

Poly[propane-1,3-diyl]diammonium
tetra- μ -selenito-trizinc dihydrate

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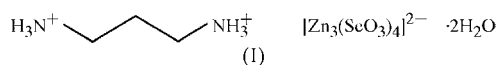
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The title compound, $(C_3H_{12}N_2)[Zn_3(SeO_3)_4] \cdot 2H_2O$, is built up from organic cations, $\{[Zn_3(SeO_3)_4]^{2-}\}_n$ macroanionic sheets and water molecules. The inorganic component of the structure is notable for incorporating both octahedrally and tetrahedrally coordinated Zn atoms. A network of N—H \cdots O and O—H \cdots O hydrogen bonds helps to establish the layered structure. The six-coordinate Zn atom has site symmetry $\bar{1}$, and one C and the two water O atoms have site symmetry m .

Comment

Organically templated inorganic networks have been intensively studied in the last few years and a vast variety of new structures have been described (Cheetham *et al.*, 1999). Many zinc-containing compounds have been reported, with a large majority of these containing tetrahedral ZnO_4 groups in combination with phosphate, hydrogen phosphite, arsenate, selenite, *etc.*, oxo-anions (*e.g.* Ritchie & Harrison, 2004). Here, we describe the synthesis and structure of the title compound, $(C_3H_{12}N_2)[Zn_3(SeO_3)_4] \cdot 2H_2O$, (I) (Fig. 1), which contains both octahedral and tetrahedral Zn centres. Compound (I) is quite distinct from $(C_3H_{12}N_2)[Zn(SeO_3)_2]$ (Millange *et al.*, 2004), which contains chains built up from vertex-sharing ZnO_4 tetrahedra and SeO_3 pyramids.



There are two Zn sites in (I). Atom Zn1 (site symmetry $\bar{1}$) adopts a fairly regular octahedral coordination (Table 1) with a mean Zn—O distance of 2.109 (2) Å [range of *cis* bond angles is 85.85 (9)–94.65 (9)°]. Atom Zn2 is the central atom of a somewhat distorted ZnO_4 tetrahedron, with a mean Zn—O distance of 1.964 (2) Å and O—Zn—O angles varying from 102.48 (10) to 122.01 (10)° (spread = 19.5°).

The two selenite groups in (I) show the usual pyramidal geometry, with mean Se—O values of 1.695 (2) and 1.693 (2) Å for the Se1- and Se2-centred polyhedra, respectively. The O—Se—O bond angles are clustered into the very

narrow range of 101.35 (12)–102.52 (11)° (spread = 1.2°). The unobserved lone pair of the Se^{IV} atom is presumed to point in the direction of the fourth tetrahedral vertex (Verma, 1999). Atoms Se1 and Se2 are displaced from the planes of their three attached O atoms by 0.7472 (14) and 0.7564 (14) Å, respectively.

There are six framework O atoms in (I). Atom O1 is terminal to Se1 and does not bond to Zn, whereas atoms O2, O4 and O5 are bicoordinate to one Se and one Zn atom, with a mean Zn—O—Se angle of 128.1 (2)°. Finally, atoms O3 and O6 are tricoordinate to two Zn and one Se atom. The bond-angle sums for O3 and O6 are 359.5 and 353.6°, respectively. The Se1—O1 bond length is slightly shorter than the bonds between Se and O2, O4 and O5, whilst the Se—O bond lengths for the tricoordinate O atoms are significantly longer.

The complete organic cation is generated by mirror symmetry, with atom C2 lying on the reflecting plane. Other-

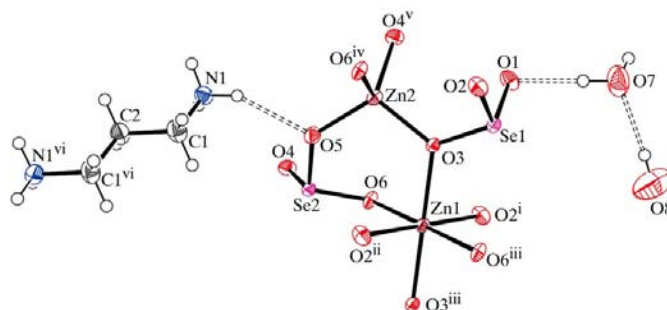


Figure 1

View of a fragment of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x + 1, y, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, y, z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $x, \frac{3}{2} - y, z$.]

