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Sodium zinc tris(dihydrogenphosphite) hydrate, $NaZn(H_2PO_3)_3\cdot H_2O$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(P–O) = 0.002 Å
R factor = 0.025
wR factor = 0.057
Data-to-parameter ratio = 26.2

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

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$NaZn(H_2PO_3)_3\cdot H_2O$ contains zigzag chains of edge-sharing alternating NaO_6 [d_{av}(Na—O) = 2.452 (2) Å] and ZnO_6 [d_{av}(Zn—O) = 2.104 (2) Å] octahedra, crosslinked by H_2PO_3 pseudo-pyramids [d_{av}(P—O_{Zn}) = 1.501 (2) Å and d_{av}(P—OH) = 1.572 (2) Å]. It is isostructural with $NaM(H_2PO_3)_3\cdot H_2O$ (M = Mn, Co).

Comment

Only a few mixed-metal phosphites containing sodium and a transition metal have been reported, including the isostructural $NaCo(H_2PO_3)_3\cdot H_2O$ (Kratochvíl *et al.*, 1982) and $NaMn(H_2PO_3)_3\cdot H_2O$ (Chmelíková *et al.*, 1986). Here, we report the synthesis and structure of the third member of this family, $NaZn(H_2PO_3)_3\cdot H_2O$, as part of our ongoing investigations of Na–M–H_3PO_3 (M = divalent transition metal) systems.

The zinc cation is octahedrally coordinated with d_{av}(Zn—O) = 2.104 (2) Å. Five of the O atoms bridge to phosphite P atoms (θ_{av} = 133.7°) and the remaining atom (O6) is part of a water molecule. A similar average Zn—O distance of 2.115 Å is found in in $Zn(H_2PO_3)_2\cdot 3H_2O$ (Ortiz-Avila *et al.*, 1989).

The three unique P^{III} atoms are coordinated by three O atoms in pseudo-pyramidal geometry, with a terminal H atom [d(P—H) = 1.32 Å] occupying the fourth tetrahedral vertex. P1 and P3 possess one P—OH vertex and make two P—O—

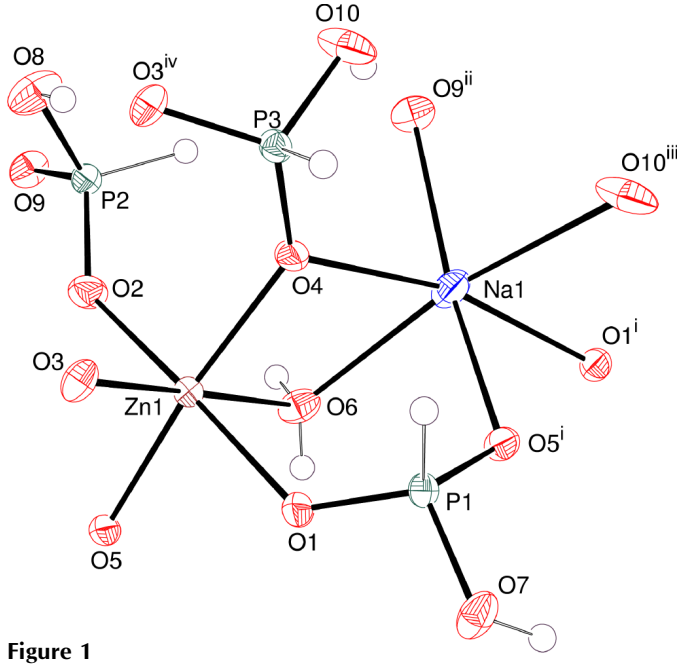

Figure 1
Fragment of $NaZn(H_2PO_3)_3\cdot H_2O$ showing the atomic connectivity (50% displacement ellipsoids). Symmetry codes as in Table 1.

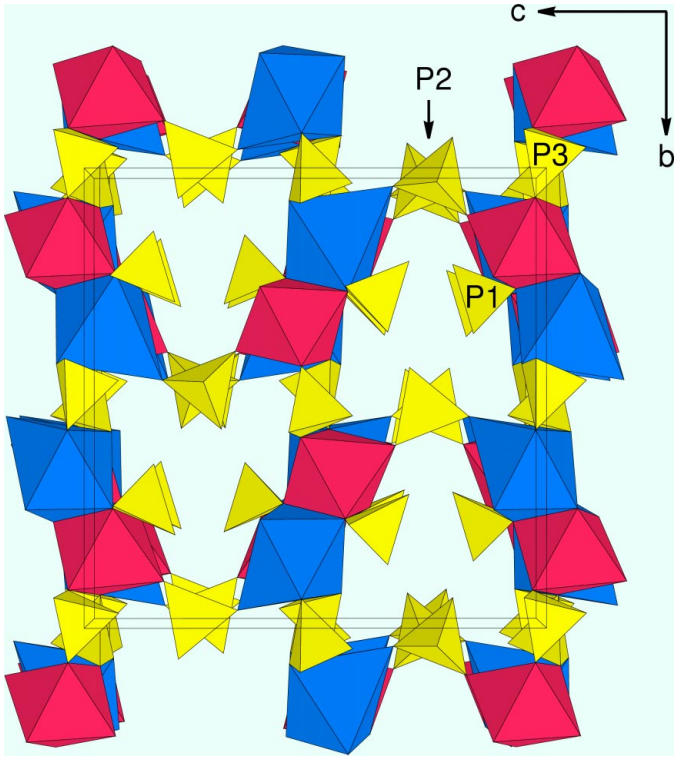

Figure 2
Polyhedral representation down [100] of the unit-cell packing in $NaZn(H_2PO_3)_3{\cdot}H_2O$ [colour key: ZnO_6 octahedra red, NaO_6 octahedra blue, phosphite tetrahedra (3 × P—O and 1 × P—H vertices) yellow].

