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Sodium Dideuteriumarsenate Monodeuterate

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Abstract. $NaD_2AsO_4.D_2O$, monoclinic, $P2_1/m$, a = 5·865 (6), b = 7·123 (6), c = 5·619 (5) Å, β = 92·58 (6)°, Z = 2, D_x = 2·63 g cm^{-3}, Mo radiation, R = 0·049 for 801 reflexions. The structure contains $AsO_2(OD)_2^-$ ions linked into (001) sheets by O–D···O hydrogen bonds, directly by pairs of bonds along **b** and *via* D_2O molecules along **a**. The sheets are joined by $NaO_4(OD_2)_2$ coordination octahedra which share edges along **b**. As–OD = 1·725 (3), As–O = 1·647, 1·689 (4), Na–OD_2 = 2·414, Na–O = 2·379, 2·534, O–D···O = 2·621, 2·781, 3·104 Å.

Introduction. Unit-cell and intensity data were measured on a Datex-automated GE XRD-6 diffractometer with Mo $K\alpha$ radiation, a θ–2θ scan at a scan speed of 2° min^{-1} in 2θ over a 2θ range of (1·80 + 0·86 tan θ), a background count for 20 s at the beginning and end of each scan, and measurement of a check reflexion, whose intensity gradually dropped by 5% during the data collection. Of 911 reflexions with $2\theta < 65°$, 807 had intensities greater than 3σ above background [$\sigma^2(I) = S + B + (0{\cdot}08\ S)^2$, where S = scan and B = background count]. Lorentz and polarization corrections were applied, but no absorption corrections were made (μ = 76 cm^{-1}).

The E statistics corresponded closely to a noncentrosymmetric distribution (mean $|E|$ = 0·88, mean $|E^2 - 1|$ = 0·68, no reflexions with $|E| > 2{\cdot}0$), and the structure was determined in space group $P2_1$ by Patterson and electron-density methods. Refinement of As, Na, and O parameters proceeded smoothly by full-matrix least-squares techniques; however, the refined structure corresponded closely to space group $P2_1/m$, there were many large correlation coefficients between parameters (as large as 0·94 between positional parameters of the two O atoms related by a mirror plane in $P2_1/m$), and some thermal parameters were non-positive-definite. Refinement was therefore continued and completed satisfactorily in the centrosymmetric space group (largest correlation 0·6 between overall scale and As thermal parameters). A difference synthesis computed at R = 0·052 contained density fluctuations as high as ±2 e Å^{-3} near the As positions, the only other significant features being three peaks of about 1 e Å^{-3} in plausible deuterium positions. Final refinement with anisotropic thermal parameters for non-deuterium atoms and isotropic parameters for

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deuterium atoms converged at $R = 0{\cdot}049$ and $R_w = 0{\cdot}062$ for 801 observed reflexions (six strong, low-order reflexions were given zero weight because of suspected extinction errors); for all 911 reflexions, $R = 0{\cdot}057$ and $R_w = 0{\cdot}062$.*

The function minimized was $\Sigma w(F_o - F_c)^2$; the weighting scheme $\sqrt{w} = 1$ when $|F_o| \leq 10$, $\sqrt{w} = 10/|F_o|$ when $|F_o| > 10$, $\sqrt{w} = 0{\cdot}05$ for unobserved reflexions, was chosen since it gave best constancy of $w(F_o - F_c)^2$ values. The maximum shifts in the final cycle were $0{\cdot}01\sigma$ for non-deuterium parameters, and $0{\cdot}07\sigma$ for deuterium parameters. An additional cycle of refinement with $w = 1/\sigma^2(F)$, with $\sigma(F)$ derived from the previously calculated $\sigma(I)$, gave a maximum shift of $1{\cdot}5\sigma$ in a parameter, a goodness-of-fit of 1·2, but less uniform values of $w(F_o - F_c)^2$ and slightly higher standard deviations; the final parameters were taken as those from the previous empirical weighting scheme. Atomic scattering factors were those of Stewart, Davidson & Simpson (1965) for D, and those of Cromer & Mann (1968) for As, Na^+, and O, with anomalous-dispersion correction for As (Cromer & Liberman, 1970). Local versions of standard crystallographic computer programs were used throughout. Final positional parameters are given in Table 1, and interatomic distances and angles in Table 2.

The thermal motion of the $AsO_2(OD)_2^-$ ion was analysed in terms of the rigid-body modes of translation and libration (Schomaker & Trueblood, 1968) with use of the computer program *MGTLS*. The ion corresponds very closely to a rigid body (r.m.s. $\Delta U_{ij} = 0{\cdot}0002$ Å^2); the translational motion is not far from isotropic, with r.m.s. displacements of 0·119, 0·107, and 0·103 Å along the principal axes, and the librational motion is more anisotropic, r.m.s. rotations 4·53, 4·25, and 2·41°. The As–O bond lengths were corrected for libration (Cruickshank, 1956) with a shape parameter of 0·08 for all atoms; bond-angle corrections were not significant.

