

The *catena*-arsenite chain anion, [AsO₂]_n³⁻: (H₃NCH₂CH₂NH₃)_{0.5}[AsO₂] and NaAsO₂ (revisited)

Clare Lee and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen
AB24 3UE, Scotland

Correspondence e-mail: w.harrison@abdn.ac.uk

Received 17 March 2004

Accepted 29 March 2004

Online 30 April 2004

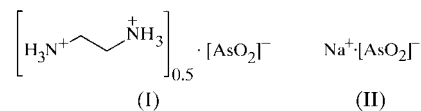
The title compounds contain the *catena*-arsenite [AsO₂]_n³⁻ unit, in which the As^{III} atom is pyramidally coordinated to one terminal and two bridging O atoms, resulting in an infinite anionic chain. Ethylenediammonium *catena*-arsenite, (C₂H₁₀N₂)_{0.5}[AsO₂], is the first example of this anion in the company of an organic cation. The ethylenediammonium species interact with the [AsO₂]⁻ chains by way of N—H...O hydrogen bonds. The structure of sodium *catena*-arsenite, Na[AsO₂] [Menary (1958). *Acta Cryst.* **11**, 742–743], has been redetermined to yield more reliable geometrical parameters. The As—O distances are normal and the Na⁺ cation is seven-coordinate [Na—O = 2.285 (4)–3.063 (4) Å] in a distorted capped trigonal prismatic geometry.

Comment

The [AsO₃]³⁻ arsenite group shows a distinctive pyramidal geometry, due to the stereochemically active lone pair of electrons on the As^{III} species, with an electron configuration of [core]4s²4p¹. This geometry is quite distinct from the tetrahedral coordination invariably displayed by the [As^VO₄]³⁻ arsenate group. A number of minerals and synthetic compounds containing isolated pyramidal [AsO₃]³⁻ ions are known, examples being reinerite, Zn₃(AsO₃)₂ (Ghose *et al.*, 1977), and the unusual arsenite–chloride finnemanite, Pb₅(AsO₃)₃Cl (Effenberger & Pertlik, 1979).

Arsenite groups may polymerize (or condense) *via* vertices into extended units, the simplest example of this being the [As₂O₅]⁴⁻ diarsenite group, which is found in paulmooreite, Pb₂As₂O₅ (Araki *et al.*, 1980). In ludlockite, PbFe₄(As₅O₁₁)₂ (Cooper & Hawthorne, 1996), as many as five AsO₃ units are fused together into [As₅O₁₁]⁷⁻ units. The polymerization of arsenite groups results in the *catena*-arsenite chain anion, [AsO₂]⁻ (or [AsO₂]_n³⁻), which was first definitively characterized by Zemann (1951) in the mineral trippkeite, CuAs₂O₄. A few years later, the same anion was found in the synthetic compound NaAsO₂ by Menary (1958). The tripp-

keite structure was redetermined to improved precision by Pertlik (1975), who also showed that the two synthetic lead *catena*-arsenite chlorides Pb(AsO₂)Cl and Pb₂(AsO₂)₃Cl contain the same chain anion (Pertlik, 1988), as does the mineral leiteite, ZnAs₂O₄ (Ghose *et al.*, 1987).



We describe here the structure of ethylenediammonium *catena*-arsenite, (H₃NCH₂CH₂NH₃)_{0.5}[AsO₂], (I), which is the first example of a *catena*-arsenite chain accompanied by organic cations. We also describe the redetermined structure of NaAsO₂, (II).

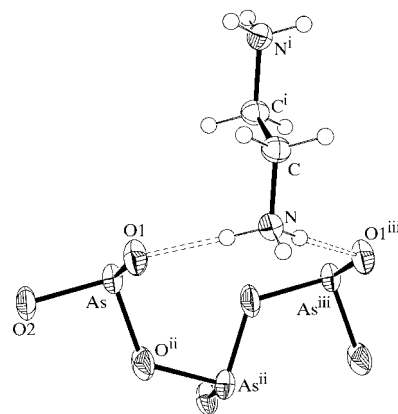


Figure 1

A view of a fragment of (I), drawn with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $\frac{1}{2} - x, y, 1 - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x, y - 1, z$.]

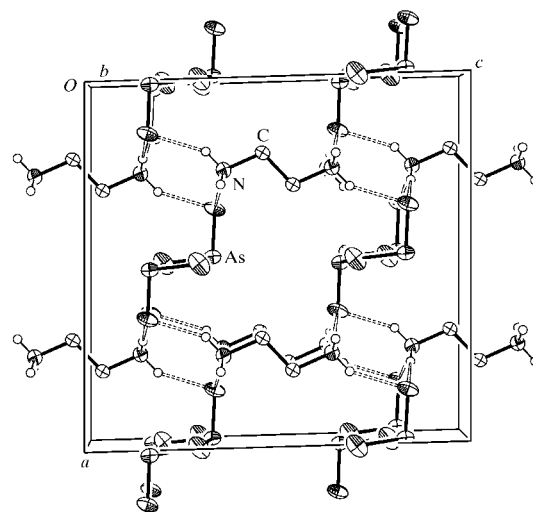


Figure 2

The unit-cell packing in (I), projected on to (010) (normal to the *catena*-arsenite chain direction). Hydrogen bonds are indicated by dashed lines.

