Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 1.5H_2O$

Zhi-Sheng Lin,[a,b,c] Ya-Xi Huang,[b,d] Yurii Prots,[b] Jing-Tai Zhao[a] and Rüdiger Kniep[b]*

[a]State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China, [b]Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40, 01187 Dresden, Germany, [c]Graduate School of Chinese Academy of Sciences, Beijing, People's Republic of China, and [d]Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, People's Republic of China
Correspondence e-mail: kniep@cpfs.mpg.de

Received 6 November 2008; accepted 14 November 2008

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(O–B) = 0.006 Å; H-atom completeness 31%; disorder in solvent or counterion; R factor = 0.040; wR factor = 0.099; data-to-parameter ratio = 15.1.

The overall hexagonal framework of the title compound, pentasodium ammonium trimanganese(II) borophosphate sesquihydrate, consists of tube-like borophosphate anions, ${}^{1}_{\infty}\{[B_3P_2O_{11}(OH)]^{4-}\}$, made up of corner-sharing PO_4 and BO_4 tetrahedra and $BO_2(OH)$ triangles, forming ten-membered ring windows. The tubes are interconnected *via* distorted MnO_6 octahedra, establishing a three-dimensional open-framework structure with two different types of ring-channels (12- and six-membered) that run along [001]. The 12-membered ring channels are occupied by NH_4^+ ions and water molecules. The ten-membered ring windows in the walls of the tubes are occupied by Na^+ ions. The remaining Na^+ ions and the water molecules, one of which is half-occupied, reside within the six-membered ring channels. The structural setup is consolidated by an O—H$\cdots$O hydrogen bond between the OH group and an opposite O atom of the framework. Donor–acceptor distances ranging from 2.80 to 3.35 Å between the ammonium N atom, water O atoms and framework O atoms indicate further hydrogen-bonding interactions.

Related literature

Reviews on the preparation, crystal chemistry and applications of borophosphates are given in Kniep *et al.* (1998) and Ewald *et al.* (2007). For isostructural compounds, see Yang, Li *et al.* (2006) for $Na_2Mn[B_3P_2O_{11}(OH)]\cdot 0.67H_2O$; Yang, Yu *et al.* (2006) for $Na_5(H_3O)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 2H_2O$; Liu *et al.* (2006) for $Na_6Cu_3[B_9P_6O_{33}(OH)_3]\cdot 2H_2O$.

Experimental

Crystal data

$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot$-1.5($H_2O$)
M_r = 2373.94
Hexagonal, $P6_3$
a = 11.9331 (2) Å
c = 12.1290 (4) Å
V = 1495.76 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.79 mm^{-1}
T = 295 K
0.08 × 0.04 × 0.04 mm

Data collection

Rigaku Mercury AFC7 CCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.779, T_{max} = 0.931
12243 measured reflections
2891 independent reflections
2784 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.099
S = 1.12
2891 reflections
191 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}
Absolute structure: Flack (1983), 1374 Friedel pairs
Flack parameter: 0.43 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O12—H1$\cdots$O4^{i}	0.86 (7)	2.11 (7)	2.959 (3)	167 (3)
O13$\cdots$O10^{ii}	–	–	2.8035 (11)	–
O13$\cdots$N^{iii}	–	–	3.077 (16)	–
O14$\cdots$O8^{iv}	–	–	3.284 (5)	–
O14$\cdots$O6^{iv}	–	–	3.333 (3)	–
N$\cdots$O13^{v}	–	–	2.988 (16)	–
N$\cdots$O3^{vi}	–	–	2.991 (3)	–
N$\cdots$O7^{v}	–	–	3.047 (3)	–

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXL97*.

This project was supported by the doctoral joint project between the Chinese Academy of Sciences and the Max-Planck Society, the State '973' project (grant No. 2007CB936704) and the Major Basic Research Programs of Shanghai (grant No. 07DJ14001).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2204).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brandenburg, K. (2004). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Ewald, B., Huang, Y.-X. & Kniep, R. (2007). *Z. Anorg. Allg. Chem.* **633**, 1517–1540.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kniep, R., Engelhardt, H. & Hauf, C. (1998). *Chem. Mater.* **10**, 2930–2934.