Table 1. *Positional parameters* (*with standard deviations in parentheses*)

Na in 2(*a*), other atoms in 2(*e*) and 4(*f*).

	x	y	z
As	0·4757 (1)	$\frac{1}{4}$	0·6899 (1)
Na	0	0	0
O(1)	0·6427 (5)	0·0684 (4)	0·8020 (5)
O(2)	0·2112 (7)	$\frac{1}{4}$	0·7768 (8)
O(3)	0·4931 (7)	$\frac{1}{4}$	0·3906 (7)
O(*W*)	−0·0487 (8)	$\frac{1}{4}$	0·2833 (8)
D(O1)	0·590 (9)	−0·034 (9)	0·736 (10)
D(*W*1)	−0·169 (33)	$\frac{1}{4}$	0·325 (37)
D(*W*2)	0·048 (16)	$\frac{1}{4}$	0·455 (18)

Table 2. *Interatomic distances* (Å) *and angles* (°) (*with standard deviations in parentheses*)

		Corrected		
As–O(1)D	1·725 (3)	1·731 (3)	O(1)–As–O(1′)	97·2 (1)
As–O(2)	1·647 (4)	1·655 (4)	O(1)–As–O(2)	114·7 (1)
As–O(3)	1·689 (4)	1·696 (4)	O(1)–As–O(3)	107·8 (1)
O(1)–D	0·87 (6)		O(2)–As–O(3)	113·3 (2)
			As–O(1)–D	107 (4)

Na–O(1)	2·379 (3)	O(*W*)–D(*W*1)	0·8 (2)
Na–O(2)	2·534 (4)	O(*W*)–D(*W*2)	1·1 (1)
Na–O(*W*)	2·414 (4)		

D(*W*1)–O(*W*)–D(*W*2)	100 (14)
O–Na–O	83·3–96·7, 180·0 (2)

X–D···Y	X···Y	X–D	D···Y	X–D···Y
O(1)–D(O1)···O(3)	2·621 (5)	0·9 (1)	1·8 (1)	175 (5)
O(*W*)–D(*W*1)···O(3)	2·781 (5)	0·8 (2)	2·0 (2)	172 (18)
O(*W*)–D(*W*2)···O(2)	3·104 (6)	1·1 (1)	2·0 (1)	177 (9)

Discussion. Sodium dihydrogenarsenate monohydrate is said to crystallize in two modifications: an orthorhombic (or pseudo-orthorhombic) form whose structure has been determined and a monoclinic form for which no X-ray data are available (Ferraris, Jones & Sowden, 1974). The structure of the first form corresponds closely to space group $P2_12_12_1$, but has been described in $P2_1$ on the basis of the observation of two weak odd-index axial reflexions in the neutron diffraction pattern. To assist in an ESR study, the structure of a fully deuterated crystal has now been determined, the material probably corresponding to the monoclinic form previously described for the hydrate (which has approximately the same $a:c$ axial ratio and β angle as the present deuterate).

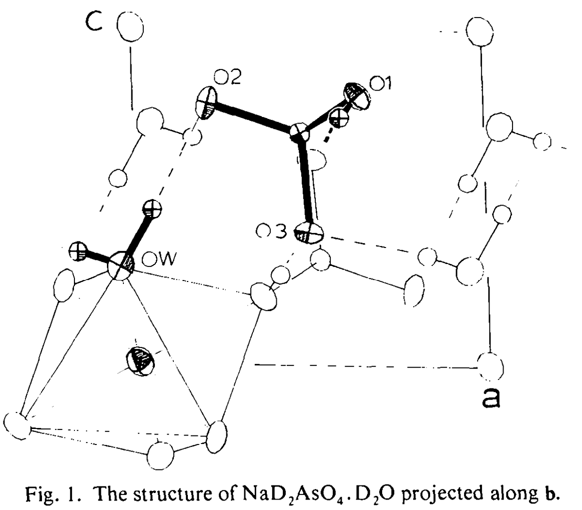

Fig. 1. The structure of $NaD_2AsO_4.D_2O$ projected along **b**.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32666 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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); $a = 12\cdot387$ (6), $b = 32\cdot04$ (1), $c = 19\cdot927$ (6) Å, $\beta = 99\cdot67$ (3)°; $D_o = 1\cdot84$ (1) g cm^{-3}, $Z = 4$, $D_c = 1\cdot836$ g cm^{-3}; $R = 0\cdot068$ 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), $\pm(01\bar{1})$ (0·047 mm), ±(101) (0·198 mm) and $\pm(\bar{1}01)$ (0·181 mm).

The intensity data were collected with an Enraf–