Arsenic Dioxide

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Abstract. AsO_2, $M_r = 107.92$, orthorhombic, *Pnma*, $a = 8.597$ (2), $b = 5.235$ (2), $c = 7.269$ (2) Å, $U = 327.1$ Å^3, $Z = 8$, $D_x = 4.382$ Mg m^{-3}, μ(Mo $K\alpha$) = 20.2 mm^{-1}. Final $R = 0.057$ for 711 unique observed reflexions. The structure consists of infinite layers. Two As and two O atoms lie on mirror planes; a third O is on a general position. The compound may be considered to contain As^{III} and As^V atoms; As^{III} is coordinated to three O atoms at right angles and As^V to four O atoms in a distorted tetrahedron.

Introduction. The compound was prepared by heating cubic As_4O_6 (Arsenolith, p.A. Merck) in an autoclave for 14 d at 533–633 K and estimated pressures of 5–50 MPa oxygen. The resulting colourless crystals were sealed in glass capillaries for crystallographic examination. Since the crystals are extremely hygroscopic, water was rigorously excluded at all stages. Chemical analysis of the product gave the composition $AsO_{1.994}$, with a hydrogen content of <0.05%.

1879 reflexions forming a quadrant in the range 7° < 2θ < 72° were collected on a Stoe four-circle diffractometer with a crystal 0.3 × 0.3 × 0.2 mm and Mo $K\alpha$ radiation. Cell dimensions were obtained by least squares from accurate centring of 24 strong reflexions. Systematic absences $0kl$, $k + l$ odd; $0k0$, k odd; and $hk0$, h odd indicated space group *Pnma* or (with a change of axes) *Pna2_1*. After Lp and empirical absorption corrections, averaging equivalent reflexions gave 845 unique reflexions, 711 with $F > 4\sigma(F)$.

The structure was solved in *Pnma* by direct methods (to locate As) and difference syntheses, and refined

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U^*
As(1)	738 (1)	2500	1731 (1)	22 (1)
As(2)	2647 (1)	2500	−1965 (1)	23 (1)
O(1)	900 (5)	−50 (6)	3196 (6)	26 (1)
O(2)	2465 (7)	2500	527 (8)	26 (1)
O(3)	−884 (8)	2500	620 (8)	33 (2)

* Equivalent isotropic U calculated from anisotropic U.

Table 2. *Bond lengths* (Å) *and angles* (°)

As(1)–O(1)	1.713 (5)	As(1)–O(2)	1.724 (7)
As(1)–O(3)	1.611 (8)	As(2)–O(2)	1.818 (7)
As(2)–O(1^i)	1.794 (5)		

O(1)–As(1)–O(2)	104.2 (3)	O(1)–As(1)–O(3)	112.4 (3)
O(2)–As(1)–O(3)	119.4 (4)	O(1)–As(1)–O(1^{ii})	102.4 (4)
O(3)–As(1)–O(1^{ii})	112.4 (3)	O(2)–As(2)–O(1^i)	89.7 (3)
O(1^i)–As(2)–O(1^{iii})	91.3 (3)	As(1)–O(1)–As(2^{iv})	124.9 (3)
As(1)–O(2)–As(2)	125.5 (4)		

Symmetry operators

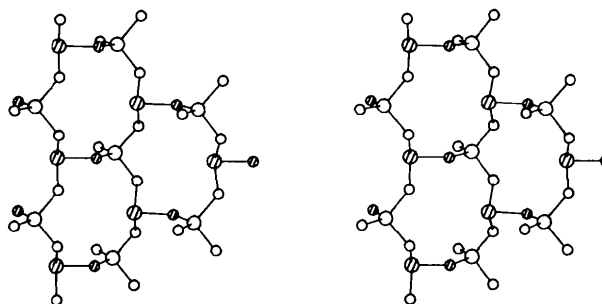| (i)	$0.5 - x$,	$0.5 + y$,	$-0.5 + z$	(iii)	$0.5 - x$,	$-y$,	$-0.5 + z$
(ii)	x,	$0.5 - y$,	z	(iv)	$0.5 - x$,	$-y$,	$0.5 + z$

Fig. 1. Stereoview of part of an infinite layer in AsO_2. Large open circles, As(1); large hatched circles, As(2); small open circles, O(1) (bridging) or O(3) (terminal); small hatched circles, O(2).

with all atoms anisotropic to a final $R' = \sum w^{1/2} \Delta/ \sum w^{1/2}|F_o| = 0.055$ and $R = 0.057$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.001F^2$. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* A diagram of the structure is given in Fig. 1.

