The structure (Fig. 1) contains tetrahedral $AsO_2(OD)_2^-$ ions, linked into sheets parallel to (001) by O—D···O bonds; the ions are joined directly along **b** by pairs of symmetry-equivalent bonds, O···O = 2·621 Å (Table 2), and along **a** by two bonds from the deuterium oxide molecule, O···O = 2·781 and 3·104 Å. All three independent bonds are close to linear (Table 2). The sheets are joined by $NaO_4(OD_2)_2$ coordination octahedra, which share edges along **b**; Na—OD_2 = 2·414, Na—O = 2·379 and 2·534 Å, with some deviation (maximum 6·7°) from 90° angles.

The $AsO_2(OD)_2^-$ ion is distorted from exact tetrahedral and from exact C_{2v} symmetry: As—O(1)D = 1·725 (3), As—O (2) = 1·647 (4), As—O(3) = 1·689 (4) Å, DO—As—OD = 97·2, O—As—O = 113·3, O—As—OD = 107·8 and 114·7 (1)°. Such distortions have been observed and discussed previously (Baur, 1974). The increase in the As—O(3) bond length, relative to As—O(2), can be related to the involvement of O(3) in stronger interionic interactions (three strong O—D···O bonds) in comparison with O(2) (one weak O—D···O bond and two weak interactions with Na). Sums of bond strengths (Brown & Shannon, 1973), computed with D atoms in ideal calculated positions, are close to valences for all the atoms except O(2) (1·8). The D_2O molecule has normal dimensions: mean O—D = 0·9 Å, D—O—D = 100°. The total environment around the O atoms is approximately trigonal planar for O(1) (angles = 107–143, mean 119°) and tetrahedral for O(2), O(3), and O(*W*) (angles = 99–123, mean 109°).

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Tetraphenylphosphonium Enneabromodibismuthate(III)

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Abstract. $[(C_6H_5)_4P]_3[Bi_2Br_9]$; monoclinic, $P2_1/n$ (alternative setting for $P2_1/c$, No. 14); a = 12·387 (6), b = 32·04 (1), c = 19·927 (6) Å, β = 99·67 (3)°; D_o = 1·84 (1) g cm^{-3}, Z = 4, D_c = 1·836 g cm^{-3}; R = 0·068 for 3561 reflexions with $I > 2\sigma(I)$. The structure consists of tetraphenylphosphonium cations and binuclear enneabromodibismuthate(III) anions with two face-sharing $BiBr_6$ octahedra.

Introduction. The main purpose of this work, as part of a systematic study of bromo- and iodobismuthates(III) (Lazarini, 1977*a*,*b*,*c*), was to establish the influence of a really large cation on the linking of hexahalobismuthate(III) groups into polynuclear species. It seems the title compound is the first known example with an $M_2X_9^{3-}$ anion without any crystallographic symmetry.

Yellow crystals of the title compound were grown by slow evaporation from an acetone solution of $[(C_6H_5)_4P]Br$ and $BiBr_3$ (3 : 2 molar ratio). The formula was determined by standard chemical analysis (found: 18·95% Bi, 33·80% Br; calculated: 19·39% Bi, 33·36% Br). A well developed crystal, selected for the intensity measurements, was characterized by the planes (with, in parentheses, the distances from the crystal faces to an arbitrary origin inside the crystal) ±(010) (0·039 mm), ±(011) (0·047 mm), ±(0$\bar{1}$1) (0·047 mm), ±(101) (0·198 mm) and ±($\bar{1}$01) (0·181 mm).

The intensity data were collected with an Enraf–

Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å), ω–2θ scan, $\theta_{min.}$ = 1°, $\theta_{max.}$ = 20°, 2θ scan width: (0·6 + 0·2 tan θ)°, aperture: (2·5 + 0·9 tan θ) mm, maximum scan time 20 s, background: a quarter of the scan time at each of the scan limits. 7225 independent reflexions were recorded and, of these, 3561 with $I > 2\sigma(I)$ (calculations based on counting statistics) were used in the structure analysis. Corrections were applied for Lorentz and polarization effects and for absorption [μ(Mo $K\alpha$) = 92·7 cm^{-1}]. The absorption corrections A^*, calculated from the measured crystal dimensions (Gaussian-grid method), range from 1·89 to 2·27. The unit-cell parameters were obtained from a least-squares fit of the θ values of 15 reflexions measured on the diffractometer. The space group $P2_1/n$ (alternative setting for $P2_1/c$, No. 14) with equivalent positions $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$ was determined from systematic absences ($h0l$: $h + l = 2n + 1$, $0k0$: $k = 2n + 1$).