Zn bridges; P2 has one terminal P═O9 bond, one P—OH bond, and makes one P—O—Zn link. The average $P-O_{Zn}$ and P—OH bond lengths are 1.501 (2) and 1.572 (2) Å, respectively. These P—O and P—OH distances are similar to their equivalent values in $NaMn(H_2PO_3)_3{\cdot}H_2O$ and $NaCo(H_2PO_3)_3{\cdot}H_2O$ (1.500 and 1.574 Å, and 1.496 and 1.567 Å, respectively).

The Na1 coordination can be described as distorted octahedral with one Na—O vertex significantly longer than the other five. The bond-valence sum (Brown, 1996) for sodium of 1.15 (ideal value = 1.00) indicates that its valence is satisfied by this coordination. The average Na—O separation of 2.452 (2) Å is similar to that found in $NaMn(H_2PO_3)_3{\cdot}H_2O$ (2.442 Å) and $NaCo(H_2PO_3)_3{\cdot}H_2O$ (2.443 Å).

The polyhedral connectivity in $NaZn(H_2PO_3)_3{\cdot}H_2O$ consists of zigzag chains of alternating ZnO_6 and NaO_6 octahedra, sharing edges by way of O1···O5 and O4···O6 pairs. The chains propagate along [100]. The octahedral chains are crosslinked by the phosphite moieties: the P2-centred group links adjacent chains in the *c* direction, and the P3 group fuses the chains in the *b* direction. Various P—OH···O and $O_wH{\cdots}O$ (*w* is water) hydrogen bonds also stabilize the structure, as described previously (Chmelíková *et al.*, 1986).

Experimental

Solutions I and II were made up as follows. I: NaOH (2.5 mmol) + H_3PO_3 (2.5 mmol) in 10 ml water; II: ZnO (2.5 mmol) + H_3PO_3 (1.5 mmol) in 10 ml water. They were mixed in a 1:1.5 ratio, stirred for 6 h, and the resulting clear solution was left to stand at room temperature. After two weeks, colourless lozenge-shaped crystals of the title compound were recovered by filtration and washing with 80% ethanol solution.

Crystal data

$NaZn(H_2PO_3)_3{\cdot}H_2O$
M_r = 349.33
Orthorhombic, *Pbca*
a = 9.0609 (4) Å
b = 14.7671 (6) Å
c = 14.8106 (6) Å
V = 1981.71 (14) Å^3
Z = 8
D_x = 2.342 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5338 reflections
θ = 2.7–32.5°
μ = 3.04 mm^{-1}
T = 298 (2) K
Cut chunk, colourless
0.23 × 0.20 × 0.13 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.541, T_{max} = 0.693
16277 measured reflections
3585 independent reflections
2756 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 32.5°
h = −7 → 13
k = −18 → 22
l = −22 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.057
S = 0.94
3585 reflections
137 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00347 (18)

Table 1
Selected geometric parameters (Å, °).

Na1—O5^{i}	2.3203 (14)	Zn1—O6	2.1810 (13)
Na1—O1^{i}	2.3257 (14)	P1—O1	1.4987 (13)
Na1—O9^{ii}	2.3292 (15)	P1—O5^{i}	1.4990 (13)
Na1—O4	2.4165 (14)	P1—O7	1.5780 (14)
Na1—O6	2.4733 (16)	P2—O9	1.4935 (13)
Na1—O10^{iii}	2.8473 (18)	P2—O2	1.5075 (13)
Zn1—O5	2.0618 (12)	P2—O8	1.5659 (14)
Zn1—O4	2.0643 (12)	P3—O4	1.4985 (13)
Zn1—O3	2.0743 (12)	P3—O3^{iv}	1.5035 (13)
Zn1—O1	2.0942 (12)	P3—O10	1.5708 (14)
Zn1—O2	2.1503 (13)		
P1—O1—Zn1	127.97 (7)	P3—O4—Zn1	132.91 (8)
P2—O2—Zn1	137.98 (8)	P1^{v}—O5—Zn1	137.11 (8)
P3^{iv}—O3—Zn1	132.32 (8)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*A*···O7^{i}	0.85	1.93	2.7622 (19)	163
O6—H6*B*···O10^{ii}	0.78	2.23	3.0034 (19)	171
O7—H7···O2^{iii}	0.93	1.66	2.5875 (18)	170
O8—H8···O3^{iv}	0.88	1.83	2.696 (2)	170
O10—H10···O9^{v}	0.89	1.69	2.5771 (19)	169

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve

structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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