different $Fe(O_h)O_4$ chains building formal $CuFe_2(O_h)_4O_8$ groups (see Fig. 1). The connection causes a shortening of the O—O edges defining the common faces: the shared O—O edges vary from 2·577 (5) to 2·638 (5) Å, the unshared ones vary from 3·010 (5) to 3·587 (5) Å in the CuO_6 polyhedron and from 2·702 (5) to 3·095 (5) Å in the $Fe(1)O_6$ and $Fe(2)O_6$ octahedra. The angles between two O atoms defining the common faces [O—Cu—O from 70·9 (1) to 82·3 (2)°, O—Fe—O from 76·5 (1) to 81·5 (2)°] are smaller than the other angles [O—Cu—O from 97·3 (2) to 107·9 (1)°, O—Fe—O from 86·9 (2) to 99·1 (2)°]. Considering the connection of the [6]-coordinated cations in $CuFe_2(OH)_2(AsO_4)_2$ the crystal structure consists of rugged layers parallel to (010). They are connected by the hydrogen bonds and arsenate tetrahedra (see Fig. 2).

The title compound contains pairs of atoms which have topologically the same environment: Fe(1)—Fe(2), As(1)—As(2), O(11)—O(21), O(12)—O(22), O(13)—O(23), O(14)—O(24), $O_h(1)$—$O_h(2)$, and H(1)—H(2). Neglecting the Cu and H atoms a theoretical cell with $a' = a$, $b' = b/2$, and $c' = c/2$, and $Z' = Z/4$ results.

The mineral hentschelite, $CuFe_2(OH)_2(PO_4)_2$, crystallizes in space group $P2_1/n$ ($a = 6{\cdot}98$, $b = 7{\cdot}79$, $c = 7{\cdot}27$ Å, $\beta = 117{\cdot}68°$; Sieber, Tillmanns & Hofmeister, 1987; Sieber, Tillmanns & Medenbach, 1987). Hentschelite is isostructural with the lazulite group minerals (Lindberg & Christ, 1959). Both the polymorphs show some structural relationships: they contain formal groups $CuFe_2(O_h)_4O_8$ formed by the face-shared polyhedra FeO_6—CuO_6—FeO_6; the $Fe(O_h)_2O_4$ octahedra are linked through corner-shared O_h atoms to form rows, the coordination polyhedra $Cu(O_h)_2O_4$ and $Fe(O_h)_2O_4$ form complicated sheets which are linked by XO_4 tetrahedra (X = P and As, respectively) and by hydrogen bonds to form a three-dimensional framework. The distinction between the crystal structures of hentschelite and of the title compound depends on the different periodicity found for the rugged sheets. The different wave pattern gives rise to the different symmetries.

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Structure of Lead(II) Arsenate(III)

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Abstract. $PbAs_2O_4$, $M_r = 421{\cdot}04$, monoclinic, $P2_1/c$, $a = 7{\cdot}037$ (3), $b = 11{\cdot}801$ (6), $c = 6{\cdot}137$ (3) Å, $\beta = 112{\cdot}99$ (3)°, $V = 469{\cdot}2$ (2) Å^3, $Z = 4$, $D_x = 5{\cdot}96$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 48{\cdot}2$ mm^{-1}, $F(000) = 720$, room temperature, $R(F) = 0{\cdot}047$ for 1654 independent reflections with $F_o > 4\sigma(F_o)$ and 65 variables. The crystal structure of $PbAs_2O_4$ consists of AsO_3 pyramids which are corner connected to form As_4O_8 rings with symmetry $\bar{1}$, bonding As—O distances from 1·790 (10) to 1·833 (9) Å, and branched As—O bond distances 1·726 (8) and 1·735 (8) Å. The As_4O_8 rings are connected by the Pb atoms to form a framework. The Pb atom has four ligands: 2·250 (8) ≤ Pb—O ≤ 2·500 (8) Å; further Pb—O distances

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are ≥ 3·104 (10) Å. Crystals of the title compound were synthesized under hydrothermal conditions at 500 (10) K.

Introduction. The trigonal pyramidal habit of an $As^{III}O_3$ group with the As atom at the apex is a consequence of the stereometric activity of the lone-pair electrons. In many cases these pyramids are combined to form chains, rings, sheets or even molecules by polymerization. A survey of arsenite minerals is given by Hawthorne (1985), and in addition details of layer arsenites have been compiled by Pertlik (1987). In connection with studies on the stereochemistry of $As^{III}O_3$ groups as well as on the connection of these groups to form condensed units (*cf.* Pertlik, 1978, 1979) the system lead–As_2O_3 was investigated under hydrothermal conditions and different solvents and the crystal structure of the title compound was investigated by X-ray methods.