Compound (I) (Fig. 1) shows $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)^{2+}$ cations and anionic $[\text{AsO}_2]^-$ chains. The geometrical parameters for the complete ethylenediammonium cation, which is generated by twofold symmetry from the unique atoms, are normal. The *catena*-arsenite chain is built up from three distinct atoms, with atom O1 forming the terminal As—O bond and atom O2 acting as the bridging atom. As expected, the geometry around As is pyramidal, with the As atom displaced from the least-squares plane of the basal O atoms by 0.886 (2) Å. Interestingly, the most prominent peak ($1.11 \text{ e } \text{Å}^{-3}$) in the final difference Fourier map for (I) is 0.74 Å from As, approximately where the lone pair of electrons is presumed to be located, and could thus correspond to a real chemical feature. As found in other well determined *catena*-arsenites (Pertlik, 1975; Ghose *et al.*, 1987), the terminal As—O_T bond in (I) [1.705 (3) Å] is distinctly shorter than the average of the bridging bonds [mean As—O_B = 1.812 (2) Å]. The O_B—As—O_B bond angle is significantly smaller than the O_B—As—O_T bond angles (Table 1).

As well as van der Waals and electrostatic forces, the organic cations and the chain anion in (I) interact by way of N—H...O hydrogen bonds (Table 2). Two of the three H—N moieties make short near-linear hydrogen bonds to arsenite O-atom acceptors, whilst the third N—H group is bifurcated to two arsenite O acceptor atoms (sum of *D*—H...*A* bond angles about atom H1 = 359°). Overall, O_T accepts three hydrogen bonds and O_B accepts one. These interactions help to define a structure (Fig. 2) in which the *catena*-arsenite chains propagate along [010] (generated by the 2₁ screw axis), crosslinked along [100] by O...H—N—H...O bonds. Interchain linking along [001] is *via* the backbone of the organic moiety. The intrachain As...As^{*i*} separation in (I) is 3.1991 (4) Å [symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$].

The structure of (II) (Fig. 3) is more or less the same as that determined by Menary (1958) using film methods, but with improved standard uncertainties. The Na⁺ cation is coordinated to seven O atoms (mean Na—O = 2.623 Å), all of which are parts of neighbouring anionic $[\text{AsO}_2]^-$ chains. The resulting NaO₇ polyhedron approximates to a distorted

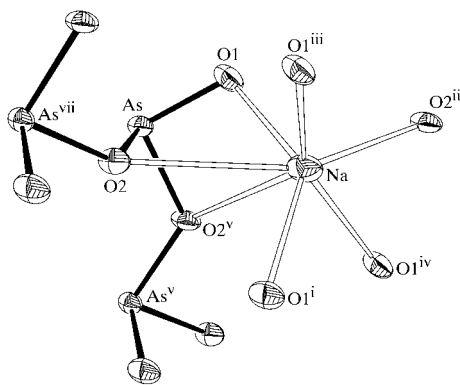


Figure 3

A view of a fragment of (II), drawn with 50% probability displacement ellipsoids. Note that atoms O1, O2 and O2^v represent a face shared between the AsO₃ and NaO₇ polyhedra. [Symmetry codes are as in Table 3; additionally: (vii) $\frac{1}{2} - x, y + \frac{1}{2}, z$.]

capped trigonal prism. The Na bond valence sum (BVS) of 1.00 (Brown, 1996) is exactly in agreement with the expected value. The As geometry is again pyramidal, with the As atom displaced from the least-squares plane of the basal O atoms by 0.912 (3) Å. The As—O distances [As—O_T = 1.684 (4) Å and mean As—O_B = 1.822 (3) Å] are similar to those found for (I). As in (I), the O_B—As—O_B bond angle is significantly smaller than the O_B—As—O_T bond angles (Table 3). By comparison, Menary's (1958) results (As—O_T = 1.600 Å, and As—O_B = 1.810 and 1.947 Å) indicated a much greater degree of distortion about As.

