

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

Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.018$ Å
 R factor = 0.052
 wR factor = 0.123
Data-to-parameter ratio = 18.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[(1,4,7,10,13,16-hexaoxocyclooctadecane)-caesium(I)] di- μ_2 -diselenido-bis[selenidoarsenate(III)]

The title compound, $[\text{Cs}(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{As}_2\text{Se}_6]$, contains two independent centrosymmetric $[\text{As}_2\text{Se}_6]^{2-}$ counter-anions, in which AsSe_3 pyramids are linked by two Se—Se bonds into a chair-shaped six-membered ring. Four of the Se atoms of the first $[\text{As}_2\text{Se}_6]^{2-}$ anion coordinate the Cs atoms of dimeric $[\{\text{Cs}(18\text{-crown-6})\}_2(\mu\text{-As}_2\text{Se}_6)]$ units that are joined by additional O...Cs interactions into polymeric sheets. In contrast, all six Se atoms of the second $[\text{As}_2\text{Se}_6]^{2-}$ anion coordinate Cs atoms within discrete $[\{\text{Cs}(18\text{-crown-6})\}_2(\mu\text{-As}_2\text{Se}_6)]$ dimers.

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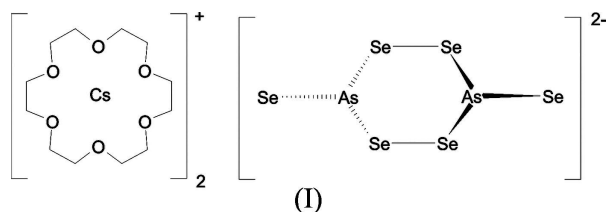
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Comment

In contrast to 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 selenidoarsenates(III) containing two or more arsenic atoms. These all contain AsSe_3 pyramids as building units, which are typically connected by shared corners or Se—Se bonds into either discrete ring-shaped anions or infinite chains. Only one example of edge-sharing of AsSe_3 pyramids has been reported, namely in the *trans*- $[\text{As}_2\text{Se}_4]^{2-}$ anions of $\text{Ba}_2\text{As}_2\text{Se}_5$ (Cordier *et al.*, 1985), a phase which also contains isolated $[\text{AsSe}_3]^{3-}$ anions. Although $[\text{As}_3\text{Se}_6]^{3-}$ anions with a chair-shaped As_3Se_3 ring have been structurally characterized in both $[\text{Sr}(\text{en})_4]_2\text{As}_3\text{Se}_6\text{Cl}$ (en = ethylenediamine; Sheldrick & Kaub, 1985) and $[\text{Mn}(\text{dien})_2]_3[\text{As}_3\text{Se}_6]_2$ (dien = diethylenetriamine; Fu *et al.*, 2005), many more examples containing the bis[$(\mu_2$ -diselenido)selenidoarsenate(III)] anion $[\text{As}_2\text{Se}_6]^{2-}$ have been isolated in the presence of larger counter-cations. This likewise chair-shaped dimeric anion comprises two AsSe_3 pyramids connected by two Se—Se bonds and has been reported in $(\text{NEt}_4)_2[\text{As}_2\text{Se}_6]$ (Smith *et al.*, 1998), $(\text{PPh}_4)_2[\text{As}_2\text{Se}_6]$ (Ansari *et al.*, 1992), $(\text{PPh}_4)_2[\text{As}_2\text{Se}_6] \cdot 2\text{CH}_3\text{CN}$ (Czado & Müller, 1998), $[\text{M}(\text{en})_3][\text{As}_2\text{Se}_6]$ (Fu *et al.*, 2005) and $[\text{Na}(2.2.2\text{-crypt})]_2[\text{As}_2\text{Se}_6]$ [2.2.2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo(8.8.8)hexacosane; Belin & Charbonnel, 1982]. The known structurally characterized 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 $A\text{AsSe}_3 \cdot x\text{H}_2\text{O}$ ($A = \text{K}$, $x = 1$; $A = \text{Rb}$ and Cs , $x = \frac{1}{2}$; Sheldrick & Kaub, 1986). Whereas the $[\text{AsSe}_2]^-$ chains of the former phases contain corner-bridged AsSe_3 pyramids, these building units are connected by Se—Se bonds in the $[\text{AsSe}_3]^-$ chains of the latter selenidoarsenates(III).

