

## Hexagonal

R32  
 $a = 5.6969 (6) \text{ \AA}$   
 $c = 23.523 (3) \text{ \AA}$   
 $V = 661.15 (13) \text{ \AA}^3$   
 $Z = 3$   
 $D_x = 5.064 \text{ Mg m}^{-3}$   
 $D_m$  not measured

## Cell parameters from 1199

reflections  
 $\theta = 1.00\text{--}27.49^\circ$   
 $\mu = 26.678 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Platelet  
 $0.13 \times 0.10 \times 0.03 \text{ mm}$   
 Colourless

## Data collection

Bruker SMART1000 CCD  
 area-detector diffractometer  
 $\omega$  scans  
 Absorption correction:  
 analytical face-indexed  
 $T_{\min} = 0.071, T_{\max} = 0.512$

1452 measured reflections  
 348 independent reflections  
 $R_{\text{int}} = 0.069$   
 $\theta_{\text{max}} = 27.49^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -7 \rightarrow 4$   
 $l = -30 \rightarrow 27$   
 Intensity decay: 0.14%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.057$   
 $S = 1.187$   
 348 reflections  
 28 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 20.9824P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.343 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.097 \text{ e \AA}^{-3}$

Extinction correction:  
*SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient:  
 0.0025 (3)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)  
 Racemic twinning:  
*SHELXL97*  
 Fractional contribution:  
 0.51 (6)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

	x	y	z	$U_{\text{eq}}$
O1	0.0534 (15)	0.3162 (15)	0.1040 (2)	0.0149 (14)
O2	0.2617 (18)	0	0	0.0135 (19)
Ta	0	0	0.064809 (17)	0.0067 (2)
Na	0	0	0.2020 (2)	0.0170 (11)
Ca1	0	0	0.36845 (9)	0.0086 (5)
Ca2	0	0	1/2	0.0104 (6)

Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

Ta—O1 <sup>i</sup> ( $\times 3$ )	1.907 (7)	Na—O1 <sup>v</sup> ( $\times 3$ )	2.848 (8)
Ta—O2 <sup>i</sup> ( $\times 3$ )	2.133 (7)	Ca1—O2 <sup>vi</sup> ( $\times 3$ )	2.287 (6)
Ta—Ta <sup>ii</sup>	3.0490 (9)	Ca1—O1 <sup>vii</sup> ( $\times 3$ )	2.443 (7)
Ta—Na	3.227 (6)	Ca1—Ca2	3.094 (2)
Ta—Ca1 <sup>iii</sup>	3.3624 (6)	Ca2—O1 <sup>viii</sup> ( $\times 6$ )	2.350 (6)
Na—O1 <sup>iv</sup> ( $\times 3$ )	2.343 (8)		
O1—Ta—O1 <sup>i</sup>	98.6 (2)	O2 <sup>vi</sup> —Ca1—O2 <sup>vi</sup>	107.72 (9)
O1—Ta—O2 <sup>i</sup>	137.0 (2)	O2 <sup>vi</sup> —Ca1—O1 <sup>xii</sup>	62.71 (16)
O1 <sup>i</sup> —Ta—O2 <sup>i</sup>	124.3 (2)	O2 <sup>x</sup> —Ca1—O1 <sup>xii</sup>	127.1 (3)
O1 <sup>v</sup> —Ta—O2 <sup>i</sup>	75.0 (3)	O2 <sup>xiii</sup> —Ca1—O1 <sup>xii</sup>	125.0 (2)
O2 <sup>i</sup> —Ta—O2 <sup>v</sup>	74.5 (3)	O1 <sup>xiii</sup> —Ca1—O1 <sup>vii</sup>	80.8 (2)
O1 <sup>iv</sup> —Na—O1 <sup>ix</sup>	112.75 (16)	O1 <sup>viii</sup> —Ca2—O1 <sup>xii</sup>	118.6 (4)
O1 <sup>iv</sup> —Na—O1 <sup>v</sup>	126.45 (17)	O1 <sup>viii</sup> —Ca2—O1 <sup>vii</sup>	150.6 (4)
O1 <sup>ix</sup> —Na—O1 <sup>v</sup>	70.7 (2)	O1 <sup>xiii</sup> —Ca2—O1 <sup>vii</sup>	84.8 (2)
O1 <sup>x</sup> —Na—O1 <sup>v</sup>	113.8 (3)	O1 <sup>vii</sup> —Ca2—O1 <sup>xiv</sup>	80.3 (3)
O1 <sup>v</sup> —Na—O1 <sup>i</sup>	61.1 (2)		

