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The solid solution $Co_{4.32}Mn_{2.68}(HPO_4)_4(PO_4)_2$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(P–O) = 0.001 Å; disorder in main residue; R factor = 0.027; wR factor = 0.064; data-to-parameter ratio = 32.1.

Single crystals of the solid solution cobalt manganese tetrakis(hydrogen phosphate) bis(phosphate), $Co_{4.32}Mn_{2.68}(HPO_4)_4(PO_4)_2$, have been prepared under hydrothermal conditions. The compound crystallizes in the $Fe_7(PO_4)_6$ structure type and is isotypic with the Co and Mn end members of the solid solution $Co_{7-x}Mn_x(HPO_4)_4(PO_4)_2$. The structure is based on a three-dimensional framework of distorted edge-sharing MO_6 and MO_5 polyhedra (M = Co or Mn) which are interlinked by corner-sharing with PO_4 tetrahedra. The four metal positions are statistically occupied by Co and Mn. Strong hydrogen bonds between the OH groups of the HPO_4 tetrahedra and the O atoms help to consolidate the crystal structure. Except for one metal site located on a position with $\overline{1}$ symmetry, all atoms are on general positions.

Related literature

The hydrothermal preparation of transition metal phosphates has been described for M = Fe (Zhou *et al.*, 2002), Co (Lightfoot & Cheetham, 1988) and Mn (Riou *et al.*, 1987). For isotypic phosphates with M = Co or Mn, see: $M_5(OH)_5(PO_4)_2$ (Ruszala *et al.*, 1977), $M(H_2PO_4)_2{\cdot}2H_2O$ (Boudjada & Durif, 1979; Effenberger, 1992), $M_5(HPO_4)_2(PO_4)_2(H_2O)_4$ (Han *et al.*, 2006; Menchetti & Sabelli, 1973; Gerault *et al.*, 1987) and $M_7(HPO_4)_4(PO_4)_2$ (Riou *et al.*, 1987; Lightfoot *et al.*, 1988). The solid solution series $Mn_{5-x}Co_x(HPO_4)_2(PO_4)_2(H_2O)_4$ (x = 1.25, 2, 2.5 and 3) was characterized by Larrea *et al.* (2007). The geometry of the PO_4 tetrahedron has been reviewed by Nord (1986).

Experimental

Crystal data

$Co_{4.32}Mn_{2.68}(HPO_4)_4(PO_4)_2$
M_r = 974.07
Triclinic, $P\overline{1}$
a = 6.5119 (12) Å
b = 7.9623 (12) Å
c = 9.5799 (10) Å
α = 104.428 (3)°
β = 109.180 (1)°
γ = 101.389 (3)°
V = 432.64 (11) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 6.65 mm^{-1}
T = 293 (2) K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: none
10685 measured reflections
5484 independent reflections
4111 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.064
S = 1.05
5484 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 1.06 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.82 e Å^{-3}

Table 1
Selected bond lengths (Å).

$M1$—O11	2.0833 (11)	$M4$—O10	2.0604 (11)
$M1$—O3$^{\rm i}$	2.0890 (11)	$M4$—O8	2.0926 (12)
$M1$—O1$^{\rm ii}$	2.0911 (11)	$M4$—O2$^{\rm ix}$	2.0976 (11)
$M1$—O11$^{\rm iii}$	2.1208 (11)	$M4$—O5$^{\rm v}$	2.1081 (12)
$M1$—O7$^{\rm iv}$	2.1288 (12)	$M4$—O1$^{\rm ii}$	2.2034 (12)
$M1$—O5$^{\rm v}$	2.1322 (12)	P1—O1	1.5274 (12)
$M2$—O12	2.1390 (11)	P1—O2	1.5310 (11)
$M2$—O12$^{\rm vi}$	2.1390 (11)	P1—O4	1.5486 (11)
$M2$—O4$^{\rm vi}$	2.1710 (11)	P1—O3	1.5777 (11)
$M2$—O4	2.1710 (11)	P2—O8	1.5257 (12)
$M2$—O8$^{\rm vii}$	2.2430 (12)	P2—O6	1.5285 (12)
$M2$—O8$^{\rm ii}$	2.2430 (12)	P2—O5	1.5300 (12)
$M3$—O9$^{\rm ii}$	2.0748 (11)	P2—O7	1.5799 (12)
$M3$—O6$^{\rm vii}$	2.0882 (12)	P3—O9	1.5298 (11)
$M3$—O9$^{\rm viii}$	2.1032 (11)	P3—O11	1.5400 (11)
$M3$—O10	2.1149 (11)	P3—O10	1.5445 (11)
$M3$—O4	2.1320 (11)	P3—O12	1.5512 (11)
$M3$—O2$^{\rm ix}$	2.2199 (11)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1P···O12$^{\rm x}$	0.85 (3)	1.63 (3)	2.4663 (18)	169 (3)
O7—H2P···O6$^{\rm xi}$	0.85 (2)	1.77 (2)	2.6143 (18)	172 (3)