Liu, W., Huang, Y.-X., Cardoso, R., Schnelle, W. & Kniep, R. (2006). *Z. Anorg. Allg. Chem.* **632**, 2413.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yang, T., Li, G., Ju, J., Liao, F., Xiong, M. & Lin, J. (2006). *J. Solid State Chem.* **179**, 2534–2540.
Yang, M., Yu, J., Di, J., Li, J., Chen, P., Fang, Q., Chen, Y. & Xu, R. (2006). *Inorg. Chem.* **45**, 3588–3593.

supporting information

Acta Cryst. (2008). E**64**, i82–i83 [doi:10.1107/S1600536808037884]

$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 1.5H_2O$

Zhi-Sheng Lin, Ya-Xi Huang, Yurii Prots, Jing-Tai Zhao and Rüdiger Kniep

S1. Comment

In the past several years, borophosphates have attracted extensive attention due to their rich structural chemistry and potential applications as catalysts (Kniep *et al.*, 1998; Ewald *et al.*, 2007). Although a large variety of borophosphate anions has been reported, tube-like borophosphate anions are particularly rare (Liu *et al.*, 2006; Yang *et al.*, 2006*a*; Yang *et al.*, 2006*b*). Up to now, only two manganese compounds containing borophosphate tubes, *viz.* $Na_2Mn[B_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (Yang *et al.*, 2006*a*) and $Na_5(H_3O)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 2H_2O$ (Yang *et al.*, 2006*b*) are listed in the literature. Here, we report on an ammonium substituted sodium manganese borophosphate, $Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 1.5H_2O$.

The crystal structure of the title compound comprises tube-like borophosphate anions, ${}_{\infty}^{1}\{[B_3P_2O_{11}(OH)]^{4-}\}$, which are built from 12-membered rings of alternating BO_4 and PO_4 tetrahedra, further interlinked by sharing common O-corners of neighbouring rings, and loop-branched by $BO_2(OH)$ triangles resulting in 10-membered ring windows on the walls of the tubes (Fig. 1). The manganese atoms are in a distorted octahedral coordination, surrounded by four oxygen atoms from phosphate tetrahedra (O1, O2, O5, O6) and two oxygen atoms from borate tetrahedra (O10, O11). The Mn-coordination octahedra interconnect the neighboring borophosphate tubes to form a three-dimensional framework with two different types of channels (Fig. 2), namely 6- and 12-membered ring channels. The 12-membered ring channels are occupied by NH_4^+ ions and water molecules; the 10-membered ring windows in the walls of the tubes are occupied by Na^+ ions. The remaining Na^+ ions and water molecules reside in the 6-membered ring channels. The structural setup is consolidated by an O—H···O hydrogen bond between the OH group and an opposite O atom of the framework. Donor-acceptor distances ranging from 2.8 to 3.35 Å between the ammonium N atom, water O atoms and framework O atoms indicate further hydrogen bonding interactions, but the corresponding H atoms were not located.

S2. Experimental

Transparent, colourless single crystals of the title compound were synthesized hydrothermally from a mixture of H_3BO_3 (32.2 mmol), $Mn(CH_3COO)_2\cdot 4H_2O$ (3 mmol), $(NH_4)_2HPO_4$ (6.4 mmol), NaF (5 mmol), and water (133.4 mmol). The educt mixture was transferred into a Teflon-lined stainless steel autoclave (internal volume 25 ml) and kept at 513 K for five days. The autoclave was cooled down to ambient temperature by removing out of the oven. The reaction products were washed with hot distilled water (333 K) until the boric acid was completely removed. Finally, the solids were dried in air at 333 K. Hexagonal prismatic crystals were selected for single-crystal diffraction. The NH_4^+ content was determined by elemental analysis and confirmed by IR spectroscopy.

S3. Refinement

The measured crystal was racemically twinned with an approximate twin fraction of 2:3. The hydrogen position bonded to O12 was found in a difference Fourier map and was refined freely. The hydrogen positions of the ammonium N atom and of the uncoordinated water atoms at O13 and O14 were not localized. The occupancy of O13 was refined to 0.50 (2). In the last refinement cycle this value was fixed to 0.50.