From the above list, it is apparent that the discrete $[\text{As}_3\text{Se}_6]^{3-}$ and $[\text{As}_2\text{Se}_4]^{2-}$ anions have all previously been isolated in the presence of voluminous counter-cations, whose central atoms exhibit either tetrahedral or octahedral binding

environments. As not only the charge and size but also the shape of the counter-cations are known to influence the connectivity and nuclearity of main group chalcogenido-metalate anions (Sheldrick & Wachhold, 1998; Sheldrick, 2000), we considered it to be of interest to employ the $[\text{Cs}(18\text{-crown-6})]^+$ cation (18-crown-6 = 1,4,7,10,13,16-hexaoxocyclooctadecane), in which the Cs^+ exhibits a coordination deficit.



The title compound $[\text{Cs}(18\text{-crown-6})]_2[\text{As}_2\text{Se}_6]$, (I), once again contains crystallographically centrosymmetric $[\text{As}_2\text{Se}_6]^{2-}$ anions, but, in contrast to the previously characterized examples, these now participate directly in the coordination sphere of the counter-cations (Table 1). As illustrated in Figs. 1 and 2, the independent caesium cations of (I), Cs1 and Cs2, are both coordinated by six O atoms of an 18-crown-6 macrocycle and lie, respectively, 1.41 (1) and 1.35 (1) Å from the mean planes of these atoms. Atom Cs1 is coordinated by the bridging Se1 atom and the terminal Se3 atom of the first $[\text{As}_2\text{Se}_6]^{2-}$ anion. In contrast, all three crystallographically independent Se atoms of the second centrosymmetric $[\text{As}_2\text{Se}_6]^{2-}$ anion participate in the ninefold coordination of Cs2, leading to the formation of $[\{\text{Cs}(18\text{-crown-6-}\kappa^6\text{O})\}_2(\mu\text{-As}_2\text{Se}_6\text{-}\kappa^6\text{Se})]$ dimeric units. The likewise ninefold coordination environment of atom Cs1 is completed by atom O7 from a symmetry-related crown ether, thereby generating polymeric $[\{\text{Cs}(18\text{-crown-6-}\kappa^7\text{O})\}_2(\mu\text{-As}_2\text{Se}_6\text{-}\kappa^4\text{Se})]$ sheets (Fig. 3). As illustrated by the packing diagram of

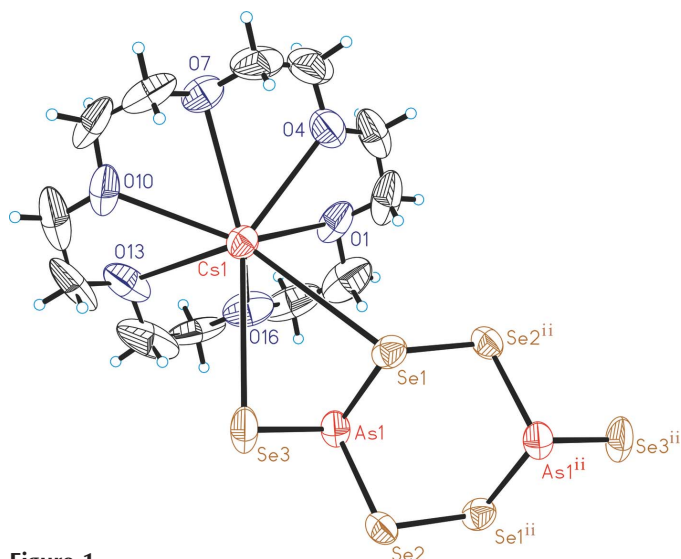


Figure 1
The coordination of Cs1 in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (ii) $-x + 1, -y, -z$.]

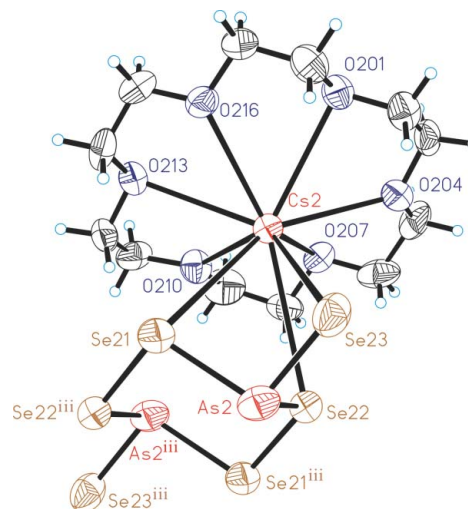


Figure 2
The coordination of Cs2 in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (iii) $-x + 1, -y, -z + 1$.]