Symmetry codes: (x) $-x, -y, -z$; (xi) $-x+1, -y+3, -z+1$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2131).

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supplementary materials

Acta Cryst. (2007). E**63**, i168-i169 [**doi:10.1107/S1600536807031352**]

The solid solution $Co_{4.32}Mn_{2.68}(HPO_4)_4(PO_4)_2$

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Comment

A large variety of Co(II) and Mn(II) phosphates is known and many of the corresponding compounds crystallize isotypically, for instance $Mn_5(OH)_5(PO_4)_2$ and $Co_5(OH)_5(PO_4)_2$ (Ruszala *et al.*, 1977), $Mn(H_2PO_4)_2{\cdot}2H_2O$ and $Co(H_2PO_4)_2{\cdot}2H_2O$ (Boudjada & Durif, 1979; Effenberger, 1992), $Mn_5(HPO_4)_2(PO_4)_2(H_2O)_4$ and $Co_5(HPO_4)_2(PO_4)_2(H_2O)_4$ (Han *et al.*, 2006; Menchetti & Sabelli, 1973; Gerault *et al.*, 1987), and $Mn_7(HPO_4)_4(PO_4)_2$ and $Co_7(HPO_4)_4(PO_4)_2$ (Riou *et al.*, 1987; Lightfoot & Cheetham, 1988). Hydrothermal and solvothermal methods have been used to synthesize numerous novel transition metal phosphates with three-dimensional framework structures such as Fe (Zhou *et al.*, 2002), Co (Lightfoot *et al.*, 1988) and Mn (Riou *et al.*, 1987) containing phosphates.

The title compound, (I), is a solid solution in the series $Co_{7-x}Mn_x(HPO_4)_4(PO_4)_2$ with $x = 2.68$, and crystallizes in the $Fe_7(PO_4)_6$ structure type. It is isotypic with the end members $M_7(HPO_4)_4(PO_4)_2$ (M = Mn, Co). The asymmetric unit of the structure is shown in Fig. 1. The crystal structure consists of a complex framework built up from edge-sharing MO_6 and MO_5 polyhedra that are linked *via* corner-sharing with PO_4 tetrahedra into a three-dimensional framework (Fig. 2). The four metal positions are statistically occupied by Co and Mn. The metal position M2 is located on an inversion centre and has a slightly distorted octahedral coordination environment while the M1 and M3 sites exhibit more distorted octahedra. The metal position M4 is surrounded by five O atoms to give a coordination polyhedron which is best described as an irregular trigonal bipyramid (Fig. 2, Table 1).

The M—O distances range from 2.0604 (11) Å to 2.2430 (12) Å and agree with those found in the solid solution $Mn_{5-x}Co_x(HPO_4)_2(PO_4)_2(H_2O)_4$ (x = 1.25, 2, 2.5 and 3; Larrea *et al.*, 2007). The fully deprotonized orthophosphate groups deviate slightly from the ideal tetrahedral geometry, with P—O bond lenghts ranging from 1.5298 (11) to 1.5512 (11) Å, which is in good agreement with those reported for other divalent-metal compounds with PO_4 groups (Nord, 1986). The two HPO_4 groups exhibit elongated P—O bonds of 1.5777 (11) Å (P1—O3) and 1.5799 (12) Å (P2—O7) which is characteristic for P—OH distances of acidic phosphates and confirms the location of the H atoms (Table 1). Strong O—H···O hydrogen bonds help to consolidate the crystal structure (Table 2).