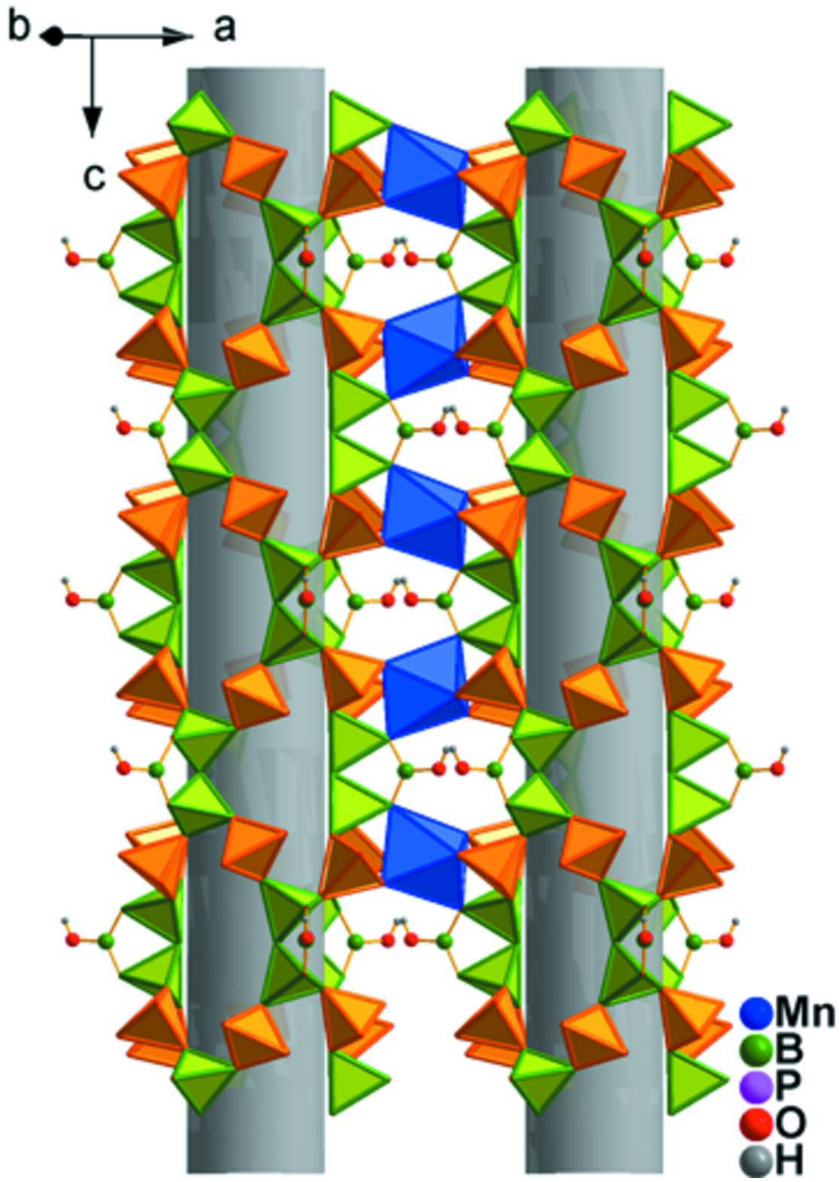

Figure 1

Borophosphate tubes in the crystal structure of $Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3].1.5H_2O$ interconnected by MnO_6 coordination octahedra.