Table 1. *Final positional parameters* (×10^5) *for* Bi *and* Br *atoms with standard deviations in parentheses*

	x	y	z
Bi(1)	48459 (12)	40545 (5)	22913 (7)
Bi(2)	43514 (12)	34885 (5)	40252 (7)
Br(1)	69324 (31)	40943 (15)	20166 (20)
Br(2)	44993 (36)	48986 (14)	20729 (22)
Br(3)	40152 (35)	38585 (15)	9550 (20)
Br(4)	27684 (31)	39568 (13)	28974 (19)
Br(5)	51255 (33)	31536 (12)	27323 (20)
Br(6)	57721 (33)	42050 (13)	37709 (19)
Br(7)	61058 (32)	31650 (14)	48785 (20)
Br(8)	36407 (34)	38781 (15)	50734 (20)
Br(9)	30016 (38)	28075 (15)	40938 (25)

Table 2. *Final positional parameters* (×10^4) *and thermal parameters* (×10^3) *for* P *and* C *atoms with standard deviations in parentheses*

The isotropic temperature factor is in the form: $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

	x	y	z	U (Å^2)
P(1)	5666 (8)	847 (3)	4331 (5)	39 (3)
P(2)	4595 (8)	810 (3)	738 (5)	36 (3)
P(3)	9113 (9)	2479 (3)	1951 (5)	47 (3)
C(1)	5997 (28)	1377 (10)	4124 (16)	32 (9)
C(2)	5202 (34)	1687 (14)	4091 (20)	59 (12)
C(3)	5469 (34)	2084 (14)	3938 (20)	58 (12)
C(4)	6527 (34)	2180 (13)	3854 (19)	56 (12)
C(5)	7323 (33)	1904 (13)	3916 (19)	56 (12)
C(6)	7108 (28)	1469 (11)	4073 (17)	40 (10)
C(7)	4651 (28)	640 (11)	3645 (17)	38 (10)
C(8)	4089 (31)	906 (13)	3147 (19)	51 (11)
C(9)	3290 (34)	729 (13)	2634 (20)	55 (12)
C(10)	3100 (30)	321 (12)	2657 (18)	47 (10)
C(11)	3582 (35)	54 (13)	3114 (21)	61 (12)
C(12)	4432 (31)	215 (12)	3651 (19)	50 (11)
C(13)	6818 (26)	523 (10)	4398 (16)	25 (9)
C(14)	7289 (32)	446 (12)	3795 (19)	50 (11)
C(15)	8161 (31)	188 (12)	3810 (18)	44 (10)
C(16)	8622 (33)	11 (13)	4407 (21)	57 (12)
C(17)	8257 (35)	100 (13)	5042 (21)	55 (12)
C(18)	7362 (31)	346 (12)	5018 (18)	47 (11)
C(19)	5115 (28)	856 (11)	5113 (16)	33 (9)
C(20)	5837 (31)	1052 (12)	5660 (19)	50 (11)
C(21)	5452 (32)	1082 (12)	6288 (20)	53 (11)
C(22)	4428 (33)	925 (13)	6335 (20)	57 (11)
C(23)	3714 (39)	733 (15)	5796 (24)	64 (14)
C(24)	4131 (32)	695 (12)	5186 (19)	47 (11)
C(25)	4552 (31)	1274 (12)	1203 (19)	45 (11)
C(26)	3748 (38)	1578 (16)	978 (23)	70 (14)
C(27)	3655 (41)	1932 (16)	1371 (25)	80 (15)
C(28)	4443 (38)	2022 (14)	1918 (23)	65 (13)
C(29)	5244 (38)	1745 (15)	2128 (23)	73 (14)
C(30)	5351 (32)	1371 (12)	1785 (20)	51 (12)
C(31)	5750 (31)	528 (12)	1117 (19)	44 (11)
C(32)	5739 (37)	337 (14)	1755 (22)	60 (13)
C(33)	6649 (32)	96 (12)	2078 (19)	58 (11)
C(34)	7560 (35)	72 (14)	1751 (22)	62 (12)
C(35)	7584 (34)	243 (13)	1143 (21)	60 (12)
C(36)	6673 (29)	457 (11)	793 (17)	36 (10)
C(37)	4769 (26)	956 (11)	−127 (16)	30 (9)
C(38)	3978 (31)	783 (12)	−678 (19)	47 (11)
C(39)	4146 (36)	878 (14)	−1343 (22)	66 (13)
C(40)	5052 (33)	1119 (13)	−1427 (20)	52 (11)
C(41)	5746 (31)	1304 (12)	−900 (19)	49 (11)
C(42)	5634 (30)	1198 (12)	−216 (18)	38 (10)