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

Since the Flack parameter (Flack, 1983) was refined to about 0.4 for both configurations of the absolute structure, we used the racemic twin instruction at the final refinement of the structure parameters with *SHELXL97* (Sheldrick, 1997). The refined fractional contribution parameter was 0.51 (6).

Data collection: *SMART* (Bruker, 1997a). Cell refinement: *SMART*. Data reduction: *XPREP* (Bruker, 1997b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ATOMS* (Dowty, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1255). Services for accessing these data are described at the back of the journal.

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## An extreme case of ZnO<sub>6</sub> octahedral distortion in trizinc tris(selenite) hydrate, Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O

WILLIAM T. A. HARRISON

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland. E-mail: w.harrison@abdn.ac.uk

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## Abstract

Trizinc tris[trioxoselenate(IV)] hydrate, Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O, is built up from ZnO<sub>6</sub> octahedra [ $d_{\text{av}}(\text{Zn—O}) =$

2.127(2) Å] and  $\text{SeO}_3$  pyramids [ $d_{\text{av}}(\text{Se—O}) = 1.693(2)$  Å], sharing vertices and edges. One of the zinc octahedra is exceptionally distorted. The title compound is isostructural with  $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  and  $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ .

### Comment

Several well characterized zinc (hydrogen) selenite hydrates are known, including  $\text{ZnSeO}_3 \cdot \text{H}_2\text{O}$  (Engelen *et al.*, 1996),  $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$  (Gladkova & Kondrashev, 1964),  $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Kondrashev *et al.*, 1979) and  $\text{Zn}(\text{HSeO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Engelen *et al.*, 1995). In all these phases, zinc is octahedrally coordinated by O atoms and the  $[\text{SeO}_3]^{2-}$  selenite group adopts its characteristic pyramidal coordination, with the selenium lone pair assumed to occupy the fourth tetrahedral vertex. In this paper, we report the hydrothermal synthesis and structure of the new phase  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  which is isostructural with  $\text{Co}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  (Wildner, 1991) and  $\text{Ni}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  (Wildner, 1991; McManus *et al.*, 1991).

There are four distinct  $\text{ZnO}_6$  groups and three  $\text{SeO}_3$  pyramids in  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$ . Zn1 and Zn2 occupy inversion centres and adopt fairly regular octahedral geometries [ $d_{\text{av}}(\text{Zn1—O}) = 2.104(2)$  Å and  $d_{\text{av}}(\text{Zn2—O}) = 2.110(2)$  Å]. Their bond-valence sums (BVS), calculated by the Brown (1996) method, are  $\text{BVS}(\text{Zn1}) = 2.07$  and  $\text{BVS}(\text{Zn2}) = 2.05$  (expected 2.00).  $\text{Zn3O}_6$  is significantly distorted, with  $d_{\text{av}}(\text{Zn3—O}) = 2.115(2)$  Å and  $\text{BVS}(\text{Zn3}) = 1.99$ . The Zn3—O10 link represents a coordinated water molecule, although the H atoms were not found in the present study. The minimum O—Zn3—O *cis* bond angle is  $71.0(1)^\circ$ . The  $\text{Zn4O}_6$  group [ $d_{\text{av}}(\text{Zn4—O}) = 2.180(2)$  Å,  $\text{BVS}(\text{Zn4}) = 1.91$ ] is exceptionally distorted, with four short Zn—O bonds in the range 1.98–2.07 Å and two very long additional bonds at greater than 2.48 Å. *cis*-O—Zn—O bond angles range from  $65.7(1)$  to  $115.2(1)^\circ$ . The displacement of the Zn atom from the best centre (Balić Zunić & Makovicky, 1996) of its octahedron is 0.34 Å. The two O9 atoms could almost be described as ‘anomalously close’ next-nearest neighbours. In this case, the displacement of the Zn atom from the best centre of the remaining four O atoms arranged in ‘see-saw’ ( $\text{SF}_4$ -like) geometry is only 0.07 Å, but its BVS is reduced to the unreasonably small value of 1.67 based on only four Zn—O contributors.