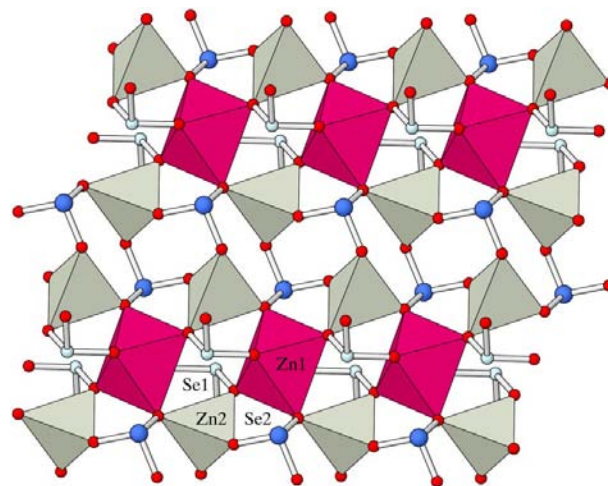


Figure 2

A view of part of an (010) macroanionic layer in (I), with the ZnO_6 and ZnO_4 groups represented by polyhedra.

wise its geometrical parameters are normal. Two uncoordinated water molecules complete the structure of (I). Both water O atoms (O7 and O8) have site symmetry *m*. The H atoms attached to O8 also lie in the reflecting plane.

The polyhedral connectivity in (I) results in distinctive infinite macroanionic sheets of stoichiometry $[\text{Zn}_3(\text{SeO}_3)_4]_n^{2n-}$ which propagate in (010). Considered in isolation, the Zn1O_6 and Zn2O_4 groups form chains that propagate along [100]. Each Zn1O_6 octahedron is linked to two neighbouring Zn1O_6 moieties by a pair of Zn2O_4 tetrahedra, forming 'four-ring' (four-polyhedra) loops. The chains are crosslinked along [001] by the Se2 atoms, forming a sheet. Finally, the Se1–O1 fragments are attached to the four-ring loops, both above and below the plane (Fig. 3).

The organic cation and water molecules occupy the inter-layer regions of the structure and interact with the inorganic sheets by way of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). Each $-\text{NH}_3^+$ moiety makes two simple $\text{N}-\text{H}\cdots\text{O}$ links and one bifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O})$ link, thus serving as a pillar or bridge between the (010) inorganic layers. This pillaring *via* hydrogen bonds is quite different from the direct ligand-like $\text{Zn}-\text{N}$ bond that can occur in some networks containing Zn (Ritchie & Harrison, 2004).

The O7 water molecule in (I) also bridges the layers, in an $\text{O1}\cdots\text{H}-\text{O7}-\text{H}\cdots\text{O1}(x, \frac{1}{2}-y, z)$ configuration. Finally, the O8 water molecule behaves in a similar way, but the acceptor

O atoms are parts of O7 water molecules and not framework O atoms. It is notable that the terminal (non-Zn bound) O1 atom accepts three hydrogen bonds.

Compound (I) complements a handful of other templated phases containing octahedral Zn atoms. The novel phase $(\text{C}_6\text{H}_{17}\text{N}_3)_2[\text{Zn}_7(\text{PO}_4)_6]$ (Kongshaug *et al.*, 2000) contains ZnO_6 groups incorporated into a chabazite-like tetrahedral ZnO_4/PO_4 framework [$\text{C}_6\text{H}_{17}\text{N}_3^{2+}$ is the 1-(2-aminoethyl)-piperazinium dication]. The partially cobalt-substituted phase $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Zn}_{3-x}\text{Co}_x(\text{HPO}_3)_4(\text{H}_2\text{O})_2]$ ($x \simeq 0.83$; Shi *et al.*, 2004) contains *trans*- $\text{Zn}(\text{H}_2\text{O})_2\text{O}_4$ octahedra as part of a three-dimensional architecture incorporating the organic cations ($\text{C}_4\text{H}_{12}\text{N}_2^{2+}$ is the piperazinium dication).

Experimental

A mixture of 1,3-diaminopropane (0.37 g, 5 mmol), aqueous 0.5 M ' H_2SeO_3 ' solution (*i.e.* dissolved SeO_2 ; 20 ml, 10 mmol) and ZnO (0.407 g, 5 mmol) was heated to 353 K for 2 d in a plastic bottle. Product recovery by vacuum filtration and rinsing with water and acetone yielded blocks of (I) accompanied by some white powder.