Experimental. Single crystals suitable for X-ray work were grown under hydrothermal conditions in a steel vessel lined with 'Teflon'. A mixture of 1 g native lead (powder) and 1 g cubic diarsenic trioxide (GR) was inserted; the reaction space (~6 ml) was filled to 80% with acetic acid (glacial GR, min. 96%) saturated at room temperature with ammonium acetate (GR). After 10 d heating to 500 (10) K isometric crystals of the title compound up to 0·1 mm in size were observed. For identification the approximate ratios of the elements Pb and As were determined by X-ray fluorescence analysis; the stoichiometric formula was determined from crystal structure analysis.

Synthetic crystal, 0·10 × 0·10 × 0·10 mm, crystallographic forms {120} and {001}; Stoe four-circle diffractometer AED2, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from 75 reflections, $39° \le 2\theta \le 51°$; $2\theta/\omega$ scan mode, minimum of 50 steps per reflection increased for α_1–α_2 splitting, step width 0·03°, step time 0·5 to 1·5 s per step, eight steps each side for background correction; three standard reflections, interval 2 h, intensity variation 12%; 3667 measured reflections, $6° \le 2\theta \le 70°$ (h: −11→11, k: −19→19, l: 0→9), 2062 reflections in unique data set ($R_{\rm int}$ = 0·071), 1654 reflections with $F_o > 4\sigma(F_o)$ used for refinement; one ψ scan for absorption correction (transmission factors 0·028 to 0·079), corrections for Lorentz and polarization effects. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography,* 1974). Calculations performed with program system *STRUCSY* (Stoe & Cie, 1984). The atomic coordinates of the Pb atom were found from interpretation of a Patterson map, the coordinates of the other atoms by Fourier methods. Several cycles of full-matrix least-squares refinement on F with anisotropic thermal parameters gave R = 0·047, wR = 0·047, $w = [\sigma(F_o)]^{-2}$, 65 variables, goodness of fit 2·79, max. $\Delta/\sigma < 10^{-3}$, max. and min. heights in final difference Fourier map 4·2 and −7·7 e Å^{-3}, isotropic secondary-extinction coefficient g (Zachariasen, 1967) 7·6 (3) × 10^{-6}. Final atomic coordinates and equivalent isotropic temperature parameters are given in Table 1.*

Table 1. *Atomic fractional coordinates* (*with e.s.d.'s in parentheses*) *and equivalent isotropic temperature parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Pb	0·01608 (6)	0·15152 (4)	0·09637 (7)	0·017
As(1)	0·6225 (1)	0·3559 (1)	0·0044 (2)	0·015
As(2)	0·2938 (2)	0·4173 (1)	0·2160 (2)	0·017
O(1)	0·8153 (11)	0·2714 (7)	0·1970 (12)	0·016
O(2)	0·1936 (13)	0·3033 (8)	0·0271 (14)	0·020
O(3)	0·7905 (13)	0·4740 (9)	0·0047 (17)	0·026
O(4)	0·5582 (12)	0·4148 (9)	0·2435 (15)	0·025

Discussion. The Pb atom is coordinated in a one-sided manner to four O atoms, 2·250 (8) ≤ Pb—O ≤ 2·500 Å, ⟨Pb—O⟩ = 2·385 Å. The bond strengths calculated according to Brown & Wu (1976) are 0·59, 0·50, 0·35, and 0·33 v.u. Two additional O-atom ligands with weaker electrostatic interactions (bond strengths 0·10 and 0·09 v.u.) follow at Pb—O distances of 3·104 (10) and 3·199 (8) Å. Further O atoms exceed the shortest Pb—As distance of 3·548 (1) Å. Each PbO_4 coordination polyhedron shares two common O—O edges [2·79 (1) Å] with two further PbO_4 polyhedra resulting in chains of ${}^1_\infty[PbO_2]$ parallel to [001]. Part of such a chain is given in Fig. 1; it shows the most relevant stereochemical data as interatomic distances and bond angles. A consequence of the connection of the PbO_4 coordination polyhedra by common O—O edges is the short Pb—Pb distance of 3·849 (1) Å. Consideration of the additional O-atom ligands produces no further connection of the Pb coordination polyhedra. The interconnection by the arsenite groups is responsible for a Pb—Pb distance of 3·746 (1) Å between Pb atoms of different chains.

The two crystallographically different As atoms are [3] coordinated to O atoms with ⟨As(1)—O⟩ = 1·795 and ⟨As(2)—O⟩ = 1·776 Å (Table 2). The AsO_3 groups are corner connected to form As_4O_8 rings. This connection is the reason for the difference in the individual As—O bond lengths: the As—O bond lengths to bonding O atoms from 1·790 (10) to 1·833 (9) Å are definitely longer than the two branched As—O bond lengths of 1·726 (8) and 1·735 (8) Å. A comparable

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51182 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As_4O_8 ring with similar distances within the ring was determined in the crystal structure of stenhuggarite, $CaFeSbAs_2O_7$ (Coda, Dal Negro, Sabelli & Tazzoli, 1977): bonding As—O = 1·801 (6) and 1·826 (7) Å, branched As—O = 1·736 (7) Å. The As_4O_8 ring has symmetry $\bar{1}$ in $PbAs_2O_4$; in stenhuggarite a $\bar{4}$ axis cuts the centre of the ring perpendicularly. Attention is drawn to the different orientation of the AsO_3 groups within one ring: in $PbAs_2O_4$ the apices of two neighbouring pyramids point in the same direction, in stenhuggarite the apices of each of the two opposite pyramids point in the same direction. The polymerization of arsenite groups is common in crystal structures (Pertlik, 1978), but ring formation is rare; only in the compound $Cu_2As_3O_6CH_3COO$, known as the pigment 'Schweinfurter Grün' (Pertlik, 1977), have As_3O_6 rings been determined up to now.