The three selenite groups in  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  all adopt pyramidal coordination, with  $d_{\text{av}}(\text{Se1—O}) = 1.688(2)$  Å,  $\text{BVS}(\text{Se1}) = 4.19$ ,  $d_{\text{av}}(\text{Se2—O}) = 1.698(2)$  Å,  $\text{BVS}(\text{Se2}) = 4.08$ , and  $d_{\text{av}}(\text{Se3—O}) = 1.692(2)$  Å,  $\text{BVS}(\text{Se3}) = 4.14$  (expected BVS for Se = 4.00). The O—Se—O bond angles range from the unusually low value of  $92.7(2)$  (Wildner, 1991) to  $106.0(2)^\circ$ , compared to an average for this ion of  $101^\circ$ , as surveyed by Fischer & Zemmann (1974).

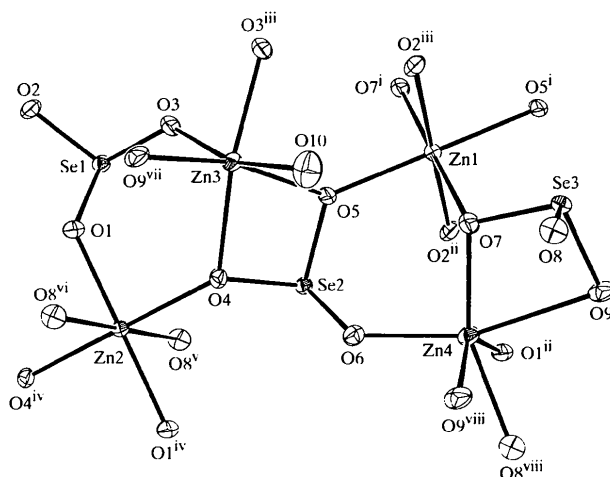


Fig. 1. ORTEP-3 (Farrugia, 1997) view of a fragment of  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  (50% displacement ellipsoids). The symmetry codes are as in Table 1.

The oxygen coordinations include bicoordinate to Zn + Se (O2 and O6), tricoordinate to  $2\text{Zn} + \text{Se}$  (O1, O3, O4, O5, O7 and O8) and in the case of O9, four-coordinate to  $3\text{Zn} + \text{Se}$ . O10 is the O atom of the water molecule.

The polyhedral connectivity in  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  involves a complex three-dimensional network of  $\text{ZnO}_6$  and  $\text{SeO}_3$  groups linked by Zn—O—Zn and Zn—O—Se bonds as described previously (McManus *et al.*, 1991; Wildner, 1991). The edge-sharing interactions between pairs of  $\text{ZnO}_6$  groups and  $\text{ZnO}_6 + \text{SeO}_3$  groups (Fig. 1) are worthy of note. The  $\text{Zn3O}_6$  and  $\text{Zn4O}_6$  octahedra are both dimerized about inversion centres to result in  $\text{Zn}_2\text{O}_{10}$  moieties. Zn3 and Se2 are linked *via* an edge

