 -480	3 589 -517		1 -98 -111
4 2036 -2160	1 112 175	6 250 180	5 -108 -52	4 315 -276	H= 0 L=15	2 206 -142
5 211 -198	5 -132 -33	7 -65 60	6 -96 -238	5 246 -234		3 -81 104
6 959 845	6 337 -321			6 347 328	1 431 -473	
7 -99 -140	7 207 179	H= 0 L=11	H= 2 L=12		3 674 679	H= 5 L=16
8 659 -663				H= 4 L=13	5 -77 -82	
	H= 5 L= 9	L 1346 1266	0 439 447			0 564 546
H# 4 L# 8		3 1678 -1759	1 533 562	0 559 495	H= 1 (-15	1 262 262
	0 /33 /13	\$ 435 365	2 -88 86	1 245 -212		2 113 147
0 1186 1127	7 - 97 100	1 12/5 -1243	3 347 -385	2 232 -234	1 -104 13	
1 812 -809	2 -01 100		4 436 332		2 -106 13	H= 0 [.17
	4 417 442		3 303 278	300 307	3 330 203	
3 846 466	5 -105 -719	0 151 140	0 09 ~36	, ,,, ,,,,		1 344 337
4 570 64U	A -95 -57	1 661 610	wa 3	8 141 -203	2 141 201	
A -128 144	7 852 -777	2 -90 -66		HR 5 1413	H= 2 L=15	
7 000 0/6		3 732 -783	0 493 314			0 -87 -93
	H= 0 L=10	4 -94 54	1 -91 -0	0 327 -345	0 598 567	1 284 -285
H= 5 L= 8	5 269 -231	5 309 240	2 812 934	1 -104 83	1 - 100 78	2 -81 136
		6 -104 16	3 -91 159	2 -101 -142	2 418 -379	3 -72 99
0 318 277	0 2312 2526	7 452 -535	4 299 248	3 -96 240	3 346 -3+1	
1 957 1031	2 465 -438		5-100 102	4 234 -206	4 495 415	H= 2 L=17
2 980 1151	1037 1011	H- 2 L-11	6 402 367	5 361 302	5 -68 -117	
3 573 -627			7 -62 163			0 459 420
4 -89 106	8 310 343			H= 0 L+14	No 3 1013	1 -11 -12
5 1044 873	HB 1 1.010	2 -86 36	He & Le12		0 -101 144	2 200 -289
5 60 5 439	A= 1 1-10	3 448 478	0 -100 -141	0 243 304	1 772 251	3 143 -124
	0 509 -421	4 218 -227	1 1044 1134	4 346 313	2 -97 10	He 3 1817
H# 0 1. 9	1 -83 57	5 644 575	2 209 -267	A ASA -AAT	3 490 -402	
	2 750 -707	6 97 15	3 1112 -1032		4 -80 116	0 367 346
1 1519 1437	3 -89 -43	7 566 530	4 -125 -115	H= 1 L=14		1 -74 -18
3 1191 -1068	4 234 -220		5 635 619		H= 4 L=15	2 437 -447
5 979 1013	5 -94 -100	н= 3 L=11	6 -94 -72	0 656 -690		
7 474 -474	6 301 -259			1 719 -788	0 -115 -184	H= 4 L+17
	7 -96 73	0 344 -348	H= 5 L-12	2 820 800	1 260 305	
H= 1 L= 9		1 480 542		3 660 684	2 -109 -90	0 483 412
	H- 2 L-10	2 174 189	0 1085 -1070	4 735 -541	3 -100 -45	1 -77 35
0 1194 -1032		3 239 -255	1 190 -293	5 502 -493	4 -86 -105	2 369 -567
1 551 -533	1 800 -868	5 507 5AT	2 -107 -141	o 486 470		
2 1210 1183	2 1442 -1425	· · · · · · · · · · · · · · · · · · ·	3 -103 24			H- 0 L-18
3 474 4421	509 560	7 -76 -55	- 536 -731	- 5 Fate	0 141 -171	0 - 10 //
5 853 -000	-64 -117		3 348 -329	0 1124 1144	1 198 154	2 279 640
A A90 AA2	5 501 -544	He 4 1 .11	a -o> 100	1 494 -468	2 -81 106	
7 629 -640	0 010 -527		No. 0. 1.473	2 -105 95	3 -72 -104	H= 1 1=28
8 383 -427	7 -80 127	0 598 621		3 535 449		
		1 875 -917	1 136 183	4 738 760	H= 0 L=16	0 167 147
H= 2 L= 9	H= 3 L=10	2 -109 -19	3 630 -637	5 269 -249		1 626 -607
		3 234 272	5 -100 73		0 -99 76	
0 783 -685	0 429 -370	4 544 462	7 265 -502	H= 3 L=14	2 -95 -145	H= 2 L=18
1 349 291	1 558 507	> 1015 - 995			→ -77 75	0 -328 -476

Table 3. Bond lengths and angles in PBr₇

Bond leng	ths
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 ang	les
Br(1)-P-Br(2)	$110.4 \pm 0.3^{\circ}$
Br(1)-P-Br(3)	109.8 ± 0.3
Br(2)-P-Br(3)	109·1 <u>+</u> 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 PBr7.

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

The PBr₄⁺ ion in PBr₇ is very similar in configuration to the PBr₄⁺ ion in PBr₅. It is nearly tetrahedral with all angles in the range 107–110° and all bond distances in the range $2 \cdot 16 - 2 \cdot 18$ Å.

The tribromide ion in PBr₇ 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 Br₂, 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 NH₄I₃ (Mooney, 1935) and CsI₃ (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 $3 \cdot 1 - 3 \cdot 4$ Å range while the nearest approaches to Br(4) and Br(6) are all greater than $3 \cdot 8$ Å. Since the van der Waals radius of bromine is $1 \cdot 95$ 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 ne	ighbors of	atoms	in	Br-
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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_{1}^{-} , 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 0.1β 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 PBr₇. In this case, however, the modification for the effect of the cation was greater since the distortion in $Br_{\overline{3}}$ is greater than in I_3^- . Hence, the Coulomb integral on Br(5) was increased by 0.3β . 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 Br3⁻.

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 PBr₇. 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 Sn₂S₃

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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 $a=8\cdot864$, $b=14\cdot020$, $c=3\cdot747$ 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 MCdCl₃ 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.