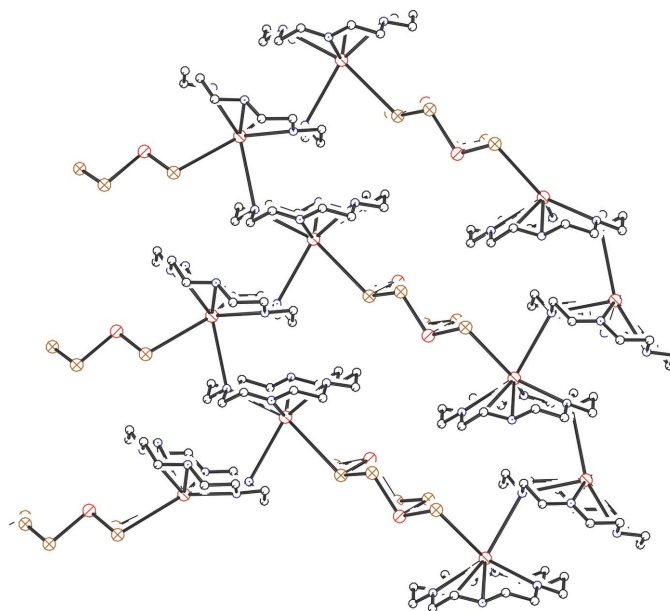


Figure 3
 $[\{\text{Cs}(18\text{-crown-6-}\kappa^7\text{O})\}_2(\mu\text{-As}_2\text{Se}_6\text{-}\kappa^4\text{Se})]$ sheets involving Cs1. H atoms have been omitted.

Fig. 4, such sheets are separated by layers of $[\{\text{Cs}(18\text{-crown-6-}\kappa^6\text{O})\}_2(\mu\text{-As}_2\text{Se}_6\text{-}\kappa^6\text{Se})]$ dimers in the crystal structure of (I). The metrical details for the $[\text{As}_2\text{Se}_6]^{2-}$ anions are consistent with those reported for other salts of $[\text{As}_2\text{Se}_6]^{2-}$.

Our present results suggest that the lower charge of $[\text{As}_2\text{Se}_6]^{2-}$ in comparison to $[\text{As}_3\text{Se}_6]^{3-}$ or species of higher nuclearity will lead to the former anion being the preferred partner of large monocations, even when these exhibit an initial coordination deficit.

Experimental

As (37.41 mg, 0.5 mmol), Se (98.7 mg, 1.25 mmol), 18-crown-6 (66.08 mg, 0.25 mmol) and Cs_2CO_3 (126.92 mg, 0.5 mmol) were

heated to 393 K in methanol (0.4 ml) in a sealed glass tube. After 80 h, the solution was cooled to 293 K at 2 K h^{-1} to afford $[\text{Cs}(\text{18-crown-6})]_2[\text{As}_2\text{Se}_6]$, (I), in 47% yield.

Crystal data

$[\text{Cs}(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{As}_2\text{Se}_6]$
 $M_r = 1418.04$
 Monoclinic, $P2_1/n$
 $a = 21.930 (4) \text{ \AA}$
 $b = 8.4753 (17) \text{ \AA}$
 $c = 24.041 (5) \text{ \AA}$
 $\beta = 102.77 (3)^\circ$
 $V = 4357.8 (15) \text{ \AA}^3$
 $Z = 4$

$D_x = 2.161 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 36 reflections
 $\theta = 4.6\text{--}17.1^\circ$
 $\mu = 8.24 \text{ mm}^{-1}$
 $T = 292 (2) \text{ K}$
 Prism, orange
 $0.23 \times 0.19 \times 0.14 \text{ mm}$

Data collection

Siemens P4 four-circle diffractometer
 ω scans
 Absorption correction: ψ scan (XPREP in SHELXTL-Plus; Sheldrick, 1995)
 $T_{\min} = 0.175$, $T_{\max} = 0.315$
 7836 measured reflections
 7578 independent reflections