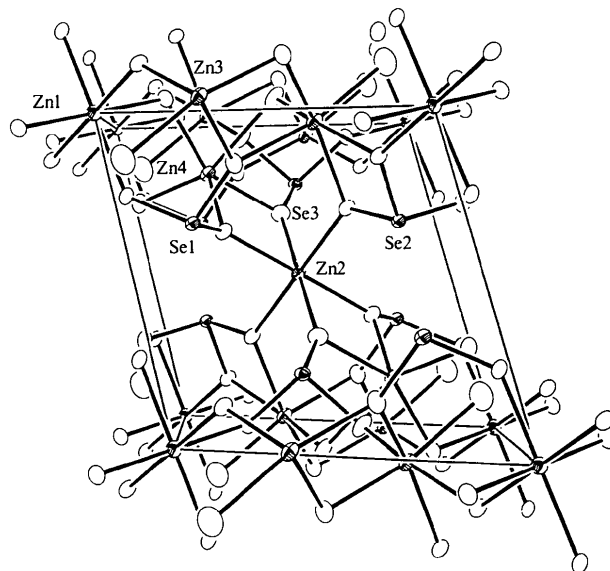


Fig. 2. View down [001] of the unit-cell packing in  $\text{Zn}_3(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$  showing the pseudo-channels associated with the  $\text{Se}^{\text{IV}}$  lone pairs.

(atoms O4 and O5) resulting in very small O4—Zn3—O5 and O4—Se2—O5 bond angles (Table 1). The Zn4-centered edge-shared (*via* 2 × O9) pair of octahedra has the novel feature of two selenite groups 'wedged' (Wildner, 1991) between them, with each pyramid sharing two of its edges (O8··O9 and O7··O9) with the Zn<sub>4</sub>O<sub>10</sub> group. The extremely acute O8—Zn4—O9 and O7—Zn4—O9 bond angles can be correlated with this feature. When the structure of Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O is viewed in projection down [001] (Fig. 2), there appear to be channels, but these are associated with the selenium lone pairs and probably do not represent space accessible by other chemical species.

The equivalent Ni atom to Zn4 in Ni<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O is rather differently distorted, with five short (1.98–2.15 Å) Ni—O bonds and one very long [2.403 (2) Å] link. The displacement of the Ni atom from its octahedral best centre is 0.16 Å. In Co<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O, the equivalent Co atom was described as 4+2 coordinated, with Co—O bond lengths in the ranges 1.98–2.07 Å and 2.23–2.31 Å, respectively. Its best-centre displacement is 0.21 Å. As discussed by Wildner (1991), these unusual geometries can to some extent be correlated with various edge-sharing interactions between pairs of MO<sub>6</sub> groups (*M* = Ni, Co) and MO<sub>6</sub> and SeO<sub>3</sub> groups.

## Experimental

A mixture of 'H<sub>2</sub>SeO<sub>3</sub>' solution (dissolved SeO<sub>2</sub>) (4 ml, 0.5 M), Zn(NO<sub>3</sub>)<sub>2</sub> solution (2 ml, 1 M), KOH solution (2 ml, 1 M) and water (6 ml) was sealed in a 23 ml teflon-lined hydrothermal bomb which was heated to 423 K for 2 d. The bomb was removed from the furnace and cooled to ambient temperature over a period of 2–3 h. Air stable perfectly faceted transparent single crystals of Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (maximum linear dimension = 0.8 mm) were recovered by vacuum filtration, rinsing with acetone and drying in air.

### Crystal data

Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O  
*M<sub>r</sub>* = 595.07  
 Triclinic  
*P* $\bar{1}$   
*a* = 8.0432 (3) Å  
*b* = 8.0805 (3) Å  
*c* = 8.8836 (3) Å  
 $\alpha$  = 65.119 (1)°  
 $\beta$  = 67.516 (1)°  
 $\gamma$  = 68.326 (1)°  
*V* = 468.77 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 4.216 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 2770 reflections  
 $\theta$  = 2.6–37.7°  
 $\mu$  = 19.300 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Rhomb  
 0.15 × 0.13 × 0.11 mm  
 Colourless

### Data collection

Bruker SMART1000 CCD  
 area-detector diffractometer  
 Area-detector scans

6653 measured reflections  
 4747 independent reflections  
*R*<sub>int</sub> = 0.027  
 $\theta_{\max}$  = 38.32°

Absorption correction:  
 analytical (*XPREP* in  
*SMART*; Bruker, 1999)  
*T*<sub>min</sub> = 0.070, *T*<sub>max</sub> = 0.121

