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Sodium zinc hydroxide selenite, $NaZn_2(OH)(SeO_3)_2$

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Fig. 1. Fragment of the $NaZn_2(OH)(SeO_3)_2$ structure (50% displacement ellipsoids) showing the bonding environments of the cations. Symmetry codes are as in Table 2.

Abstract

The title compound, sodium dizinc hydroxide bis-(selenite), $NaZn_2(OH)(SeO_3)_2$, contains a dense poly-hedral network of octahedral ZnO_6, pyramidal SeO_3 and tetrahedral NaO_4 units [$d_{av}(Zn—O) = 2.120\,(2)$, $d_{av}(Se—O) = 1.700\,(1)$ and $d_{av}(Na—O) = 2.316\,(2)$ Å]. It is isostructural with $NaCo_2(OH)(SeO_3)_2$.

Comment

$NaZn_2(OH)(SeO_3)_2$ (Figs. 1 and 2) is isostructural with $NaCo_2(OH)(SeO_3)_2$ (Wildner, 1995). It is built up from a three-dimensional network of edge- and vertex-sharing ZnO_6, SeO_3 and NaO_4 groups.

The Na1 atom, with site symmetry *m*, is tetrahedrally coordinated by four O-atom near neighbours [$d_{av}(Na—O) = 2.316\,(2)$ Å]. Its bond valence sum (Brown, 1996) is 1.00, exactly as expected. The Zn1 (site symmetry $\bar{1}$) and Zn2 (site symmetry *m*) atoms are coordinated octahedrally by O atoms [$d_{av}(Zn1—O) = 2.102\,(2)$ and $d_{av}(Zn2—O) = 2.138\,(2)$ Å]. Both Se atoms have site symmetry *m* and display their characteristic pyramidal geometry [$d_{av}(Se1—O) = 1.699\,(1)$ and $d_{av}(Se2—O) = 1.701\,(1)$ Å], with the fourth tetrahedral vertex assumed to be occupied by the Se^{IV} lone pair (Engelen *et al.*, 1996).

Of the five O atoms in the structure, O1 is bonded to two Zn and one Na atom, O2 and O4 are bonded to Na, Zn and Se, O3 is bonded to three Zn, and O5 is bonded to two Zn and one Se atom. The H atom is bonded to O3, completing a tetrahedron about the O atom. No
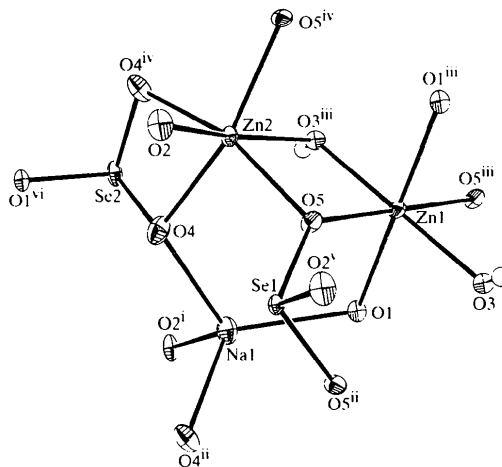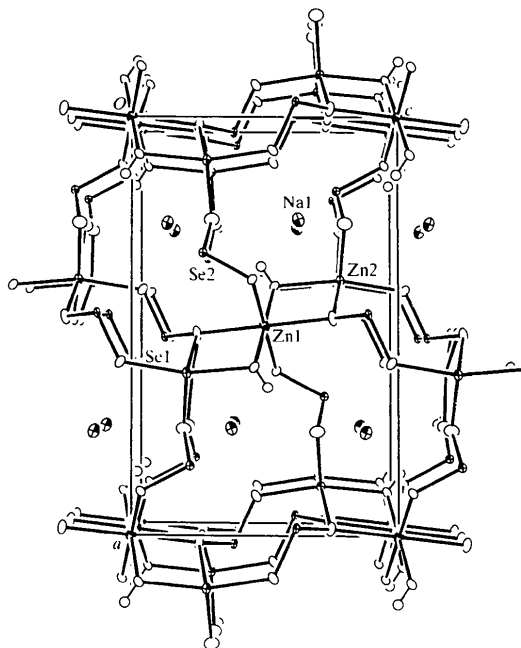

Fig. 2. View down [010] of the $NaZn_2(OH)(SeO_3)_2$ structure, showing the pseudo-channels occupied by Na^+ cations.

hydrogen bond links with $d(H\cdots O) < 2.5$ Å arise from this situation.

The polyhedral connectivity in this phase is the same as that in $NaCo_2(OH)(SeO_3)_2$ (Wildner, 1995), resulting in chains of edge- and corner-sharing ZnO_6 groups propagating along [010] in a manner reminiscent of the α-Co_2SiO_4 structure (Morimoto *et al.*, 1974; Wildner, 1995). Se atoms (as selenite groups) crosslink these formal $[Co/Zn_2O_7H]^{9-}$ chains in the [100] and [001] directions, resulting in small [010] channels occupied by the Na^+ cations.

