Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Caesium dimethyldiselenidoarsenate(V)

Tobias Van Almsick and William S. Sheldrick*

Lehrstuhl für Analytische Chemie,
Ruhr-Universität Bochum, Universitätsstrasse
150, 44780 Bochum, Germany

Correspondence e-mail:
william.sheldrick@rub.de

Received 4 November 2005
Accepted 15 November 2005
Online 23 November 2005

Key indicators

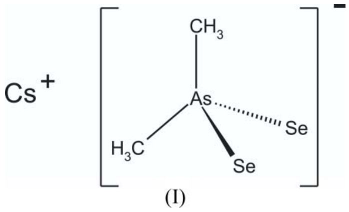
Single-crystal X-ray study
T = 292 K
Mean σ(As–C) = 0.018 Å
R factor = 0.047
wR factor = 0.125
Data-to-parameter ratio = 25.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $Cs[As(CH_3)_2Se_2]$, contains discrete tetrahedral dimethyldiselenidoarsenate(V) anions and Cs cations, with As and Cs located on a crystallographic twofold rotation axis. A distorted octahedral coordination is observed for the caesium counter-cation, with Cs···Se distances in the range 3.706 (2)–3.762 (2) Å.

Comment

The isolated $AsSe_4^{3-}$ anion has been structurally characterized in $[Li(NH_3)_4]_3AsSe_4$ (Korber & Grothe, 2001), $Na_3AsSe_4\cdot 9H_2O$ (Krebs *et al.*, 1990), Rb_3AsSe_4 and Cs_3AsSe_4 (Wachhold & Sheldrick, 1996), $Rb_3AsSe_4\cdot Se_6$ and $Cs_3AsSe_4\cdot 2Cs_2As_2Se_4\cdot 6Te_4Se_2$ (Wachhold & Sheldrick, 1997), as well as in $Ba_2AsSe_4(OH)\cdot 2H_2O$ (Kaub, 1986). In contrast, examples of substituted selenidoarsenate(V) anions are limited to $[AsO_3Se]^{3-}$, $[As(CH_2CN)Se_3]^{2-}$ and $[AsPh_2Se_2]^{-}$, in respectively $Na_3(AsO_3Se)\cdot 12H_2O$ (Krebs *et al.*, 1990), $[K(2.2.2\text{-crypt})]_2[As(CH_2CN)Se_3]$ (2.2.2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Smith *et al.*, 1998) and $(pipH_2)(AsPh_2Se_2)$ (pipH = piperidine; Kanda *et al.*, 1998). Methanolothermal conditions (Sheldrick & Wachhold, 1997; Sheldrick & Wachhold, 1998) were employed for the preparation of the alkali metal tetraselenidoarsenates(V) Rb_3AsSe_4 and Cs_3AsSe_4 from As_2Se_3 and Se in the presence of M_2CO_3 (M = Rb, Cs) at 453 K. The unique $[As(CH_2CN)Se_3]^{2-}$ anion of $[K(2.2.2\text{-crypt})]_2[As(CH_2CN)Se_3]$ was obtained by reaction of K, As, Se and (2.2.2-crypt) in NH_3 at 195 K followed by acetonitrile extraction of the solid products and subsequent crystallization. We therefore postulated that it might be possible to isolate analogous methylselenidoarsenates(V) such as $[As(CH_3)Se_3]^{2-}$ or $[As(CH_3)_2Se_2]^{-}$ from methanolic selenidoarsenate solutions under oxidizing crystallization conditions.



(I)

To this end, $CsAsSe_3\cdot 0.5H_2O$ (Sheldrick & Kaub, 1986) was dissolved in methanol at 463 K and, following cooling to 293 K, the mother liquor was left to crystallize in air. For the given As:Se ratio of 1:3, the formation of a substituted selenidoarsenate(V) was to be expected.

The $[As(CH_3)_2Se_2]^{-}$ anions of the resulting title compound $Cs[As(CH_3)_2Se_2]$, (I), display crystallographic twofold rota-

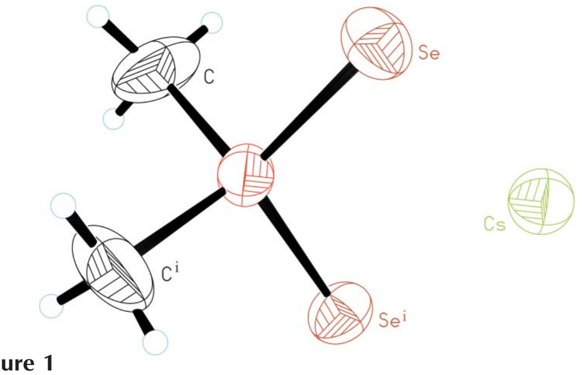


Figure 1
The $[As(CH_3)_2Se_2]^-$ anion and Cs cation of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1$, y, $-z + \frac{1}{2}$.]