Experimental

$CoCl_6{\cdot}6H_2O$ (0.90 g), $MnCl_2$ (0.10 g), H_3PO_4 (0.5 ml, 75wt%) and H_2O (7 ml) were mixed and transferred into a 23 ml Teflon-lined stainless steel autoclave and heated at 453 K for 3 d. Then the autoclave was cooled to room temperature at a rate of 10 K h^{-1}. The crystalline material was separated by filtration, washed with distilled water and dried in air at room temperature. Two varieties of crystals were obtained, one with pink and one with purple colour. Single-crystal X-ray diffraction revealed that the pink crystals belong to the solid solution $Mn_{5-x}Co_x(HPO_4)_2(PO_4)_2(H_2O)_4$ (Larrea *et al.*, 2007), whereas the purple crystals could be assigned to the title compound (I). Their composition is in good agreement with the results of the energy dispersive spectrometrical (EDS) analysis (weight percentage): Mn, 14.5%; Co, 26.9%; P, 19.2% and O, 39.4%.

Refinement

The site occupation factors for all metal sites were refined with their sums constrained to unity. The metal positions M1 are occupied by 73% Co and 27% Mn, M2 by 42% Co and 58% Mn, M3 by 80% Co and 20% Mn, and M4 by 54% Co and 58% Mn. H atoms of the hydrogenphosphate anion were localized in Fourier maps and were refined isotropically, with an O—H distance restraint of 0.85 (1) Å. The highest peak and the deepest hole in the final Fourier map are located 0.36 and 0.38 Å, respectively, from O1.

Figures

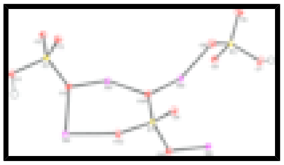

Fig. 1. The asymmetric unit of (I) with atom labels (*M* = Co, Mn), drawn with displacement ellipsoids at the 50% probability level for all non-H atoms. H atoms are given as spheres of arbitrary radius.

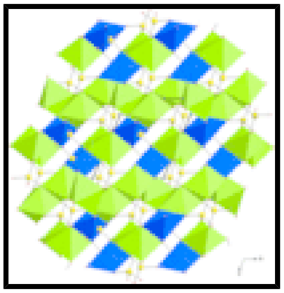

Fig. 2. Polyhedral representation of (I) showing the framework structure as viewed along the *b* axis. MO_5 polyhedra are displayed in blue and MO_6 polyhedra in green.

cobalt manganese tetrakis(hydrogen phosphate) bis(phosphate)

Crystal data

$Co_{4.32}Mn_{2.68}(HPO_4)_4(PO_4)_2$	$Z = 1$
$M_r = 974.07$	$F_{000} = 469.6$
Triclinic, $P\overline{1}$	$D_x = 3.739$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
$a = 6.5119$ (12) Å	Cell parameters from 9895 reflections
$b = 7.9623$ (12) Å	θ = 2.4–40.1°
$c = 9.5799$ (10) Å	μ = 6.65 mm^{-1}
α = 104.428 (3)°	$T = 293$ (2) K
β = 109.180 (1)°	Prism, colourless
γ = 101.389 (3)°	0.10 × 0.10 × 0.10 mm
$V = 432.64$ (11) Å^3	

Data collection

Bruker APEXII CCD area-detector	4111 reflections with $I > 2\sigma(I)$

diffractometer	
Monochromator: graphite	$R_{\text{int}} = 0.022$
$T = 100(2)$ K	$\theta_{\text{max}} = 40.4^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.4^\circ$
Absorption correction: none	$h = -11 \rightarrow 9$
10685 measured reflections	$k = -13 \rightarrow 14$
5484 independent reflections	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.8077P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5484 reflections	$\Delta\rho_{\text{max}} = 1.06$ e Å^{-3}
171 parameters	$\Delta\rho_{\text{min}} = -0.82$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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)
Co3	0.38449 (3)	0.45668 (3)	0.10926 (2)	0.00799 (5)	0.796 (12)
Mn3	0.38449 (3)	0.45668 (3)	0.10926 (2)	0.00799 (5)	0.204 (12)
Co1	0.05082 (4)	0.71421 (3)	0.51524 (2)	0.00797 (5)	0.729 (12)
Mn1	0.05082 (4)	0.71421 (3)	0.51524 (2)	0.00797 (5)	0.271 (12)
Co2	0.0000	0.0000	0.0000	0.00878 (7)	0.418 (16)
Mn2	0.0000	0.0000	0.0000	0.00878 (7)	0.582 (16)
Co4	0.28343 (4)	0.81332 (3)	0.28480 (3)	0.00936 (6)	0.424 (12)
Mn4	0.28343 (4)	0.81332 (3)	0.28480 (3)	0.00936 (6)	0.576 (12)
P1	0.22577 (6)	0.14388 (5)	−0.22339 (4)	0.00662 (7)	
P3	−0.08771 (6)	0.42078 (5)	0.17407 (4)	0.00616 (7)	