The pairs of oxygen atoms O(1)—O(2) and O(3)—O(4) have topologically the same environment. The atoms O(1) and O(2) are approximately [3] coordinated by two Pb atoms and one As atom. The atoms O(3) and O(4) are coordinated to two As atoms and in addition to one distant Pb atom. The type structure of $PbAs_2O_4$ is given in Fig. 2 in an orthogonal projection on (001).

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

As(1)—O(1)	1·726 (8)	O(1)—O(3)	2·64 (1)
As(1)—O(3)	1·827 (9)	O(1)—O(4)	2·57 (1)
As(1)—O(4)	1·833 (9)	O(3)—O(4)	2·68 (1)
As(2)—O(2)	1·735 (8)	O(2)—O(3)	2·64 (1)
As(2)—O(3)	1·790 (10)	O(2)—O(4)	2·72 (1)
As(2)—O(4)	1·802 (8)	O(3)—O(4)	2·67 (1)
Pb—O(1)—Pb	109·0 (3)	O(1)—As(1)—O(3)	96·0 (4)
Pb—O(1)—As(1)	117·3 (3), 125·8 (3)	O(1)—As(1)—O(4)	92·6 (4)
Pb—O(2)—Pb	106·0 (4)	O(3)—As(1)—O(4)	94·1 (4)
Pb—O(2)—As(2)	116·5 (3), 125·8 (3)	O(2)—As(2)—O(3)	97·0 (4)
As(1)—O(3)—As(2)	121·5 (4)	O(2)—As(2)—O(4)	100·7 (4)
As(1)—O(4)—As(2)	120·0 (3)	O(3)—As(2)—O(4)	96·1 (4)

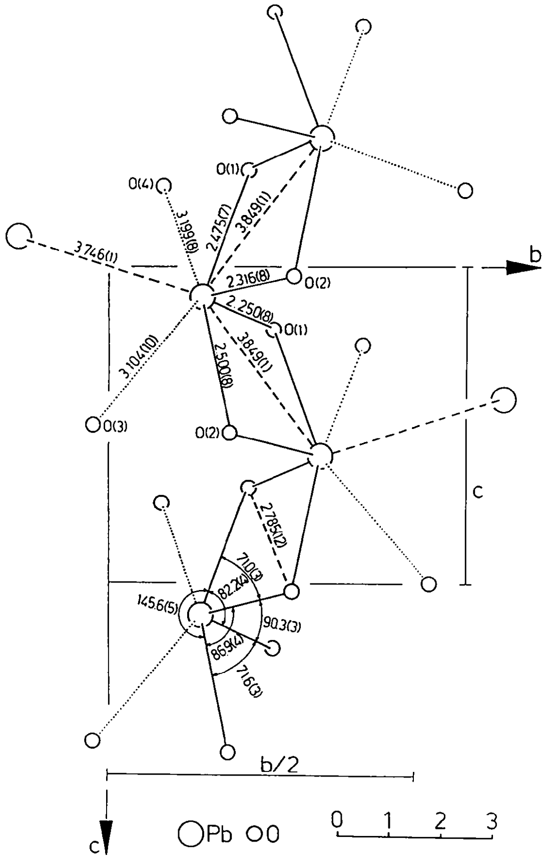

Fig. 1. Stereochemistry and connection of the Pb atoms in $PbAs_2O_4$ in a projection onto (100). Interatomic distances (Å) and bond angles (°) are indicated.

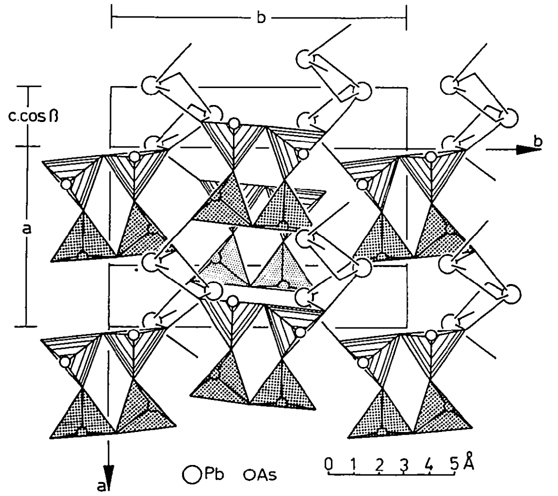

Fig. 2. The crystal structure of $PbAs_2O_4$ in a projection parallel to (001). The basal planes of the arsenite groups are dotted, the other faces are hatched.

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