In the unit-cell packing in (II) (Fig. 4), the *catena*-arsenite chains propagate along [010], as generated by *b*-glide symmetry, resulting in an intrachain As...As^{*ii*} separation of 3.2121 (7) Å [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$]. The face- and edge-sharing NaO₇ groups are sandwiched between the $[\text{AsO}_2]^-$ chains and crosslink them in the *a* direction, resulting in neutral (001) slabs of stoichiometry NaAsO₂. The As^{III} lone-pair electrons appear to be directed into the inter-slab region. The shortest interblock As...O and As...As contacts are 3.762 (3) and 3.6844 (7) Å, respectively. This is quite reminiscent of the situation in ludlockite (Cooper & Hawthorne, 1996), in which the $[\text{As}_5\text{O}_{11}]^{7-}$ units face each other.

The geometrical parameters for the $[\text{AsO}_2]^-$ units in (I) and (II) are broadly consistent with the equivalent data for CuAs₂O₄ and ZnAs₂O₄. In particular, the As—O_B bond

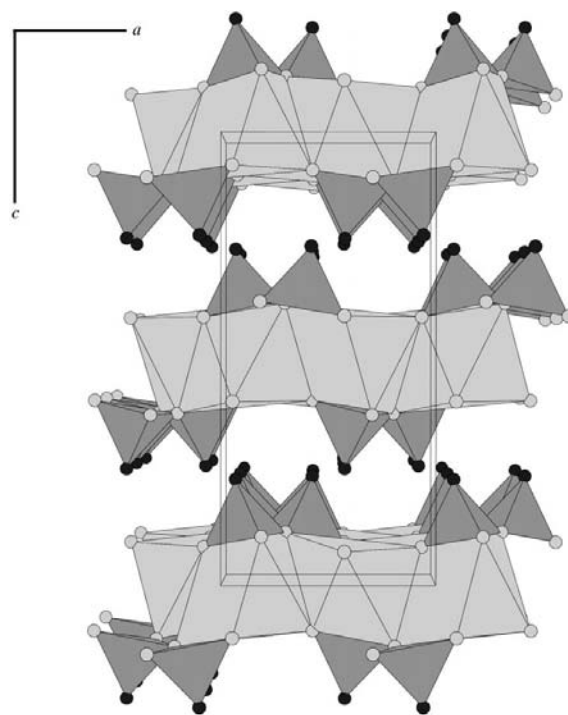


Figure 4

A polyhedral representation of the unit-cell packing in (II), projected on to (010). The NaO₇ polyhedra are shown with light shading and the AsO₃ groups are represented by AsO₃*E* tetrahedra (dark shading), where the dummy atom *E* (very dark shading), placed 1.0 Å from As, represents the lone pair of electrons. The *catena*-arsenite chains propagate towards the viewer.

lengths are clustered in the narrow range of 1.806 (2)–1.829 (3) Å. The As–O_T bond lengths show somewhat greater variability, which might be due to the different bonding situations of the O atoms in question: the O_T atom in (I) [1.705 (3) Å] only accepts hydrogen bonds, whereas the O_T atom in CuAs₂O₄ (1.765 Å) is also bonded to two Cu atoms. However, there are also some significant differences. For example, the O_B–As–O_B bond angle of 100.3° in CuAs₂O₄ is significantly larger than the O_B–As–O_T bond angle (95.9°), which is the reverse of the situation for (I), (II) and ZnAs₂O₄ (Ghose *et al.*, 1987).

Experimental

For (I), a mixture of As₂O₃ (1 g), ethylenediamine (0.5 g) and water (10 ml) was heated to 353 K in a plastic bottle for 48 h. Upon cooling, the resultant solids were filtered off, yielding some plate-shaped crystals of (I) accompanied by substantial amounts of undissolved or recrystallized As₂O₃. We have not yet succeeded in making (I) in purer form. For (II), a commercial sample (Sigma Chemical Co.) of NaAsO₂ was recrystallized from methanol, in which it is sparingly soluble. The resulting crystal quality is poor.

Compound (I)

Crystal data

(C₂H₁₀N₂)_{0.5}[AsO₂]
M_r = 137.98
 Monoclinic, *I*2/a
a = 12.7854 (8) Å
b = 4.6647 (3) Å
c = 13.3343 (9) Å
 β = 91.7380 (10)°
V = 794.89 (9) Å³
Z = 8
D_x = 2.306 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 2219 reflections
 θ = 3.1–32.5°
 μ = 8.37 mm⁻¹
T = 293 (2) K
 Plate, colourless
 0.31 × 0.29 × 0.02 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.131, *T_{max}* = 0.850
 3520 measured reflections

1430 independent reflections
 1181 reflections with *I* > 2σ(*I*)
R_{int} = 0.037
 θ_{max} = 32.5°
h = -16 → 19
k = -7 → 5
l = -19 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.039
wR(*F*²) = 0.115
S = 1.05
 1430 reflections
 48 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0792*P*)² + 0.139*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.11 e Å⁻³
 Δρ_{min} = -1.68 e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0032 (8)

Table 1

Selected geometric parameters (Å, °) for (I).