P2	0.41114 (6)	1.23356 (5)	0.37360 (5)	0.00817 (7)
O4	0.22221 (19)	0.18779 (14)	−0.05752 (13)	0.00969 (18)
O2	0.44797 (18)	0.24541 (14)	−0.22778 (13)	0.00928 (18)
O6	0.4801 (2)	1.38550 (15)	0.31163 (14)	0.0130 (2)
O7	0.27261 (19)	1.29718 (16)	0.47367 (14)	0.0125 (2)
O5	0.61929 (19)	1.20780 (16)	0.48908 (14)	0.0124 (2)
O3	0.2064 (2)	−0.06486 (14)	−0.27465 (13)	0.01030 (19)
O8	0.26319 (19)	1.05504 (14)	0.24010 (13)	0.0118 (2)
O10	0.12308 (18)	0.53885 (14)	0.16495 (13)	0.00955 (18)
O9	−0.30343 (17)	0.46328 (14)	0.08719 (13)	0.00871 (18)
O11	−0.05564 (19)	0.45695 (14)	0.34663 (12)	0.00933 (18)
O12	−0.1130 (2)	0.21731 (14)	0.09879 (14)	0.0118 (2)
O1	0.01773 (19)	0.16985 (14)	−0.33822 (13)	0.00999 (18)*
H1P	0.184 (5)	−0.105 (4)	−0.205 (3)	0.050*
H2P	0.341 (5)	1.401 (2)	0.545 (3)	0.050*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co3	0.00736 (9)	0.00902 (9)	0.00765 (9)	0.00258 (6)	0.00323 (7)	0.00255 (7)
Mn3	0.00736 (9)	0.00902 (9)	0.00765 (9)	0.00258 (6)	0.00323 (7)	0.00255 (7)
Co1	0.00849 (9)	0.00820 (9)	0.00707 (9)	0.00228 (6)	0.00329 (7)	0.00231 (7)
Mn1	0.00849 (9)	0.00820 (9)	0.00707 (9)	0.00228 (6)	0.00329 (7)	0.00231 (7)
Co2	0.00994 (14)	0.00837 (12)	0.00859 (13)	0.00261 (10)	0.00466 (11)	0.00262 (10)
Mn2	0.00994 (14)	0.00837 (12)	0.00859 (13)	0.00261 (10)	0.00466 (11)	0.00262 (10)
Co4	0.00927 (10)	0.00836 (9)	0.01135 (10)	0.00333 (7)	0.00496 (8)	0.00313 (7)
Mn4	0.00927 (10)	0.00836 (9)	0.01135 (10)	0.00333 (7)	0.00496 (8)	0.00313 (7)
P1	0.00609 (15)	0.00688 (14)	0.00704 (15)	0.00198 (11)	0.00281 (12)	0.00232 (11)
P3	0.00582 (14)	0.00670 (13)	0.00642 (15)	0.00232 (11)	0.00254 (12)	0.00254 (11)
P2	0.00638 (15)	0.00853 (14)	0.00817 (16)	0.00225 (11)	0.00178 (12)	0.00199 (12)
O4	0.0116 (5)	0.0090 (4)	0.0076 (4)	0.0015 (3)	0.0045 (4)	0.0017 (3)
O2	0.0076 (4)	0.0090 (4)	0.0111 (5)	0.0009 (3)	0.0049 (4)	0.0027 (3)
O6	0.0136 (5)	0.0119 (4)	0.0119 (5)	0.0006 (4)	0.0037 (4)	0.0057 (4)
O7	0.0089 (5)	0.0161 (5)	0.0107 (5)	0.0037 (4)	0.0044 (4)	0.0010 (4)
O5	0.0090 (5)	0.0195 (5)	0.0099 (5)	0.0072 (4)	0.0031 (4)	0.0056 (4)
O3	0.0146 (5)	0.0071 (4)	0.0104 (5)	0.0032 (4)	0.0069 (4)	0.0024 (3)
O8	0.0111 (5)	0.0104 (4)	0.0097 (5)	0.0009 (4)	0.0022 (4)	0.0010 (4)
O10	0.0072 (4)	0.0103 (4)	0.0113 (5)	0.0017 (3)	0.0047 (4)	0.0033 (4)
O9	0.0063 (4)	0.0119 (4)	0.0083 (4)	0.0038 (3)	0.0021 (4)	0.0043 (4)
O11	0.0122 (5)	0.0097 (4)	0.0058 (4)	0.0036 (3)	0.0030 (4)	0.0028 (3)
O12	0.0161 (5)	0.0078 (4)	0.0136 (5)	0.0050 (4)	0.0081 (4)	0.0029 (4)