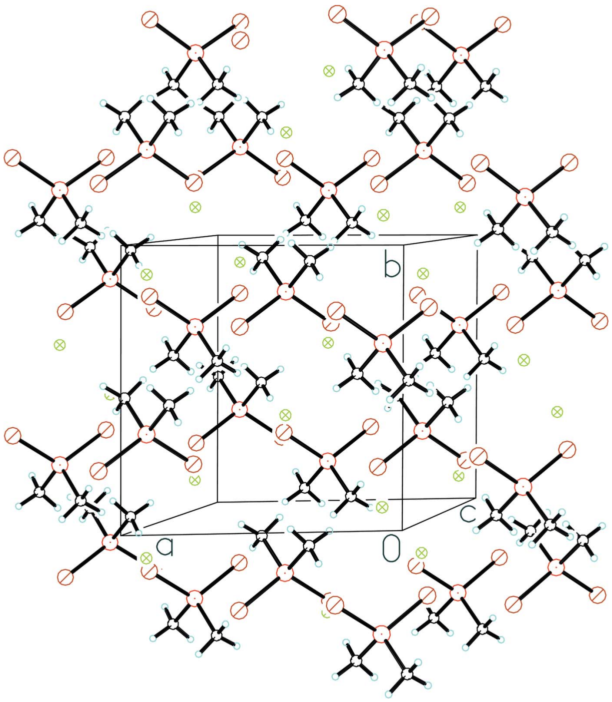


Figure 2
Projection of the structure of (I) perpendicular to [001]. Atom colour codes: Cs green cross-hatched circles, C black shaded circles, Se orange hatched circles, As red dotted circles, H blue open circles.

tion symmetry with Cs and As located on a twofold rotation axis. The caesium counter-cations are coordinated in a distorted octahedral fashion through six symmetry-related Se atoms (Table 1). A significant shortening is observed for the As—Se bond length [2.262 (2) Å] of (I) in comparison with the tetraselenidoarsenate(V) anions of Rb_3AsSe_4 and Cs_3AsSe_4, for which distances in the range 2.306 (3)–2.336 (3) Å were reported (Wachhold & Sheldrick, 1996). This marked bond strengthening is in accordance with the increase in the formal bond order from 1.25 in $AsSe_4^{3-}$ to 1.5 in $[As(CH_3)_2Se_2]^-$. As a result of the partial double-bond character of the participating As—Se bonds, the Se—As—Se angle [117.5 (1)°] is much wider than the C—As—C angle of 106.4 (1)°.

Experimental

$CsAsSe_3 \cdot 0.5H_2O$ (300 mg, 136.1 mmol) (Sheldrick & Kaub, 1986) was heated to 463 K in methanol (0.8 ml) in a sealed glass tube. After cooling to 293 K, the mother liquor was separated from the solid contents and allowed to evaporate slowly in air to afford colourless crystals of (I) in 28% yield.

Crystal data

$Cs^+ \cdot C_2H_6AsSe_2^-$
$M_r = 395.82$
Monoclinic, $C2/c$
$a = 9.858$ (2) Å
$b = 10.027$ (2) Å
$c = 9.787$ (2) Å
$\beta = 115.92$ (3)°
$V = 870.1$ (3) Å^3
$Z = 4$

$D_x = 3.022$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
$\theta = 6.1$–14.9°
$\mu = 16.30$ mm^{-1}
$T = 292$ (2) K
Block, colourless
0.12 × 0.10 × 0.08 mm

Data collection

Siemens $P4$ four-circle diffractometer
ω scans
Absorption correction: ψ-scan (*XPREP* in *SHELXTL-Plus*; Sheldrick, 1995)
$T_{\min} = 0.153$, $T_{\max} = 0.275$
807 measured reflections
759 independent reflections

574 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.125$
$S = 1.08$
759 reflections
30 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 8.7148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cs—Se^i	3.7063 (17)	Cs—Se^v	3.7617 (17)
Cs—Se^{ii}	3.7063 (17)	As—C^{iii}	1.924 (14)
Cs—Se	3.7509 (18)	As—C	1.924 (14)
Cs—Se^{iii}	3.7509 (18)	As—Se	2.2621 (15)
Cs—Se^{iv}	3.7617 (17)	As—Se^{iii}	2.2621 (15)
C^{iii}—As—C	106.4 (12)	C^{iii}—As—Se^{iii}	108.4 (5)
C^{iii}—As—Se	107.9 (5)	C—As—Se^{iii}	107.9 (5)
C—As—Se	108.4 (5)	Se—As—Se^{iii}	117.45 (10)

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

The methyl H atoms were refined as riding, with C—H = 0.96 Å and $U_{\rm iso}(H) = 1.5 U_{\rm eq}(C)$. The methyl group was allowed to rotate but not to tip. The highest peak in the final difference Fourier synthesis is sited 0.93 Å from As and the deepest hole 0.87 Å from As.

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; 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-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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