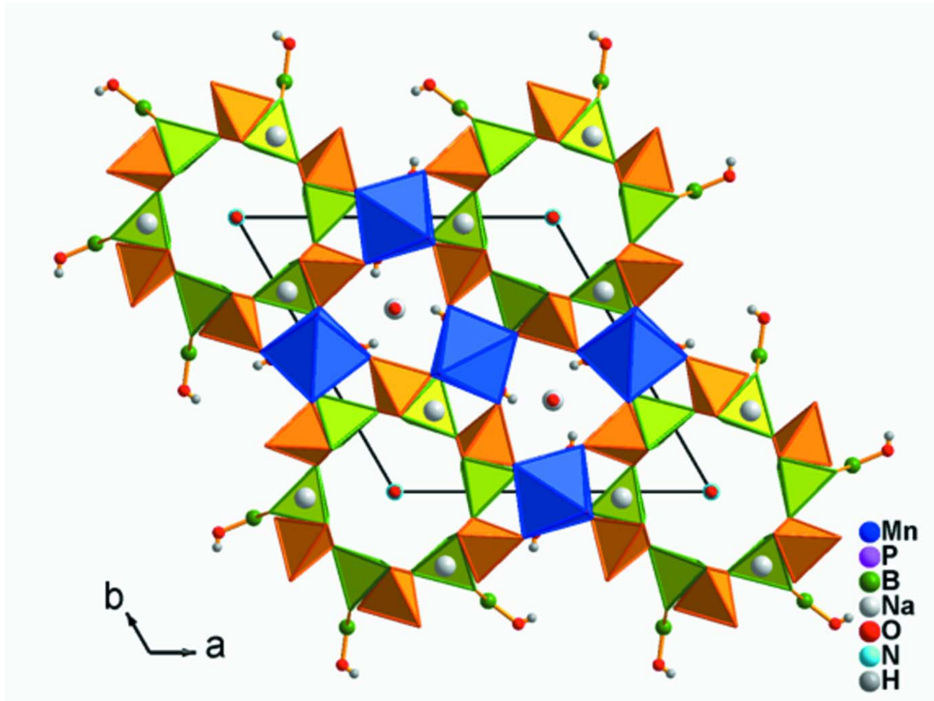

Figure 2

The overall framework of $Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3].1.5H_2O$ viewed along [001], showing the resulting channel-system.

Pentasodium ammonium trimanganese(II) borophosphate sesquihydrate

Crystal data

$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot1.5(H_2O)$
$M_r = 2373.94$
Hexagonal, $P6_3$
Hall symbol: P 6c
$a = 11.9331$ (2) Å
$c = 12.1290$ (4) Å
$V = 1495.76$ (6) Å^3
$Z = 1$
$F(000) = 1164$
$D_x = 2.635$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7346 reflections
$\theta = 2.0$–$33.6°$
$\mu = 1.79$ mm^{-1}
$T = 295$ K
Prism, colourless
0.08 × 0.04 × 0.04 mm

Data collection

Rigaku Mercury AFC7 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.779$, $T_{max} = 0.931$
12243 measured reflections
2891 independent reflections
2784 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.0°$
$h = -16 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.099$
$S = 1.12$
2891 reflections
191 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 2.5644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.81$ e Å^{-3}
Absolute structure: Flack (1983), 1374 Friedel pairs
Absolute structure parameter: 0.43 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Mn2	0.50444 (6)	0.50073 (7)	0.04544 (11)	0.01330 (12)	
P1	0.62139 (9)	0.81051 (9)	0.00965 (7)	0.0111 (2)	
P2	0.37924 (9)	0.19394 (10)	0.08857 (7)	0.0120 (2)	
B1	0.2928 (4)	0.2502 (4)	0.6961 (4)	0.0118 (7)	
B2	0.2992 (4)	0.2504 (5)	0.8974 (4)	0.0151 (8)	
B3	0.4938 (3)	0.4004 (3)	0.7921 (5)	0.0159 (6)	
O1	0.5750 (3)	0.6785 (3)	0.9591 (3)	0.0169 (6)	
O2	0.7011 (3)	0.9084 (3)	0.9177 (2)	0.0162 (6)	
O3	0.7199 (3)	0.8385 (3)	0.1043 (2)	0.0150 (6)	
O4	0.5126 (3)	0.8296 (3)	0.0515 (3)	0.0177 (5)	
O5	0.2925 (3)	0.0953 (3)	0.1789 (2)	0.0152 (5)	
O6	0.4181 (3)	0.3245 (3)	0.1360 (3)	0.0179 (6)	
O7	0.2859 (3)	0.1639 (3)	0.9886 (3)	0.0182 (6)	
O8	0.6857 (3)	0.5090 (3)	0.0545 (3)	0.0175 (6)	
O9	0.5731 (3)	0.6364 (3)	0.1961 (3)	0.0147 (5)	
O10	0.26579 (18)	0.17981 (18)	0.7974 (3)	0.0132 (3)	
O11	0.4355 (3)	0.3637 (3)	0.8933 (3)	0.0157 (6)	
O12	0.6273 (2)	0.4785 (2)	0.7907 (3)	0.0235 (5)	
H1	0.648 (7)	0.498 (7)	0.723 (6)	0.07 (2)*	
Na1	0.71486 (14)	0.73129 (14)	0.8014 (2)	0.0273 (3)	
Na2	0.3333	0.6667	0.9533 (3)	0.0251 (6)	
N	0.0000	0.0000	0.0452 (12)	0.0243 (10)	
Na3	0.6667	0.3333	0.9477 (3)	0.0248 (6)	

