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Bis(1,4,7-triazacyclononane-κ^3N)manganese(II) di-μ-diselenido-bis[selenidoarsenate(III)]

Anna Kromm and William S. Sheldrick*

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

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

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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.010 Å
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 17.7

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

The title compound, $[Mn(C_6H_{15}N_3)_2][As_2Se_6]$, contains a sandwich-like centrosymmetric complex cation with two tridentate 9-aneN_3 (1,4,7-triazacyclononane) ligands, which coordinate the Mn^{II} atom in an octahedral manner. $AsSe_3$ pyramids are linked by two Se—Se bonds into the centrosymmetric chair-shaped six-membered ring of the $[As_2Se_6]^{2-}$ counter-anions.

Comment

In contrast to thio- and selenidoantimonates containing trivalent antimony (Sheldrick & Wachhold, 1998; Van Almsick & Sheldrick, 2005*a*), only a limited number of structural types are known for the corresponding oligo- and polymeric selenidoarsenates (Sheldrick, 2000). In selenidoarsenates(III), $AsSe_3$ pyramids are typically connected by shared corners or Se—Se bonds into either discrete ring-shaped anions or infinite chains. Cyclic $[\{AsSe_2\}_n]^{n-}$ anions have been structurally characterized in $Ba_2As_2Se_5$ (Cordier *et al.*, 1985) for n = 2, in $[Sr(en)_4]_2(As_3Se_6)Cl$ (en = ethylenediamine; Sheldrick & Kaub, 1985) and $[Mn(dien)_2]_3[As_3Se_6]_2$ (dien = diethylenetriamine; Fu *et al.*, 2005) for n = 3, and in $Cs_4As_4Se_8$ (Van Almsick & Sheldrick, 2006*a*) for n = 4. Polymeric $[AsSe_2]^-$ chains are present in the alkali metal phases $AAsSe_2$ [A = Na (Eisenmann & Schäfer, 1979) and A = K–Cs (Sheldrick & Häusler, 1988)]. Edge bridging of $AsSe_3$ pyramids and bipyramidal As_2Se_4 units with direct As—As bonds is observed in the discrete $[As_4Se_6]^{2-}$ anions of $(PPh_4)_2[As_4Se_6]$ (Ansari *et al.*, 1992) and $[K(2.2.2\text{-crypt})]_2$ $[As_4Se_6]$ (2.2.2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Smith *et al.*, 1996) and in the polymeric chains of $Cs_2As_4Se_6$ (Van Almsick & Sheldrick, 2006*b*).

The linkage of $AsSe_3$ pyramids into infinite chains has only been observed for the phases $AAsSe_3.xH_2O$ (A = K, x = 1; A = Rb and Cs, x = 0.5; Sheldrick & Kaub, 1986). In contrast, the dimeric chair-shaped $[As_2Se_6]^{2-}$ comprising two $AsSe_3$ pyramids connected by two Se—Se bonds has been isolated in the presence of a variety of large cations, as reported in $(NEt_4)_2[As_2Se_6]$ (Smith *et al.*, 1998), $(PPh_4)_2[As_2Se_6]$ (Ansari *et al.*, 1992), $(PPh_4)_2[As_2Se_6]$. $2CH_3CN$ (Czado & Müller, 1998), $[M(en)_3][As_2Se_6]$ (M = Mn, Ni; Fu *et al.*, 2005), $[Na(2.2.2\text{-crypt})]_2[As_2Se_6]$ (Belin & Charbonnel, 1982) and $[Cs(18\text{-crown-}6)]_2[As_2Se_6]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxocyclooctadecane; Van Almsick & Sheldrick, 2005*b*). We considered it of interest to employ a centrosymmetric sandwich-like transition-metal-containing counter-cation to isolate a selenidoarsenate under solvothermal conditions.

The title compound $[Mn(9\text{-ane}N_3)_2][As_2Se_6]$, (I) (9-ane$N_3$ = 1,4,7-triazacyclononane), represents the first selenidoarsenate(III) with a centrosymmetric cation and once again contains

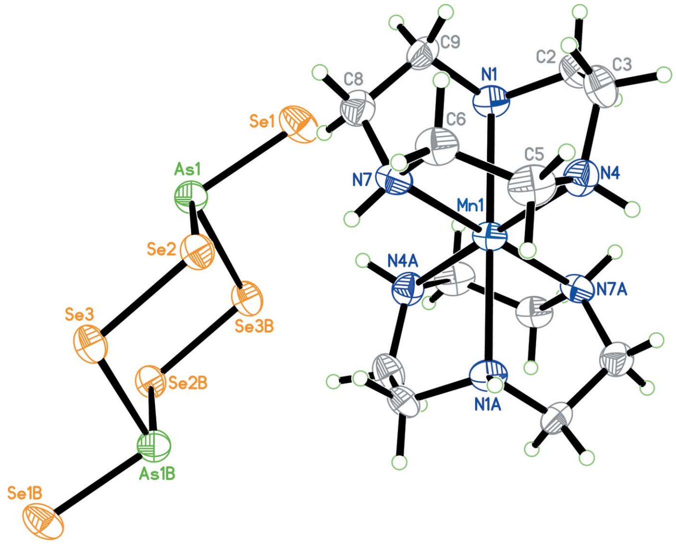


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (A) $-x, 2-y, 1-z$, (B) $-x, 1-y, 1-z$.]

