

## Tetracaesium octaselenidotetraarsenate(III)

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## Key indicators

Single-crystal X-ray study  
 $T = 292$  K  
Mean  $\sigma(\text{Se}-\text{As}) = 0.002$  Å  
 $R$  factor = 0.037  
 $wR$  factor = 0.099  
Data-to-parameter ratio = 26.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{Cs}_4\text{As}_4\text{Se}_8$ , contains discrete cyclic  $[\text{As}_4\text{Se}_8]^{4-}$  anions consisting of corner-sharing  $\text{AsSe}_3$  pyramids. A twist-chair conformation is observed for the eight-membered  $\text{As}_4\text{Se}_4$  rings, which exhibit a crystallographic inversion centre. Both of the crystallographically independent  $\text{Cs}^+$  cations contain eight Se atoms in their coordination spheres.

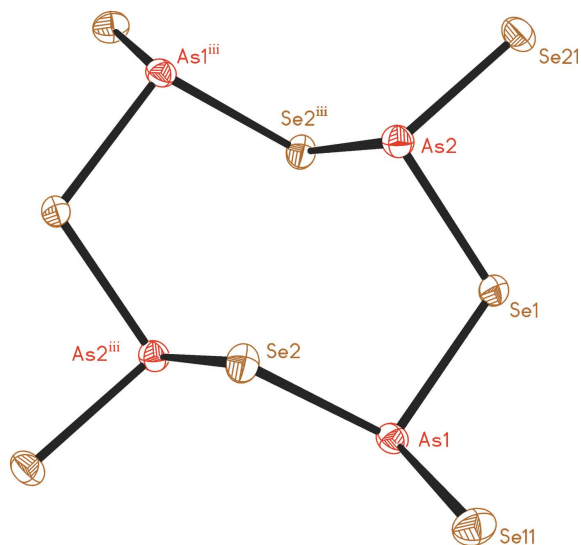
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## Comment

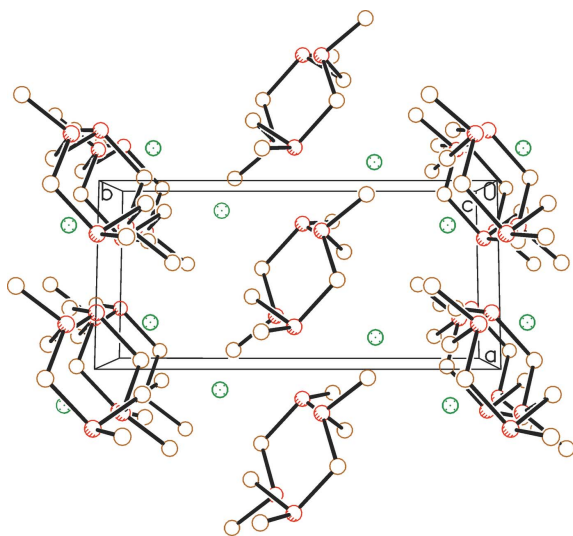
In contrast with the rich structural diversity exhibited by both thioarsenates(III) and thio- and selenidoantimonates(III) (Sheldrick & Wachhold, 1998; Sheldrick, 2000), only a very limited number of structural types are known for the corresponding oligo- and polymeric selenidoarsenates(III). These all contain  $\text{AsSe}_3$  pyramids as building units, which are typically connected by shared corners or Se–Se bonds into discrete cyclic anions or infinite chains. The *trans*- $[\text{As}_2\text{Se}_4]^{2-}$  anions of  $\text{Ba}_2\text{As}_2\text{Se}_5$  (Cordier *et al.*, 1985) provide the only reported example of edge-sharing. Although cyclic  $[\text{As}_3\text{Se}_6]^{3-}$  anions comprising three corner-sharing  $\text{AsSe}_3$  pyramids have been structurally characterized in both  $[\text{Sr}(\text{en})_4]_2[\text{As}_3\text{Se}_6]\text{Cl}$  (en is ethylenediamine; Sheldrick & Kaub, 1985*a*) and  $[\text{Mn}(\text{dien})_2]_3[\text{As}_3\text{Se}_6]_2$  (dien is diethylenetriamine; Fu, Guo, Liu *et al.*, 2005), many more examples containing  $[\text{As}_2\text{Se}_6]^{2-}$  have been isolated in the presence of large counter-cations. Recent structural studies of this chair-shaped dimeric anion with its two Se–Se-linked  $\text{AsSe}_3$  pyramids have been reported for  $[\text{Cs}(18\text{-crown-6})]_2[\text{As}_2\text{Se}_6]$  (18-crown-6 is 1,4,7,10,13,16-hexaoxocyclododecane; van Almsick & Sheldrick, 2005) and  $[\text{M}(\text{en})_3][\text{As}_2\text{Se}_6]$  ( $M = \text{Mn}$  or  $\text{Fe}$ ; Fu, Guo, Liu *et al.*, 2005). The known polymeric selenidoarsenates(III) are restricted to the phases  $A\text{AsSe}_2$  [ $A = \text{Na}$  (Eisenmann & Schäfer, 1979) and  $A = \text{K}-\text{Cs}$  (Sheldrick & Häusler, 1988)] and  $A\text{AsSe}_3 \cdot x\text{H}_2\text{O}$  ( $A = \text{K}$  and  $x = 1$ , or  $A = \text{Rb}$  or  $\text{Cs}$  and  $x = 0.5$ ; Sheldrick & Kaub, 1986). Whereas the  $[\text{AsSe}_2]^-$  chains of the former metaselenidoarsenates(III) contain corner-bridged  $\text{AsSe}_3$  pyramids, these building units are connected by Se–Se bonds in the  $[\text{AsSe}_3]^-$  chains of  $A\text{AsSe}_3 \cdot x\text{H}_2\text{O}$ .