O13	0.0000	0.0000	0.8007 (19)	0.041 (2)*	0.50
O14	0.3333	0.6667	0.7692 (9)	0.090 (3)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn2	0.0140 (2)	0.01171 (19)	0.0136 (2)	0.00596 (15)	−0.00045 (17)	0.00050 (14)
P1	0.0127 (4)	0.0114 (4)	0.0093 (4)	0.0061 (3)	0.0005 (3)	0.0014 (3)
P2	0.0128 (4)	0.0126 (4)	0.0103 (4)	0.0061 (4)	−0.0003 (4)	0.0009 (3)
B1	0.0110 (17)	0.0120 (17)	0.0113 (18)	0.0050 (14)	0.0000 (15)	0.0011 (15)
B2	0.018 (2)	0.0153 (18)	0.014 (2)	0.0096 (16)	0.0016 (16)	0.0004 (16)
B3	0.0135 (13)	0.0121 (12)	0.0206 (17)	0.0054 (10)	0.0010 (19)	0.0038 (19)
O1	0.0212 (13)	0.0161 (12)	0.0113 (14)	0.0079 (11)	0.0016 (11)	0.0013 (10)
O2	0.0210 (14)	0.0136 (12)	0.0125 (12)	0.0076 (11)	0.0022 (11)	0.0018 (10)
O3	0.0168 (13)	0.0148 (12)	0.0128 (14)	0.0075 (10)	−0.0020 (11)	0.0041 (10)
O4	0.0158 (12)	0.0161 (12)	0.0214 (14)	0.0081 (11)	0.0002 (11)	−0.0001 (11)
O5	0.0188 (13)	0.0134 (12)	0.0129 (12)	0.0078 (10)	0.0019 (11)	0.0022 (10)
O6	0.0211 (13)	0.0129 (12)	0.0184 (15)	0.0074 (11)	0.0021 (12)	0.0014 (11)
O7	0.0179 (14)	0.0180 (13)	0.0150 (15)	0.0061 (11)	−0.0019 (12)	0.0034 (11)
O8	0.0124 (11)	0.0162 (12)	0.0229 (14)	0.0064 (10)	0.0007 (11)	−0.0036 (11)
O9	0.0159 (12)	0.0160 (12)	0.0086 (12)	0.0053 (10)	0.0001 (11)	−0.0001 (11)
O10	0.0151 (8)	0.0132 (8)	0.0117 (8)	0.0074 (7)	−0.0023 (13)	−0.0018 (13)
O11	0.0146 (12)	0.0156 (12)	0.0142 (14)	0.0055 (10)	−0.0013 (11)	−0.0007 (11)
O12	0.0143 (10)	0.0297 (12)	0.0193 (13)	0.0055 (9)	−0.0020 (14)	0.0008 (15)
Na1	0.0289 (7)	0.0381 (7)	0.0212 (7)	0.0215 (6)	−0.0001 (10)	−0.0012 (11)
Na2	0.0238 (8)	0.0238 (8)	0.0278 (15)	0.0119 (4)	0.000	0.000
N	0.0161 (12)	0.0161 (12)	0.041 (3)	0.0081 (6)	0.000	0.000
Na3	0.0241 (8)	0.0241 (8)	0.0261 (14)	0.0121 (4)	0.000	0.000

Geometric parameters (Å, º)