Geometric parameters (Å, °)

M1—O11	2.0833 (11)	P1—O4	1.5486 (11)
M1—O3$^{\rm i}$	2.0890 (11)	P1—O3	1.5777 (11)
M1—O1$^{\rm ii}$	2.0911 (11)	P2—O8	1.5257 (12)
M1—O11$^{\rm iii}$	2.1208 (11)	P2—O6	1.5285 (12)

M1—O7^{iv}	2.1288 (12)	P2—O5	1.5300 (12)
M1—O5^{v}	2.1322 (12)	P2—O7	1.5799 (12)
M2—O12	2.1390 (11)	P3—O9	1.5298 (11)
M2—O12^{vi}	2.1390 (11)	P3—O11	1.5400 (11)
M2—O4^{vi}	2.1710 (11)	P3—O10	1.5445 (11)
M2—O4	2.1710 (11)	P3—O12	1.5512 (11)
M2—O8^{vii}	2.2430 (12)	O2—M4^{ix}	2.0976 (11)
M2—O8^{ii}	2.2430 (12)	O2—M3^{ix}	2.2199 (11)
M3—O9^{ii}	2.0748 (11)	O6—M3^{x}	2.0882 (12)
M3—O6^{vii}	2.0882 (12)	O7—M1^{iv}	2.1288 (12)
M3—O9^{viii}	2.1032 (11)	O7—H2P	0.85 (3)
M3—O10	2.1149 (11)	O5—M4^{v}	2.1081 (12)
M3—O4	2.1320 (11)	O5—M1^{v}	2.1322 (12)
M3—O2^{ix}	2.2199 (11)	O3—M1^{xi}	2.0890 (11)
M3—M3^{ix}	3.0824 (5)	O3—H1P	0.85 (3)
M4—O10	2.0604 (11)	O8—M2^{x}	2.2430 (12)
M4—O8	2.0926 (12)	O9—M3^{ii}	2.0748 (11)
M4—O2^{ix}	2.0976 (11)	O9—M3^{xii}	2.1032 (11)
M4—O5^{v}	2.1081 (12)	O11—M1^{iii}	2.1208 (11)
M4—O1^{ii}	2.2034 (12)	O1—M1^{ii}	2.0911 (11)
P1—O1	1.5274 (12)	O1—M4^{ii}	2.2034 (12)
P1—O2	1.5310 (11)		
O9^{ii}—M3—O6^{vii}	177.41 (4)	O1—P1—O4	110.72 (6)
O9^{ii}—M3—O9^{viii}	84.92 (4)	O2—P1—O4	114.57 (6)
O6^{vii}—M3—O9^{viii}	93.39 (4)	O1—P1—O3	108.54 (6)
O9^{ii}—M3—O10	91.88 (4)	O2—P1—O3	106.78 (6)
O6^{vii}—M3—O10	89.13 (5)	O4—P1—O3	104.08 (6)
O9^{viii}—M3—O10	161.97 (4)	O9—P3—O11	108.96 (6)
O9^{ii}—M3—O4	84.43 (4)	O9—P3—O10	110.59 (6)
O6^{vii}—M3—O4	97.60 (4)	O11—P3—O10	110.28 (6)
O9^{viii}—M3—O4	91.92 (4)	O9—P3—O12	109.91 (6)
O10—M3—O4	105.44 (4)	O11—P3—O12	108.53 (6)
O9^{ii}—M3—O2^{ix}	81.10 (4)	O10—P3—O12	108.55 (6)
O6^{vii}—M3—O2^{ix}	96.76 (4)	O8—P2—O6	111.66 (7)
O9^{viii}—M3—O2^{ix}	83.03 (4)	O8—P2—O5	111.13 (7)
O10—M3—O2^{ix}	78.94 (4)	O6—P2—O5	111.70 (7)
O4—M3—O2^{ix}	165.03 (4)	O8—P2—O7	109.60 (6)
O9^{ii}—M3—M3^{ix}	42.81 (3)	O6—P2—O7	107.40 (7)
O6^{vii}—M3—M3^{ix}	135.46 (4)	O5—P2—O7	105.06 (7)
O9^{viii}—M3—M3^{ix}	42.10 (3)	P1—O4—M3	120.45 (6)
O10—M3—M3^{ix}	132.14 (3)	P1—O4—M2	122.03 (6)