The phases  $A\text{AsSe}_3 \cdot x\text{H}_2\text{O}$  were prepared from  $\text{A}_2\text{CO}_3$  and  $\text{As}_2\text{Se}_3$  under mild hydrothermal conditions (408 K). We have now observed that the title octaselenidotetraarsenate(III),  $\text{Cs}_4\text{As}_4\text{Se}_8$ , (I), can be isolated in low yield on heating  $\text{CsAsSe}_3 \cdot 0.5\text{H}_2\text{O}$  to 463 K in methanol.

Compound (I) contains the novel crystallographically centrosymmetric  $\text{As}_4\text{Se}_8^{4-}$  anion with its eight-membered  $\text{As}_4\text{Se}_4$  ring (Fig. 1). As observed for the analogous  $\text{Sb}_4\text{S}_8^{4-}$  anion of  $[\text{Ni}(\text{dien})]_2[\text{Sb}_4\text{S}_8]$  (Bensch *et al.*, 2001), the octaselenidotetraarsenate(III) anion exhibits a twist-chair conformation. In accordance with other chalcogenidoarsen-



**Figure 1**  
The cyclic  $[\text{As}_4\text{Se}_8]^{4-}$  anion of (I), showing the atom-labelling scheme. Displacement parameters are drawn at the 50% probability level. [Symmetry code: (iii)  $1 - x, 1 - y, 1 - z$ .]



**Figure 2**  
A projection of the structure of (I) perpendicular to  $[001]$ . Cs atoms are indicated by green dotted circles, Se atoms by open brown circles and As atoms by red semi-hatched circles

ates(III) (Sheldrick & Wachhold, 1998), the more polar terminal As—Se distances [2.3092 (14) and 2.3223 (13) Å] are significantly shorter than the bridging As—Se bond lengths [2.4306 (13)–2.4676 (13) Å] within the eight-membered ring. Although the smaller  $[\text{As}_3\text{Se}_6]^{3-}$  anion has been structurally characterized in two salts (Sheldrick & Kaub, 1985*b*; Fu, Guo, Cai *et al.*, 2005), the analogous  $[\text{As}_4\text{Se}_8]^{4-}$  anion has yet to be reported.

Fig. 2 depicts a projection of the crystal structure of (I) perpendicular to  $[001]$ . Cs—Se distances in the range 3.6352 (14)–4.1289 (18) Å are observed for the eightfold coordinated counter-cations Cs1 and Cs2.

## Experimental

$\text{CsAsSe}_3 \cdot 0.5\text{H}_2\text{O}$  (300.0 mg, 0.66 mmol) (Sheldrick & Kaub, 1986) was heated to 463 K in methanol (0.8 ml) in a sealed glass tube. After 30 h, the contents were allowed to cool to room temperature at  $2.1 \text{ K h}^{-1}$  to afford red crystals of (I) in 10% yield, together with black  $\text{Cs}_2\text{As}_4\text{Se}_6$  (van Almsick & Sheldrick, 2006) in 32% yield.