Mn2—O8	2.118 (3)	O5—B1^{ix}	1.475 (5)
Mn2—O1^{i}	2.126 (3)	O5—Na1^{iv}	2.584 (3)
Mn2—O6	2.127 (3)	O6—Na1^{iv}	2.434 (4)
Mn2—O4^{ii}	2.162 (3)	O7—P2^{vii}	1.562 (3)
Mn2—O9	2.303 (3)	O8—P2^{x}	1.505 (3)
Mn2—O11^{i}	2.326 (4)	O8—Na3^{i}	2.376 (3)
Mn2—Na3^{i}	3.6069 (13)	O9—B3^{iv}	1.354 (6)
Mn2—Na2^{i}	3.6582 (12)	O9—B1^{iv}	1.493 (5)
P1—O1^{i}	1.513 (3)	O10—Na1^{iii}	2.360 (2)
P1—O4	1.514 (3)	O11—Mn2^{vii}	2.326 (4)
P1—O2^{i}	1.550 (3)	O12—Na1	2.656 (3)
P1—O3	1.555 (3)	O12—Na3	2.768 (4)
P1—Na2^{i}	3.0544 (12)	O12—H1	0.86 (8)
P1—Na1^{i}	3.094 (3)	Na1—O10^{x}	2.360 (2)
P2—O6	1.500 (3)	Na1—O6^{vi}	2.434 (4)
P2—O8^{iii}	1.505 (3)	Na1—O5^{vi}	2.584 (3)
P2—O5	1.562 (3)	Na1—P1^{vii}	3.094 (3)

P2—O7^{i}	1.562 (3)	Na1—P2^{vi}	3.118 (3)
P2—Na1^{iv}	3.118 (3)	Na1—H1	2.66 (8)
P2—Na3^{i}	3.4270 (19)	Na2—O14	2.232 (11)
B1—O10	1.430 (5)	Na2—O4^{xi}	2.370 (3)
B1—O5^{v}	1.475 (5)	Na2—O4^{vii}	2.370 (3)
B1—O3^{vi}	1.491 (5)	Na2—O4^{xii}	2.370 (3)
B1—O9^{vi}	1.493 (5)	Na2—O1^{viii}	2.817 (3)
B2—O10	1.416 (6)	Na2—O1^{ii}	2.817 (3)
B2—O7	1.466 (6)	Na2—P1^{xi}	3.0544 (12)
B2—O2^{ii}	1.494 (5)	Na2—P1^{vii}	3.0544 (12)
B2—O11	1.509 (5)	Na2—P1^{xii}	3.0544 (12)
B3—O9^{vi}	1.354 (6)	Na2—Mn2^{xi}	3.6582 (12)
B3—O11	1.371 (6)	Na2—Mn2^{xii}	3.6582 (12)
B3—O12	1.386 (4)	Na3—O8^{xiii}	2.376 (3)
O1—P1^{vii}	1.513 (3)	Na3—O8^{xiv}	2.376 (3)
O1—Mn2^{vii}	2.126 (3)	Na3—O8^{vii}	2.376 (3)
O1—Na1	2.407 (4)	Na3—O12^{iii}	2.768 (4)
O1—Na2	2.817 (3)	Na3—O12^{x}	2.768 (4)
O2—B2^{viii}	1.494 (5)	Na3—P2^{xiv}	3.4270 (19)
O2—P1^{vii}	1.550 (3)	Na3—P2^{xiii}	3.4270 (19)
O2—Na1	2.614 (4)	Na3—P2^{vii}	3.4270 (19)
O3—B1^{iv}	1.491 (5)	Na3—Mn2^{xiii}	3.6069 (13)
O4—Mn2^{viii}	2.162 (3)	Na3—Mn2^{xiv}	3.6069 (13)
O4—Na2^{i}	2.370 (3)	Na3—Mn2^{vii}	3.6069 (13)