C(43)	3397 (28)	495 (11)	730 (16)	40 (9)
C(44)	2358 (36)	692 (14)	624 (21)	70 (13)
C(45)	1438 (32)	421 (13)	612 (19)	49 (11)
C(46)	1501 (34)	4 (13)	760 (20)	54 (12)
C(47)	2521 (38)	−172 (14)	875 (22)	66 (13)
C(48)	3518 (31)	79 (12)	886 (19)	47 (11)
C(49)	9286 (28)	1935 (10)	2008 (16)	26 (9)
C(50)	10064 (35)	1726 (13)	1693 (21)	63 (12)
C(51)	10188 (44)	1271 (17)	1785 (27)	84 (17)
C(52)	9520 (42)	1077 (16)	2156 (25)	79 (16)
C(53)	8734 (43)	1271 (18)	2437 (26)	98 (16)
C(54)	8657 (41)	1681 (17)	2400 (24)	92 (16)
C(55)	8950 (32)	2673 (12)	2785 (18)	48 (11)
C(56)	8163 (32)	2945 (12)	2781 (19)	53 (11)
C(57)	8036 (35)	3104 (13)	3546 (22)	63 (13)
C(58)	8830 (38)	2955 (15)	4044 (22)	61 (14)
C(59)	9649 (38)	2659 (15)	3990 (23)	70 (14)
C(60)	9720 (33)	2513 (13)	3326 (21)	61 (12)
C(61)	7908 (31)	2606 (12)	1367 (18)	44 (11)
C(62)	7175 (39)	2313 (15)	1132 (23)	79 (14)
C(63)	6068 (40)	2405 (16)	750 (24)	98 (15)
C(64)	5910 (41)	2819 (17)	638 (24)	77 (15)
C(65)	6652 (44)	3134 (17)	844 (26)	89 (16)
C(66)	7707 (37)	3017 (14)	1215 (22)	71 (13)
C(67)	10251 (33)	2699 (13)	1696 (21)	57 (12)
C(68)	10342 (37)	2703 (14)	984 (23)	70 (14)
C(69)	11389 (34)	2833 (13)	802 (20)	53 (12)
C(70)	12250 (34)	2978 (13)	1285 (22)	59 (12)
C(71)	12111 (35)	2984 (13)	1916 (22)	60 (13)
C(72)	11215 (32)	2818 (13)	2155 (19)	54 (12)

The structure was solved by the heavy-atom method and refined by least-squares calculations with anisotropic thermal parameters for Bi and Br atoms, isotropic for P and C atoms and with anomalous-dispersion corrections for Bi, Br and P. The function minimized in the least-squares procedure was $\Sigma\, w(|F_o| - |F_c|)^2$. The weighting scheme applied was as follows: $|F_o| < 140$: $w_F = (|F_o|/140)^{2\cdot5}$, $140 < |F_o| \leq 280$: $w_F = 1\cdot0$, $|F_o| > 280$: $w_F = (280/|F_o|)^{1\cdot5}$, $\sin\theta < 0\cdot15$: $w_S = (\sin\theta/0\cdot15)^{1\cdot7}$, $0\cdot15 < \sin\theta \leq 0\cdot28$: $w_S = 1\cdot0$, $\sin\theta > 0\cdot28$: $w_S = (0\cdot28/\sin\theta)^{2\cdot3}$, $w = 0\cdot06 w_F w_S$. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was also included in the final stage of the refinement [$g = 1\cdot5(1) \times 10^{-2}$]. The positional parameters of the H atoms were calculated and included in the structure factor calculation with an isotropic temperature factor ($U = 0\cdot06$ Å^2) but were not refined. The final R values are $R = \Sigma||F_o| - |F_c||/\Sigma\,|F_o| = 0\cdot068$ and $R_w = [\Sigma\, w(F_o - F_c)^2/\Sigma\, wF_o^2]^{1/2} = 0\cdot073$ for 3561 reflexions and 401 parameters. The average parameter shift-to-error ratio was 0·2 in the final cycle. A final difference Fourier map revealed no peaks greater than 1·3 e Å^{-3}.