4539 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = 0 \rightarrow 26$
 $k = 0 \rightarrow 10$
 $l = -28 \rightarrow 27$
 3 standard reflections every 100 reflections
 intensity decay: 20%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.123$
 $S = 0.94$
 7578 reflections
 416 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.25 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00070 (7)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cs1—O16	2.997 (8)	Cs2—O210	2.999 (6)
Cs1—O4	3.087 (7)	Cs2—O204	3.044 (6)
Cs1—O10	3.107 (8)	Cs2—O216	3.064 (6)
Cs1—O13	3.214 (8)	Cs2—O201	3.195 (6)
Cs1—O1	3.220 (8)	Cs2—O213	3.196 (6)
Cs1—O7	3.236 (7)	Cs2—O207	3.206 (7)
Cs1—O7 ⁱ	3.484 (8)	Cs2—Se23	3.7502 (16)
Cs1—Se1	3.9297 (15)	Cs2—Se21	3.7557 (15)
Cs1—Se3	3.9836 (17)	Cs2—Se22	3.8090 (17)
As1—Se3	2.2833 (16)	As2—Se23	2.2762 (18)
As1—Se1	2.4210 (16)	As2—Se22	2.4364 (19)
As1—Se2	2.4214 (17)	As2—Se21	2.4404 (17)
Se1—Se2 ⁱⁱ	2.3466 (16)	Se21—Se22 ⁱⁱⁱ	2.3543 (16)
Se2—Se1 ⁱⁱ	2.3466 (16)	Se22—Se21 ⁱⁱⁱ	2.3543 (16)
Se3—As1—Se1	93.29 (6)	Se23—As2—Se22	92.26 (6)
Se3—As1—Se2	98.06 (6)	Se23—As2—Se21	98.32 (6)
Se1—As1—Se2	100.22 (6)	Se22—As2—Se21	102.41 (6)
Se2 ⁱⁱ —Se1—As1	103.69 (6)	Se22 ⁱⁱⁱ —Se21—As2	100.73 (6)
Se1 ⁱⁱ —Se2—As1	97.77 (6)	Se21 ⁱⁱⁱ —Se22—As2	105.54 (6)

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

A steady decrease in the average intensity of three monitor reflections up to a final value of 20% was observed during the course of data collection. The crystal changed in colour from orange to black, presumably due to the release of selenium.

H atoms were treated as riding, with $\text{C—H} = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The deepest hole in the final difference Fourier synthesis is 1.13 \AA from Cs2.

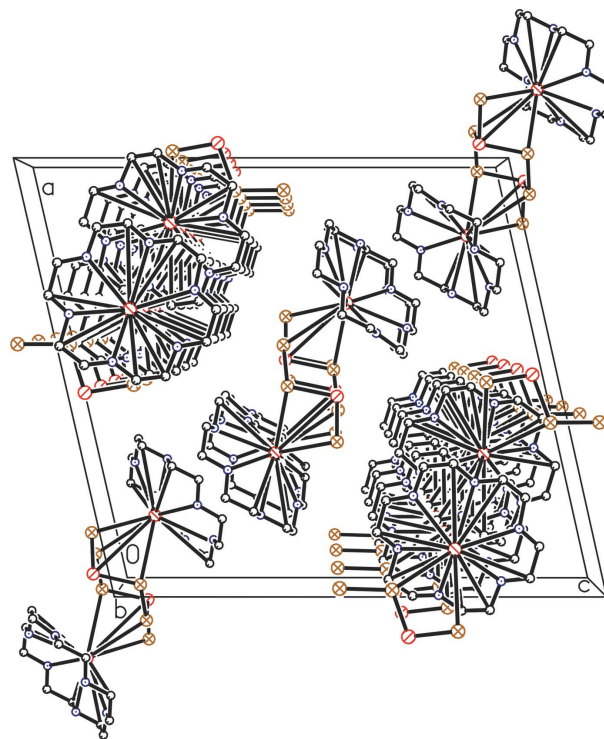


Figure 4

Projection of the structure of (I) along [010], with the following colouring scheme: caesium, red left-hatched sphere; oxygen, blue dotted sphere; carbon, black sphere; arsenic, red hatched sphere; selenium, orange hatched sphere. H atoms have been omitted.

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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