O4—M3—M3^{ix}	87.57 (3)	M3—O4—M2	116.38 (5)
O2^{ix}—M3—M3^{ix}	79.23 (3)	P1—O2—M4^{ix}	138.88 (6)
O11—M1—O3^{i}	163.60 (4)	P1—O2—M4^{ix}	138.88 (6)
O11—M1—O1^{ii}	90.18 (4)	P1—O2—M3^{ix}	123.34 (6)
O3^{i}—M1—O1^{ii}	105.01 (4)	M4^{ix}—O2—M3^{ix}	96.67 (4)
O11—M1—O11^{iii}	78.20 (5)	M4^{ix}—O2—M3^{ix}	96.67 (4)
O3^{i}—M1—O11^{iii}	87.39 (4)	P1—O2—M3^{ix}	123.34 (6)
O1^{ii}—M1—O11^{iii}	166.41 (4)	M4^{ix}—O2—M3^{ix}	96.67 (4)
O11—M1—O7^{iv}	96.03 (4)	P2—O6—M3^{x}	141.22 (7)
O3^{i}—M1—O7^{iv}	89.65 (4)	P2—O7—M1^{iv}	148.04 (7)
O1^{ii}—M1—O7^{iv}	92.17 (5)	P2—O7—H2P	114 (2)
O11^{iii}—M1—O7^{iv}	82.20 (4)	M1^{iv}—O7—H2P	94 (2)
O11—M1—O5^{v}	94.92 (4)	M1^{iv}—O7—H2P	94 (2)
O3^{i}—M1—O5^{v}	82.07 (5)	P2—O5—M4^{v}	136.06 (7)
O1^{ii}—M1—O5^{v}	79.53 (4)	P2—O5—M1^{v}	121.90 (7)
O11^{iii}—M1—O5^{v}	108.19 (4)	M4^{v}—O5—M1^{v}	98.92 (5)
O7^{iv}—M1—O5^{v}	166.27 (5)	P2—O5—M1^{v}	121.90 (7)
O12—M2—O12^{vi}	180.00 (6)	M4^{v}—O5—M1^{v}	98.92 (5)
O12—M2—O4^{vi}	90.32 (4)	P1—O3—M1^{xi}	135.93 (7)
O12^{vi}—M2—O4^{vi}	89.68 (4)	P1—O3—M1^{xi}	135.93 (7)
O12—M2—O4	89.68 (4)	P1—O3—H1P	107.8 (19)
O12^{vi}—M2—O4	90.32 (4)	M1^{xi}—O3—H1P	106 (2)
O4^{vi}—M2—O4	180.00 (5)	M1^{xi}—O3—H1P	106 (2)
O12—M2—O8^{vii}	89.04 (4)	P2—O8—M4	117.24 (7)
O12^{vi}—M2—O8^{vii}	90.96 (4)	P2—O8—M2^{x}	131.08 (7)
O4^{vi}—M2—O8^{vii}	85.96 (4)	M4—O8—M2^{x}	111.53 (5)
O4—M2—O8^{vii}	94.04 (4)	M4—O8—M2^{x}	111.53 (5)
O12—M2—O8^{ii}	90.96 (4)	P3—O10—M4	126.48 (6)
O12^{vi}—M2—O8^{ii}	89.04 (4)	P3—O10—M3	128.41 (6)
O4^{vi}—M2—O8^{ii}	94.04 (4)	M4—O10—M3	101.20 (5)
O4—M2—O8^{ii}	85.96 (4)	P3—O9—M3^{ii}	129.37 (6)
O8^{vii}—M2—O8^{ii}	180.00 (6)	P3—O9—M3^{xii}	135.51 (7)
O10—M4—O8	136.28 (5)	M3^{ii}—O9—M3^{xii}	95.08 (4)
O10—M4—O2^{ix}	83.06 (4)	P3—O9—M3^{xii}	135.51 (7)
O8—M4—O2^{ix}	105.04 (4)	M3^{ii}—O9—M3^{xii}	95.08 (4)
O10—M4—O5^{v}	95.67 (5)	P3—O11—M1	124.87 (6)
O8—M4—O5^{v}	123.79 (5)	P3—O11—M1^{iii}	132.69 (6)
O2^{ix}—M4—O5^{v}	100.18 (4)	M1—O11—M1^{iii}	101.80 (5)
O10—M4—O1^{ii}	88.72 (4)	M1—O11—M1^{iii}	101.80 (5)
O8—M4—O1^{ii}	83.01 (4)	P3—O12—M2	153.67 (7)
O2^{ix}—M4—O1^{ii}	171.24 (4)	P1—O1—M1^{ii}	137.39 (7)