As–O1	1.705 (3)	As–O2 ⁱ	1.817 (3)
As–O2	1.806 (2)		
O1–As–O2	99.04 (10)	O2–As–O2 ⁱ	93.93 (7)
O1–As–O2 ⁱ	98.57 (13)	As–O2–As ⁱⁱ	123.99 (13)

Symmetry codes: (i) 1 - *x*, *y* - ½, ½ - *z*; (ii) 1 - *x*, ½ + *y*, ½ - *z*.

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N–H1...O1 ⁱ	0.89	2.10	2.905 (4)	150
N–H1...O2 ⁱⁱ	0.89	2.58	3.318 (4)	140
N–H2...O1 ⁱⁱⁱ	0.89	1.83	2.719 (3)	174
N–H3...O1	0.89	1.82	2.701 (3)	172

Symmetry codes: (i) ½ - *x*, ½ - *y*, ½ - *z*; (ii) *x* - ½, 1 - *y*, *z*; (iii) *x*, *y* - 1, *z*.

Compound (II)

Crystal data

Na[AsO₂]
M_r = 129.91
 Orthorhombic, *Pbca*
a = 6.7762 (5) Å
b = 5.0901 (4) Å
c = 14.3098 (11) Å
V = 493.57 (7) Å³
Z = 8
D_x = 3.497 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 1514 reflections
 θ = 2.9–31.8°
 μ = 13.62 mm⁻¹
T = 293 (2) K
 Rod, colourless
 0.23 × 0.08 × 0.08 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.120, *T_{max}* = 0.336
 5152 measured reflections

894 independent reflections
 639 reflections with *I* > 2σ(*I*)
R_{int} = 0.048
 θ_{max} = 32.5°
h = -10 → 10
k = -7 → 6
l = -21 → 18

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.040
wR(*F*²) = 0.109
S = 1.01
 894 reflections
 37 parameters

w = 1/[σ²(*F_o*²) + (0.0661*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 2.97 e Å⁻³
 Δρ_{min} = -1.05 e Å⁻³

Table 3

Selected geometric parameters (Å, °) for (II).

Na–O1 ⁱ	2.285 (4)	Na–O2	2.996 (4)
Na–O1	2.397 (5)	Na–O2 ^v	3.063 (4)
Na–O2 ⁱⁱ	2.413 (4)	As–O1	1.684 (4)
Na–O1 ⁱⁱⁱ	2.420 (4)	As–O2 ^v	1.815 (3)
Na–O1 ^{iv}	2.785 (4)	As–O2	1.829 (3)
O1–As–O2 ^v	95.42 (16)	O2 ^v –As–O2	92.93 (11)
O1–As–O2	99.07 (17)	As ^{vi} –O2–As	123.66 (19)

Symmetry codes: (i) *x* - ½, ½ - *y*, 1 - *z*; (ii) ½ + *x*, ½ - *y*, 1 - *z*; (iii) 1 - *x*, 2 - *y*, 1 - *z*; (iv) 1 - *x*, 1 - *y*, 1 - *z*; (v) ½ - *x*, *y* - ½, *z*; (vi) ½ - *x*, ½ + *y*, *z*.

For (I), the H atoms were placed in calculated positions (C–H distances in the range 0.96–0.98 Å and N–H distances of 0.89 Å) and refined by riding, allowing for free rotation of the rigid NH₃ group about the C–N bond. The constraint *U*_{iso}(H) = 1.2*U*_{eq}(attached atom) was applied in all cases. For (II), the maximum difference peak was 0.82 Å from As.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1044). Services for accessing these data are described at the back of the journal.

References

- Araki, T., Moore, P. B. & Brunton, G. D. (1980). *Am. Mineral.* **65**, 340–345.
- Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.
- Bruker (1999). *SMART* (Version 5.624), *SAINTE* (Version 6.02a) and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cooper, M. A. & Hawthorne, F. C. (1996). *Can. Mineral.* **34**, 79–89.
- Dowty, E. (1999). *ATOMS*. Version 5.0.7 for Windows and Macintosh. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
- Effenberg, H. & Pertlik, F. (1979). *Tschermaks Mineral. Petrogr. Mitt.* **26**, 95–107.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Ghose, S., Boving, P., Lachapelle, W. A. & Wan, C. (1977). *Am. Mineral.* **62**, 1129–1134.
- Ghose, S., Sen Gupta, P. K. & Schlemper, E. O. (1987). *Am. Mineral.* **72**, 629–632.
- Menary, J. W. (1958). *Acta Cryst.* **11**, 742–743.
- Pertlik, F. (1975). *Tschermaks Mineral. Petrogr. Mitt.* **22**, 211–217.
- Pertlik, F. (1988). *Z. Kristallogr.* **184**, 191–201.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Zemann, J. (1951). *Tschermaks Mineral. Petrogr. Mitt.* **2**, 417–423.