All calculations were performed on the CDC Cyber 72 computer of RRC Ljubljana with the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) adapted by Professor L. Golič. Atomic scattering factors for the nonhydrogen atoms tabulated by Cromer & Mann (1968) were applied together with those tabulated by Stewart, Davidson & Simpson (1965) for H atoms and the values of $\Delta f'$ and $\Delta f''$ for anomalous-dispersion correction tabulated by Cromer & Liberman (1970).

The positional parameters of the Bi and Br atoms are listed in Table 1 and those of the P and C atoms in Table 2. Stereoscopic drawings (Johnson, 1965) of the unit-cell content with the atom-numbering system used and of the $Bi_2Br_9^{3-}$ anion are given in Figs. 1 and 2 respectively. Some important interatomic distances and angles are given in Table 3.*

Discussion. It seems that in the crystal structure the large tetraphenylphosphonium cations stabilize the large enneabromodibismuthate(III) anions with two face-sharing octahedra. Table 3 contains the uncorrected bond distances within this anion as well as those corrected for rigid-body thermal motion by the program of Filippini & Gramaccioli (1969) based on the procedure of Schomaker & Trueblood (1968), kindly provided by Professor C. M. Gramaccioli. The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32672 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

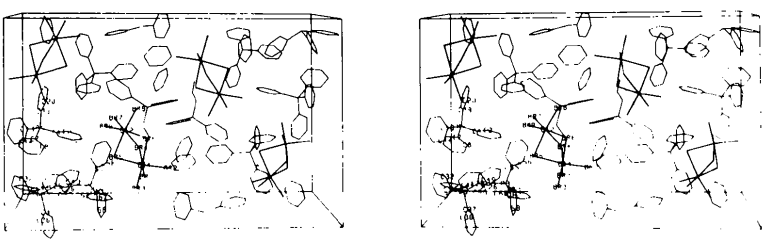

Fig. 1. A stereoscopic drawing of the unit cell viewed along [100].

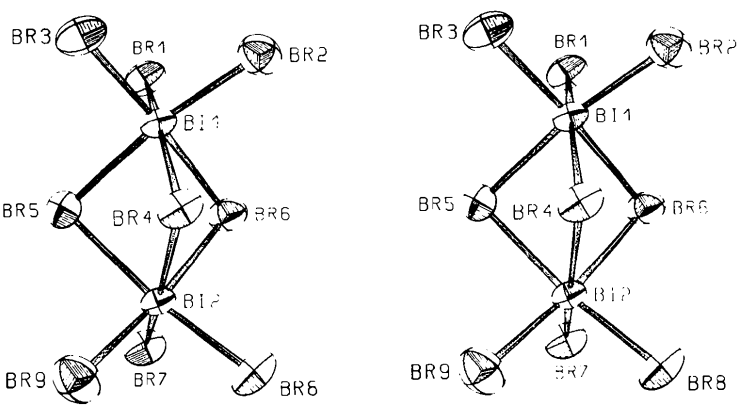

Fig. 2. A stereoscopic drawing of the $Bi_2Br_9^{3-}$ anion. The atoms are represented by thermal ellipsoids drawn at the 70% probability level.

corrected distances are all about 0·2% longer. Only uncorrected bond angles are listed in Table 3. For three different $(C_6H_5)_4P^+$ cations of the asymmetric unit only the maximum, minimum and mean distances and angles, uncorrected for thermal motion, are given. The weighted mean distances and angles ($\bar{X}$) and the average standard deviations $\sigma(\bar{X})$ were calculated as:

$$\bar{X} = \sum_i (X_i/\sigma_i^2)/\sum_i \sigma_i^{-2}, \quad \sigma(\bar{X}) = (1/\sum_i \sigma_i^{-2})^{1/2}.$$

The terminal and bridging Bi—Br distances are comparable with those found in other bromobismuthates(III). The distortions from octahedral geometry found in $Bi_2Br_9^{3-}$ are typical for bridged metal–metal systems with no metal–metal bonding (Cotton, 1967). The differences between corresponding distances and angles are not very significant and are probably due to crystal-packing forces. Unusual contacts between the phenyl rings and Br atoms were not observed.