O5^{v}—M4—O1^{ii}	77.56 (4)	P1—O1—M4^{ii}	121.67 (6)
O1—P1—O2	111.62 (6)	M1^{ii}—O1—M4^{ii}	97.21 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1P···O12^{xiii}	0.85 (3)	1.63 (3)	2.4663 (18)	169 (3)
O7—H2P···O6^{xiv}	0.85 (2)	1.77 (2)	2.6143 (18)	172 (3)

Symmetry codes: (xiii) −*x*, −*y*, −*z*; (xiv) −*x*+1, −*y*+3, −*z*+1.

Fig. 1

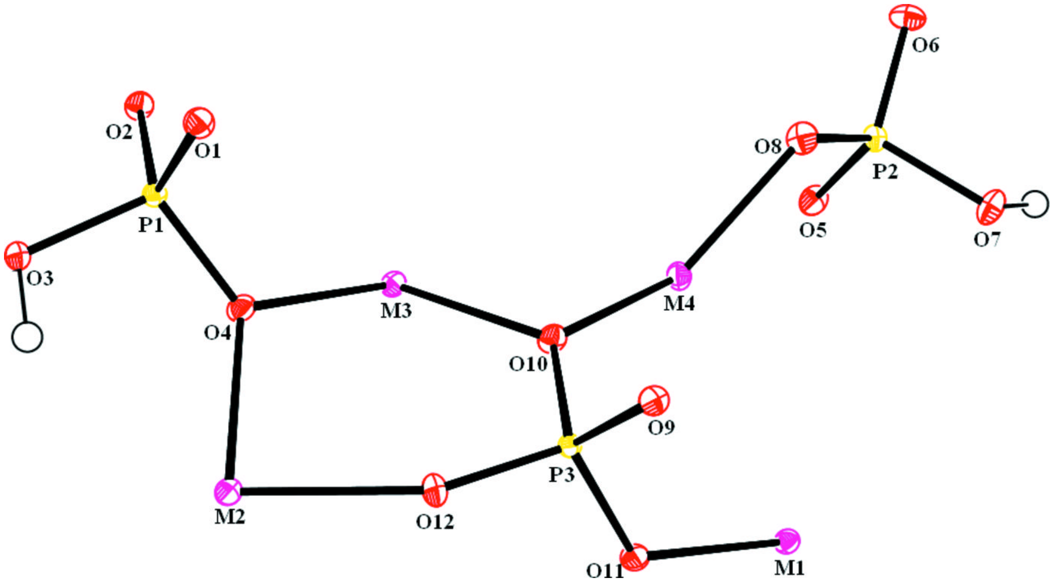

Fig. 2