Experimental

Single crystals of $NaZn_2(OH)(SeO_3)_2$ were prepared by loading ZnO (0.81 g, 10 mmol), Na_2SeO_3 (1,73 g, 10 mmol), SeO_2 (1.11 g, 10 mmol) and H_2O (12 ml) into the teflon cup of a 45 ml capacity hydrothermal bomb. This was sealed and baked for 16 h at 498 K. After cooling and recovery of 2.08 g (98% yield based on Zn) of crystalline product by vacuum filtration, the pH of the mother liquor was 9.

Crystal data

$NaZn_2(OH)(SeO_3)_2$	Mo $K\alpha$ radiation
$M_r = 424.69$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 2000
$Pnma$	reflections
$a = 13.332\,(1)$ Å	$\theta = 4-25°$
$b = 6.0756\,(5)$ Å	$\mu = 17.96$ mm^{-1}
$c = 8.3258\,(6)$ Å	$T = 298$ K
$V = 674.4\,(1)$ Å^3	Block
$Z = 4$	$0.10 \times 0.08 \times 0.05$ mm
$D_x = 4.18$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Siemens SMART area-detector diffractometer	817 reflections with $I > \sigma(I)$
ω scans	$R_{int} = 0.04$
Absorption correction:	$\theta_{max} = 27°$
multi-scan (SADABS;	$h = -17 \rightarrow 17$
Bruker, 1997a)	$k = -7 \rightarrow 7$
$T_{min} = 0.13$, $T_{max} = 0.41$	$l = -10 \rightarrow 10$
4187 measured reflections	
873 independent reflections	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0003$
$R = 0.029$	$\Delta\rho_{max} = 1.77$ e Å^{-3}
$wR = 0.032$	$\Delta\rho_{min} = -1.08$ e Å^{-3}
$S = 1.09$	Extinction correction:
817 reflections	Larson (1967)
71 parameters	Extinction coefficient: 41 (3)
H atom refined	Scattering factors from International Tables for X-ray Crystallography (Vol. IV)
Weighting: Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979): 1.03, 0.668 and 0.810	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Na1	0.24941 (15)	1/4	0.1276 (2)	0.0189
Zn1	0	0	0	0.0106
Zn2	0.11247 (3)	-1/4	0.28793 (5)	0.0099
Se1	0.02697 (3)	1/4	0.38270 (4)	0.0083
Se2	0.32950 (3)	-1/4	0.27423 (4)	0.0123
O1	0.1094 (2)	1/4	-0.0439 (3)	0.0112
O2	0.0878 (2)	-1/4	0.5321 (4)	0.0169
O3	-0.0982 (2)	1/4	-0.0367 (4)	0.0106
O4	0.24672 (17)	-0.0426 (4)	0.3029 (3)	0.0206
O5	0.01832 (18)	0.0322 (4)	0.2543 (3)	0.0136

Table 2. *Selected geometric parameters (Å, °)*

Na1—O1	2.350 (3)	Zn2—O4	2.192 (3)
Na1—O2^i	2.312 (4)	Zn2—O4^{iv}	2.192 (3)
Na1—O4	2.300 (3)	Zn2—O5	2.143 (2)
Na1—O4$''$	2.300 (3)	Zn2—O5^{iv}	2.143 (2)
Zn1—O1	2.137 (2)	Se1—O2^i	1.686 (3)
Zn1—O1^{iii}	2.137 (2)	Se1—O5	1.705 (2)
Zn1—O3	2.028 (2)	Se1—O5$''$	1.705 (2)
Zn1—O3^{iii}	2.028 (2)	Se2—O1^{vi}	1.720 (3)
Zn1—O5	2.140 (2)	Se2—O4	1.692 (2)
Zn1—O5^{iii}	2.140 (2)	Se2—O4^{iv}	1.692 (2)
Zn2—O2	2.060 (3)	O3—H1	0.75 (8)
Zn2—O3^{iii}	2.100 (3)		
Zn1—O1—Zn1$''$	90.58 (11)	Zn1$''$—O3—Zn2$'''$	102.04 (11)
Zn1—O1—Se2^i	118.3 (1)	Zn2—O4—Se2	95.54 (11)
Zn1$''$—O1—Se2^i	118.3 (1)	Zn1—O5—Zn2	97.07 (9)
Zn2—O2—Se1^v	124.07 (18)	Zn1—O5—Se1	134.33 (13)
Zn1—O3—Zn1$''$	96.97 (13)	Zn2—O5—Se1	119.96 (11)
Zn1—O3—Zn2$'''$	102.04 (11)		

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

The single H atom was located in a difference synthesis and refined isotropically without constraints. The highest difference peak is 0.90 Å from Se2 and the deepest difference hole is 0.85 Å from Se1.

Data collection: *SMART* (Bruker, 1997b). Cell refinement: *SMART*. Data reduction: *SAINT* (Bruker, 1997b). Program(s) used to refine structure: *CRYSTALS* (Watkin et al., 1997). Molecular graphics: *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *CRYSTALS*.

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