### Crystal data

$\text{Cs}_4\text{As}_4\text{Se}_8$   
 $M_r = 1463.00$   
Monoclinic,  $P2_1/n$   
 $a = 7.1572$  (13) Å  
 $b = 14.862$  (3) Å  
 $c = 10.515$  (4) Å  
 $\beta = 103.51$  (2)°  
 $V = 1087.5$  (5) Å<sup>3</sup>  
 $Z = 2$

$D_x = 4.468 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 24 reflections  
 $\theta = 5.1$ – $17.3^\circ$   
 $\mu = 26.06 \text{ mm}^{-1}$   
 $T = 292$  (2) K  
Prism, red  
 $0.12 \times 0.11 \times 0.09 \text{ mm}$

### Data collection

Siemens P4 four-circle diffractometer  
 $\omega$  scans  
Absorption correction:  $\psi$  scan (XPREP in SHELXTL; Sheldrick, 1995)  
 $T_{\text{min}} = 0.054$ ,  $T_{\text{max}} = 0.092$   
2600 measured reflections  
1916 independent reflections

1594 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = -1 \rightarrow 8$   
 $k = -1 \rightarrow 17$   
 $l = -12 \rightarrow 12$   
3 standard reflections every 97 reflections  
intensity decay: 0.1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.099$   
 $S = 1.02$   
1916 reflections  
73 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.28 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.23 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cs1—Se1 <sup>i</sup>	3.6877 (13)	Cs2—Se21 <sup>ix</sup>	3.8412 (14)
Cs1—Se11 <sup>ii</sup>	3.6966 (13)	Cs2—Se1	3.8778 (14)
Cs1—Se2 <sup>iii</sup>	3.7185 (13)	Cs2—Se11 <sup>vii</sup>	3.9099 (16)
Cs1—Se1	3.7192 (16)	Cs2—Se2	4.1289 (18)
Cs1—Se21 <sup>i</sup>	3.7518 (14)	Se1—As2	2.4306 (13)
Cs1—Se21 <sup>iv</sup>	3.8114 (16)	Se1—As1	2.4676 (13)
Cs1—Se2 <sup>v</sup>	3.8516 (13)	Se21—As2	2.3223 (13)
Cs1—Se11 <sup>v</sup>	3.8949 (16)	Se2—As1	2.4372 (13)
Cs2—Se11 <sup>vi</sup>	3.6352 (14)	Se2—As2 <sup>iii</sup>	2.4403 (15)
Cs2—Se11 <sup>vii</sup>	3.6801 (14)	Se11—As1	2.3092 (14)
Cs2—Se21 <sup>viii</sup>	3.7009 (16)	As2—Se2 <sup>iii</sup>	2.4403 (15)
Cs2—Se11	3.7377 (14)		
As2—Se1—As1	108.33 (5)	Se2—As1—Se1	101.59 (5)
As1—Se2—As2 <sup>iii</sup>	94.98 (5)	Se21—As2—Se1	96.01 (5)
Se11—As1—Se2	98.49 (5)	Se21—As2—Se2 <sup>iii</sup>	101.09 (5)
Se11—As1—Se1	104.95 (5)	Se1—As2—Se2 <sup>iii</sup>	99.18 (5)
As2 <sup>iii</sup> —Se2—As1—Se11	−155.96 (5)	As2—Se1—As1—Se2	−8.79 (6)
As2 <sup>iii</sup> —Se2—As1—Se1	96.77 (5)	As1—Se1—As2—Se21	178.95 (5)
As2—Se1—As1—Se11	−110.96 (6)	As1—Se1—As2—Se2 <sup>iii</sup>	−78.76 (6)

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x + 1, y, z$ ; (v)  $-x + 2, -y + 1, -z + 1$ ; (vi)  $x - 1, y, z$ ; (vii)  $-x + 1, -y + 1, -z$ ; (viii)  $-x, -y + 1, -z$ ; (ix)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

The highest peak in the final difference Fourier synthesis is situated 1.84 Å from atom Se11 and the deepest hole 1.76 Å from atom Cs1.

Data collection: *R3m/V Software* (Siemens, 1989); cell refinement: *R3m/V Software*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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