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Zn}_3(\text{SeO}_3)_4]\cdot 2\text{H}_2\text{O}$
 $M_r = 816.12$
 Monoclinic, $P2_1/m$
 $a = 4.9345$ (3) Å
 $b = 22.9848$ (13) Å
 $c = 8.3987$ (5) Å
 $\beta = 104.623$ (1)°
 $V = 921.71$ (9) Å³

$Z = 2$
 $D_x = 2.941$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 11.84$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 0.21 × 0.15 × 0.06 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.175$, $T_{\max} = 0.494$

7902 measured reflections
 3219 independent reflections
 2404 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 32.7^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.064$
 $S = 0.93$
 3219 reflections
 126 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.08$ e Å⁻³
 $\Delta\rho_{\min} = -0.83$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0040 (3)

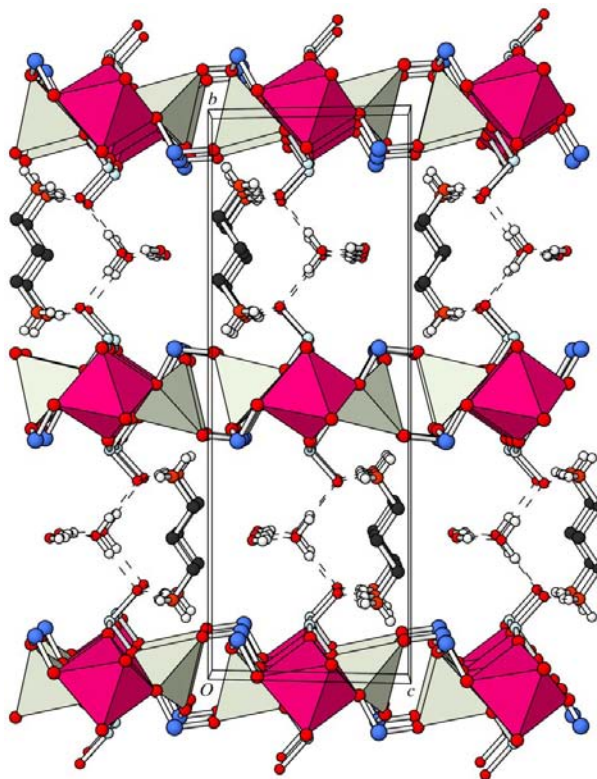


Figure 3
 The unit-cell packing in (I), viewed down [100]. Polyhedral drawing conventions are as in Fig. 2. Hydrogen bonds are indicated by dashed lines.

Table 1
 Selected geometric parameters (Å, °).

Zn1–O2 ⁱ	2.048 (2)	Se1–O1	1.674 (2)
Zn1–O3	2.136 (2)	Se1–O2	1.682 (2)
Zn1–O6	2.144 (2)	Se1–O3	1.730 (2)
Zn2–O4 ⁱⁱ	1.941 (2)	Se2–O4	1.681 (2)
Zn2–O5	1.946 (2)	Se2–O5	1.682 (2)
Zn2–O3	1.958 (2)	Se2–O6	1.715 (2)
Zn2–O6 ⁱⁱⁱ	2.011 (2)		
Se1–O2–Zn1 ⁱⁱⁱ	130.32 (13)	Se2–O5–Zn2	127.57 (14)
Se1–O3–Zn2	121.61 (12)	Se2–O6–Zn2 ⁱ	117.85 (11)
Se1–O3–Zn1	117.55 (11)	Se2–O6–Zn1	118.24 (11)
Zn2–O3–Zn1	120.34 (11)	Zn2 ⁱ –O6–Zn1	117.48 (11)
Se2–O4–Zn2 ⁱⁱ	126.44 (13)		

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $x - 1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °).

<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>
N1—H1...O5	0.89	2.26	3.081 (4)	153
N1—H1...O4 ⁱⁱⁱ	0.89	2.33	2.868 (4)	119
N1—H2...O1 ^{iv}	0.89	2.11	2.974 (4)	165
N1—H3...O1 ⁱⁱ	0.89	1.97	2.857 (4)	174
O7—H4...O1	0.90	1.90	2.800 (4)	180
O8—H5...O7	0.86	2.12	2.972 (9)	172
O8—H6...O7 ⁱ	0.97	2.02	2.988 (8)	179

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

O-bound H atoms were located in a difference map and refined as riding in their as-found relative locations, with O—H distances in the range 0.86–0.97 Å. H atoms bonded to C or N atoms were placed in idealized locations, with C—H = 0.97 Å and N—H = 0.91 Å, and refined as riding, allowing the —NH₃ group to rotate but not tilt. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases.

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 (Farrugia, 1997) and *ATOMS* (Dowty, 2002); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3033). Services for accessing these data are described at the back of the journal.

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