Discussion. As(1), As(2), O(2) and O(3) lie on special positions $x, 0.25, z$ with mirror symmetry. As(1) is coordinated by four O atoms to form a distorted tetra-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34879 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hedron: O(1) (twice) and O(2) bridge to As(2) atoms but O(3) is terminal. The As(1)–O(3) bond is considerably shorter than the others and may be considered to possess some double-bond character; the large O–As(1)–O angles involving O(3) support this view. As(2) is coordinated by three O atoms at right angles, with As–O bonds substantially longer than for As(1). It is therefore reasonable to regard As(1) and As(2) as in oxidation states $+5$ and $+3$ respectively.

The extended structure forms layers parallel to the yz plane. There are two such layers (centrosymmetrically related) per cell. Short (<3.4 Å) As–O contacts between layers are As(2)$\cdots$O(3) 2.94, 3.18; As(1)$\cdots$O(3) 3.13 Å (O atoms at $0.5 + x$, $0.5 - y$, $-0.5 - z$; $-x,-y,-z$; $-x$, $1 - y$, $-z$ respectively). Within layers the only such contact is As(2)$\cdots$O(2) 3.19 Å [O(2) at $0.5 - x$, $0.5 + y$, $-0.5 + z$; all e.s.d.'s for non-bonded distances are 0.01 Å].

The system As_2O_{4-x} has been investigated by d'Yvoire, Prades & Guérin (1969). They obtained from powder photography the cell constants 8.566, 7.271, 5.236 Å (e.s.d.'s 0.002 Å) for $x = 0$; a increased with x, e.g. $x = 0.134$ when $a = 8.618$ Å, while b and c remained constant. Since the a axis of our material is 8.597 Å, this would imply that its x is not zero ($x = 0.08$ if x and a are linearly related). There is, however, no crystallographic evidence either for a small fraction of vacant O atom sites or for short O$\cdots$O contacts caused by hydrogen bonding to OH groups derived from water.

Few crystal structure determinations have been performed in the arsenic/oxygen system, none of them of high accuracy. In lithium and sodium polyarsenates, the $(AsO_3)_n^{n-}$ ions (which contain tetrahedrally coor-

dinated As^V) show mean As–O(bridging) and As–O(terminal) lengths of 1.76 and 1.64 Å respectively, but the terminal O atoms carry a formal $0.5-$ charge and their As–O bond orders are formally 1.5 (Hilmer & Dornberger-Schiff, 1956; Liebau, 1956). In claudetite II [a monoclinic form of arsenic(III) oxide], the pyramidal AsO_3 groups have As–O distances ranging from 1.77 to 1.82 Å (average 1.79 Å), in good agreement with the As^{III}–O distances in AsO_2; the angles at As are, however, somewhat larger (average $95.5°$; Pertlik, 1975).

The antimony oxide of empirical formula SbO_2 exists in two forms. Both may be regarded as containing Sb^{III} and Sb^V; they consist of distorted Sb^VO_6 octahedra and Sb^{III} coordinated by four O atoms in a markedly one-sided manner (Rogers & Skapski, 1964; Skapski & Rogers, 1965). The structures of AsO_2 and SbO_2 are thus not closely related.

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Diammonium Nickel Diselenate Hexahydrate*

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Abstract. $(NH_4)_2Ni(SeO_4)_2.6H_2O$, monoclinic $P2_1/a$, $a = 9.334$ (3), $b = 12.628$ (4), $c = 6.370$ (2) Å, $\beta = 106.31$ (3)°, $V = 720.61$ Å^3, $D_o = 2.20$ (3), $D_c = 2.253$ Mg m^{-3}, $Z = 2$. The structure, which is isomorphous with the corresponding sulfate, has been determined by the refinement of diffractometer data to a final R value of 0.028 for 813 observed reflexions.

The metal–water distances are 2.068 (2), 2.055 (2) and 2.043 (2) Å.

Introduction. In the continuing study of the variation of hexaaqua ions of the first transition group of elements (Montgomery, 1979) the structure of the title compound has been determined.

The compound $(NH_4)_2Ni(SeO_4)_2.6H_2O$ was recrystallized by slow evaporation of an aqueous solution

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