Table 3. *Interatomic distances* (Å) *and angles* (°) *with standard deviations in parentheses*

(*a*) Bond distances in the $Bi_2Br_9^{3-}$ anion

	Uncorrected	Corrected for thermal motion
Bi(1)—Br(1)	2·733 (4)	2·739 (4)
Bi(1)—Br(2)	2·761 (5)	2·768 (5)
Bi(1)—Br(3)	2·761 (4)	2·767 (4)
Bi(1)—Br(4)	3·037 (4)	3·043 (5)
Bi(1)—Br(5)	3·020 (4)	3·027 (4)
Bi(1)—Br(6)	3·017 (4)	3·024 (4)
Bi(2)—Br(4)	3·109 (4)	3·115 (4)
Bi(2)—Br(5)	3·088 (4)	3·095 (4)
Bi(2)—Br(6)	2·987 (5)	2·994 (5)
Bi(2)—Br(7)	2·729 (4)	2·735 (4)
Bi(2)—Br(8)	2·704 (5)	2·710 (5)
Bi(2)—Br(9)	2·766 (5)	2·773 (5)

(*b*) Bond angles in the $Bi_2Br_9^{3-}$ anion (uncorrected for thermal motion)

Br(1)—Bi(1)—Br(2)	92·9 (1)	Br(4)—Bi(2)—Br(5)	79·1 (1)
Br(1)—Bi(1)—Br(3)	91·7 (1)	Br(4)—Bi(2)—Br(6)	79·9 (1)
Br(1)—Bi(1)—Br(4)	167·8 (1)	Br(4)—Bi(2)—Br(7)	166·7 (1)
Br(1)—Bi(1)—Br(5)	92·1 (1)	Br(4)—Bi(2)—Br(8)	95·0 (1)
Br(1)—Bi(1)—Br(6)	88·3 (1)	Br(4)—Bi(2)—Br(9)	95·9 (1)
Br(2)—Bi(1)—Br(3)	92·7 (1)	Br(5)—Bi(2)—Br(6)	81·4 (1)
Br(2)—Bi(1)—Br(4)	92·5 (1)	Br(5)—Bi(2)—Br(7)	93·5 (1)
Br(2)—Bi(1)—Br(5)	171·5 (1)	Br(5)—Bi(2)—Br(8)	172·8 (1)
Br(2)—Bi(1)—Br(6)	91·2 (1)	Br(5)—Bi(2)—Br(9)	92·4 (1)
Br(3)—Bi(1)—Br(4)	99·0 (1)	Br(6)—Bi(2)—Br(7)	88·1 (1)
Br(3)—Bi(1)—Br(5)	93·9 (1)	Br(6)—Bi(2)—Br(8)	93·1 (1)
Br(3)—Bi(1)—Br(6)	176·1 (1)	Br(6)—Bi(2)—Br(9)	173·1 (1)
Br(4)—Bi(1)—Br(5)	81·3 (1)	Br(7)—Bi(2)—Br(8)	91·3 (1)
Br(4)—Bi(1)—Br(6)	80·6 (1)	Br(7)—Bi(2)—Br(9)	95·4 (1)
Br(5)—Bi(1)—Br(6)	82·1 (1)	Br(8)—Bi(2)—Br(9)	92·8 (2)
Bi(1)—Br(4)—Bi(2)	82·2 (1)	Bi(1)—Br(6)—Bi(2)	84·5 (1)
Bi(1)—Br(5)—Bi(2)	82·8 (1)		

(*c*) Bond distances and angles in the $(C_6H_5)_4P^+$ cations

P—C(mean)	1·79 (1)	C—C(mean)	1·392 (7)
P—C(max)	1·83 (3)	C—C(max)	1·45 (7)
P—C(min)	1·73 (4)	C—C(min)	1·32 (6)
C—P—C(mean)	109·4 (4)	P—C—C(mean)	119·7 (6)
C—P—C(max)	112 (2)	P—C—C(max)	124 (3)
C—P—C(min)	107 (2)	P—C—C(min)	116 (3)
C—C—C(mean)	119·8 (4)		
C—C—C(max)	126 (4)		
C—C—C(min)	114 (4)		

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