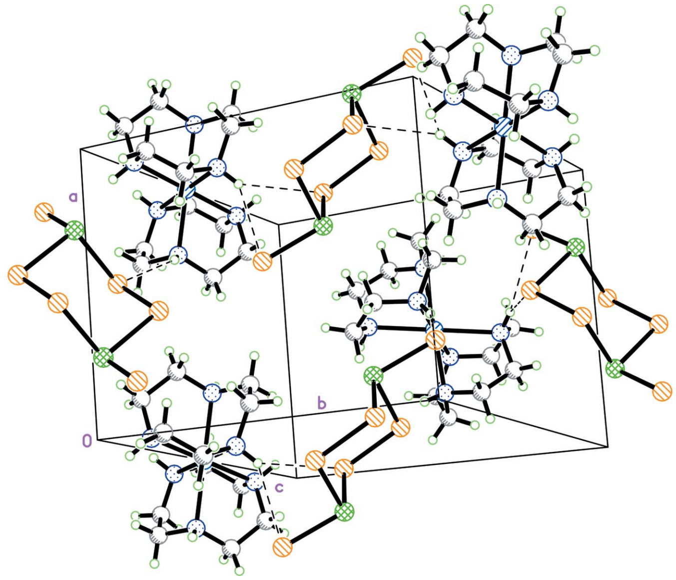
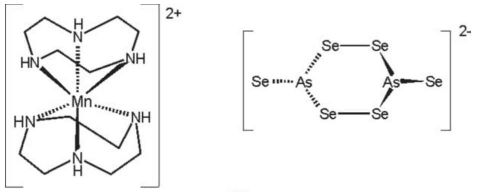


Figure 2
The packing of (I). Dashed lines indicate hydrogen bonds.

the common centrosymmetric $[As_2Se_6]^{2-}$ anion, thereby indicating that their formation is effectively independent of the shape, symmetry or charge of the bulky non-interacting counter-cation. As illustrated in Fig. 1, the anions of (I) exhibit a chair-shaped conformation with typical dimensions. The terminal more polar As1—Se1 bond exhibits a distance of 2.2879 (12) Å much shorter than those of 2.4404 (12) and 2.4252 (12) Å for the endocyclic As1—Se2 and As1—Se3($-x$, $1-y$, $1-z$) bonds. The Se2—Se3 distance of 2.3461 (11) Å lies in the typical range for polyselenide anions (Müller *et al.*, 1993). The shortest intermolecular Se···Se interaction is that between Se1 and Se2 ($\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$) with a length of 3.972 (2) Å. Cations and anions are linked by N—H···Se hydrogen bonds (Table 1) into the polymeric network shown in Fig. 2.



(I)

Experimental

As (42.8 mg, 0.57 mmol), Se (82.4 mg, 1.04 mmol) and $[MnCl_3(9\text{-aneN}_3)]$ (150.6 mg, 0.52 mmol) were heated to 463 K in a 1:1 mixture (1 ml) of CH_3OH and H_2O in the presence of Cs_2CO_3 (165.3 mg, 0.51 mmol). After 30 h, the solution was cooled to 293 K at a rate of 1.5 K h^{-1} to afford orange crystals of $[Mn(9\text{-aneN}_3)_2][As_2Se_6]$ in 70% yield.

Crystal data

$[Mn(C_6H_{15}N_3)_2][As_2Se_6]$
$M_r = 936.96$
Monoclinic, $P2_1/n$
$a = 9.222$ (3) Å
$b = 12.179$ (3) Å
$c = 11.249$ (4) Å
$\beta = 96.54$ (2)°
$V = 1255.1$ (6) Å^3
$Z = 2$
$D_x = 2.479$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 11.86$ mm^{-1}
$T = 292$ (2) K
Block, orange
0.45 × 0.25 × 0.18 mm

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 1995)
$T_{min} = 0.014$, $T_{max} = 0.120$
2908 measured reflections
2200 independent reflections
1729 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.0°$
3 standard reflections every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.110$
$S = 1.04$
2200 reflections
124 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.23$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···Se1^{i}	0.91	2.95	3.716 (6)	143
N4—H4···Se2^{i}	0.91	2.93	3.677 (6)	141
N7—H7···Se1^{ii}	0.91	2.72	3.556 (6)	152
N1—H1···Se3^{iii}	0.91	2.78	3.562 (6)	145

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

H atoms were constrained to idealized positions and refined using a riding model, with C—H = 0.97 Å, N—H = 0.91 Å and U_{iso}(H) = 1.2U_{eq}(C,N). The highest peak is located 1.17 Å from atom Se_3 and the deepest hole 0.86 Å from As1.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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