*h* = -14 → 7  
*k* = -13 → 14  
*l* = -14 → 15

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030  
*wR*(*F*<sup>2</sup>) = 0.059  
*S* = 0.978  
 4747 reflections  
 149 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0040P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.414 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -1.159 \text{ e } \text{Å}^{-3}$   
 Extinction correction:  
*SHELX97* (Sheldrick, 1997)  
 Extinction coefficient:  
 0.0765 (9)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Zn1—O5 <sup>i</sup>	2.051 (3)	Zn3—O3	2.172 (3)
Zn1—O5	2.051 (3)	Zn4—O6	1.985 (3)
Zn1—O2 <sup>ii</sup>	2.054 (3)	Zn4—O1 <sup>iii</sup>	2.020 (3)
Zn1—O2 <sup>iiii</sup>	2.054 (3)	Zn4—O7	2.041 (3)
Zn1—O7 <sup>i</sup>	2.207 (3)	Zn4—O8 <sup>viii</sup>	2.071 (3)
Zn1—O7	2.207 (3)	Zn4—O9 <sup>viii</sup>	2.481 (3)
Zn2—O1 <sup>i</sup>	2.014 (2)	Zn4—O9	2.483 (3)
Zn2—O1	2.014 (2)	Se1—O2	1.657 (2)
Zn2—O4	2.107 (3)	Se1—O3	1.697 (3)
Zn2—O4 <sup>i</sup>	2.107 (3)	Se1—O1	1.710 (3)
Zn2—O8 <sup>i</sup>	2.209 (3)	Se2—O6	1.678 (3)
Zn2—O8 <sup>ii</sup>	2.209 (3)	Se2—O4	1.706 (2)
Zn3—O9 <sup>iii</sup>	2.047 (2)	Se2—O5	1.710 (3)
Zn3—O3 <sup>iiii</sup>	2.077 (3)	Se3—O8	1.681 (3)
Zn3—O5	2.087 (2)	Se3—O7	1.696 (3)
Zn3—O10	2.141 (4)	Se3—O9	1.699 (2)
Zn3—O4	2.168 (3)		
O6—Zn4—O1 <sup>iii</sup>	103.42 (13)	O7—Zn4—O9 <sup>viii</sup>	96.65 (11)
O6—Zn4—O7	91.74 (11)	O8 <sup>viii</sup> —Zn4—O9 <sup>viii</sup>	65.70 (10)
O1 <sup>iii</sup> —Zn4—O7	115.22 (11)	O6—Zn4—O9	157.15 (10)
O6—Zn4—O8 <sup>viii</sup>	110.92 (11)	O1 <sup>iii</sup> —Zn4—O9	93.44 (11)
O1 <sup>iii</sup> —Zn4—O8 <sup>viii</sup>	78.80 (11)	O7—Zn4—O9	66.88 (10)
O7—Zn4—O8 <sup>viii</sup>	150.42 (13)	O8 <sup>viii</sup> —Zn4—O9	87.20 (11)
O6—Zn4—O9 <sup>viii</sup>	90.14 (11)	O9 <sup>viii</sup> —Zn4—O9	84.72 (9)
O1 <sup>iii</sup> —Zn4—O9 <sup>viii</sup>	144.50 (10)		

Symmetry codes: (i) 2 - *x*, -*y*, -*z*; (ii) *x*, *y* - 1, *z*; (iii) 2 - *x*, 1 - *y*, -*z*; (iv) 1 - *x*, 1 - *y*, 1 - *z*; (v) *x* - 1, 1 + *y*, *z*; (vi) 2 - *x*, -*y*, 1 - *z*; (vii) *x*, 1 + *y*, *z*; (viii) 2 - *x*, -1 - *y*, 1 - *z*.

A face-indexed absorption correction was used and perfectly developed {100}, {010} and {101} faces were found to be present. The maximum difference peak is 0.76 Å from Se3 and the deepest difference hole is 0.80 Å from Zn3.

Data collection: *SMART* (Bruker, 1999). Cell refinement: *SAINT* (Bruker, 1999). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *SHELX97*.

We thank Michael Ruf (Bruker AXS, Karlsruhe, Germany) for assistance with the data collection.

Supplementary data for this paper are available from the IUCR electronic archives (Reference: BR1257). Services for accessing these data are described at the back of the journal.

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