O8—Mn2—O1^{i}	95.34 (12)	B3^{iv}—O9—Mn2	120.6 (2)
O8—Mn2—O6	89.88 (12)	B1^{iv}—O9—Mn2	118.7 (2)
O1^{i}—Mn2—O6	174.49 (15)	B2—O10—B1	118.2 (2)
O8—Mn2—O4^{ii}	174.93 (18)	B2—O10—Na1^{iii}	115.7 (3)
O1^{i}—Mn2—O4^{ii}	88.22 (11)	B1—O10—Na1^{iii}	119.3 (3)
O6—Mn2—O4^{ii}	86.46 (12)	B3—O11—B2	117.6 (3)
O8—Mn2—O9	86.00 (12)	B3—O11—Mn2^{vii}	122.7 (2)
O1^{i}—Mn2—O9	82.24 (11)	B2—O11—Mn2^{vii}	116.6 (3)
O6—Mn2—O9	96.39 (14)	B3—O12—Na1	115.5 (2)
O4^{ii}—Mn2—O9	90.91 (12)	B3—O12—Na3	94.0 (3)
O8—Mn2—O11^{i}	93.89 (12)	Na1—O12—Na3	125.72 (15)
O1^{i}—Mn2—O11^{i}	97.79 (14)	B3—O12—H1	106 (5)
O6—Mn2—O11^{i}	83.59 (12)	Na1—O12—H1	81 (5)
O4^{ii}—Mn2—O11^{i}	89.20 (12)	Na3—O12—H1	135 (5)
O9—Mn2—O11^{i}	179.89 (14)	O10^{x}—Na1—O1	125.56 (16)
O1^{i}—P1—O4	113.43 (17)	O10^{x}—Na1—O6^{vi}	120.09 (16)
O1^{i}—P1—O2^{i}	105.09 (17)	O1—Na1—O6^{vi}	108.15 (9)
O4—P1—O2^{i}	112.12 (18)	O10^{x}—Na1—O5^{vi}	114.43 (12)
O1^{i}—P1—O3	111.51 (18)	O1—Na1—O5^{vi}	111.70 (11)
O4—P1—O3	109.4 (2)	O6^{vi}—Na1—O5^{vi}	57.80 (11)
O2^{i}—P1—O3	104.87 (18)	O10^{x}—Na1—O2	117.98 (12)
O6—P2—O8^{iii}	114.34 (17)	O1—Na1—O2	57.76 (11)
O6—P2—O5	104.92 (18)	O6^{vi}—Na1—O2	111.69 (11)

$O8^{iii}—P2—O5$	112.87 (17)	$O5^{vi}—Na1—O2$	67.76 (7)
$O6—P2—O7^{i}$	110.57 (19)	$O10^{x}—Na1—O12$	80.64 (8)
$O8^{iii}—P2—O7^{i}$	109.5 (2)	$O1—Na1—O12$	85.06 (12)
$O5—P2—O7^{i}$	104.11 (17)	$O6^{vi}—Na1—O12$	79.46 (12)
$O10—B1—O5^{v}$	109.7 (3)	$O5^{vi}—Na1—O12$	136.89 (14)
$O10—B1—O3^{vi}$	108.1 (3)	$O2—Na1—O12$	142.78 (14)
$O5^{v}—B1—O3^{vi}$	108.4 (3)	$O14—Na2—O4^{xi}$	120.17 (10)
$O10—B1—O9^{vi}$	110.9 (3)	$O14—Na2—O4^{vii}$	120.17 (10)
$O5^{v}—B1—O9^{vi}$	110.6 (3)	$O4^{xi}—Na2—O4^{vii}$	96.95 (13)
$O3^{vi}—B1—O9^{vi}$	109.0 (3)	$O14—Na2—O4^{xii}$	120.17 (10)
$O10—B2—O7$	109.1 (4)	$O4^{xi}—Na2—O4^{xii}$	96.95 (13)
$O10—B2—O2^{ii}$	109.2 (3)	$O4^{vii}—Na2—O4^{xii}$	96.95 (13)
$O7—B2—O2^{ii}$	107.9 (3)	$O14—Na2—O1^{viii}$	91.45 (9)
$O10—B2—O11$	111.2 (3)	$O4^{xi}—Na2—O1^{viii}$	57.64 (10)
$O7—B2—O11$	110.1 (4)	$O4^{vii}—Na2—O1^{viii}$	69.66 (9)
$O2^{ii}—B2—O11$	109.2 (4)	$O4^{xii}—Na2—O1^{viii}$	147.64 (16)
$O9^{vi}—B3—O11$	123.0 (3)	$O14—Na2—O1^{ii}$	91.45 (9)
$O9^{vi}—B3—O12$	120.0 (5)	$O4^{xi}—Na2—O1^{ii}$	69.66 (10)
$O11—B3—O12$	117.0 (5)	$O4^{vii}—Na2—O1^{ii}$	147.64 (16)
$P1^{vii}—O1—Mn2^{vii}$	126.55 (19)	$O4^{xii}—Na2—O1^{ii}$	57.64 (10)
$P1^{vii}—O1—Na1$	101.82 (16)	$O1^{viii}—Na2—O1^{ii}$	119.937 (9)
$Mn2^{vii}—O1—Na1$	121.96 (15)	$O14—Na2—O1$	91.45 (9)
$P1^{vii}—O1—Na2$	83.98 (13)	$O4^{xi}—Na2—O1$	147.64 (16)
$Mn2^{vii}—O1—Na2$	94.45 (11)	$O4^{vii}—Na2—O1$	57.64 (10)
$Na1—O1—Na2$	123.48 (15)	$O4^{xii}—Na2—O1$	69.66 (9)
$B2^{viii}—O2—P1^{vii}$	135.3 (3)	$O1^{viii}—Na2—O1$	119.937 (9)
$B2^{viii}—O2—Na1$	132.2 (3)	$O1^{ii}—Na2—O1$	119.937 (8)
$P1^{vii}—O2—Na1$	92.40 (14)	$O8^{xiii}—Na3—O8^{xiv}$	93.15 (13)
$B1^{iv}—O3—P1$	127.0 (3)	$O8^{xiii}—Na3—O8^{vii}$	93.15 (13)
$P1—O4—Mn2^{viii}$	127.87 (17)	$O8^{xiv}—Na3—O8^{vii}$	93.15 (13)
$P1—O4—Na2^{i}$	101.43 (16)	$O8^{xiii}—Na3—O12^{iii}$	120.52 (9)
$Mn2^{viii}—O4—Na2^{i}$	107.56 (13)	$O8^{xiv}—Na3—O12^{iii}$	78.10 (11)
$B1^{ix}—O5—P2$	131.9 (3)	$O8^{vii}—Na3—O12^{iii}$	145.34 (9)
$B1^{ix}—O5—Na1^{iv}$	133.0 (2)	$O8^{xiii}—Na3—O12^{x}$	78.10 (10)
$P2—O5—Na1^{iv}$	94.29 (14)	$O8^{xiv}—Na3—O12^{x}$	145.34 (9)
$P2—O6—Mn2$	125.0 (2)	$O8^{vii}—Na3—O12^{x}$	120.52 (9)
$P2—O6—Na1^{iv}$	102.20 (17)	$O12^{iii}—Na3—O12^{x}$	77.89 (13)
$Mn2—O6—Na1^{iv}$	128.53 (15)	$O8^{xiii}—Na3—O12$	145.34 (9)
$B2—O7—P2^{vii}$	127.6 (3)	$O8^{xiv}—Na3—O12$	120.52 (9)
$P2^{x}—O8—Mn2$	128.59 (17)	$O8^{vii}—Na3—O12$	78.10 (10)
$P2^{x}—O8—Na3^{i}$	122.40 (16)	$O12^{iii}—Na3—O12$	77.89 (13)
$Mn2—O8—Na3^{i}$	106.59 (13)	$O12^{x}—Na3—O12$	77.89 (13)
$B3^{iv}—O9—B1^{iv}$	119.0 (3)		

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) −*x*+*y*, −*x*+1, *z*; (iii) −*y*+1, *x*−*y*, *z*; (iv) −*x*+1, −*y*+1, *z*−1/2; (v) *x*−*y*, *x*, *z*+1/2; (vi) −*x*+1, −*y*+1, *z*+1/2; (vii) *x*, *y*, *z*+1; (viii) −*y*+1, *x*−*y*+1, *z*; (ix) *y*, −*x*+*y*, *z*−1/2; (x) −*x*+*y*+1, −*x*+1, *z*; (xi) −*y*+1, *x*−*y*+1, *z*+1; (xii) −*x*+*y*, −*x*+1, *z*+1; (xiii) −*x*+*y*+1, −*x*+1, *z*+1; (xiv) −*y*+1, *x*−*y*, *z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H1···O4^{xv}	0.86 (7)	2.11 (7)	2.959 (3)	167 (3)
O13···O10^{xvi}			2.8035 (11)	
O13···N^{xvii}			3.077 (16)	
O14···O8^{v}			3.284 (5)	
O14···O6^{v}			3.333 (3)	
N···O13^{i}			2.988 (16)	
N···O3^{xviii}			2.991 (3)	
N···O7^{i}			3.047 (3)	

Symmetry codes: (i) *x*, *y*, *z*−1; (v) *x*−*y*, *x*, *z*+1/2; (xv) *x*−*y*+1, *x*, *z*+1/2; (xvi) −*x*+*y*, −*x*, *z*; (xvii) −*x*, −*y*, *z*+1/2; (xviii) *x*−1, *y*−1, *z*.