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$BaMn^{II}_2Mn^{III}(PO_4)_3$

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Key indicators: single-crystal X-ray study; T = 296 K; mean σ(P–O) = 0.002 Å; R factor = 0.020; wR factor = 0.055; data-to-parameter ratio = 15.3.

The title compound, barium trimanganese tris(orthophosphate), was synthesized hydrothermally. Its structure is isotypic with the lead and strontium analogues $AMn^{II}_2Mn^{III}(PO_4)_3$ (A = Pb, Sr). Except for two O atoms on general positions, all atoms are located on special positions. The Ba and one P atom exhibit $mm2$ symmetry, the Mn^{II} atom $2/m$ symmetry, the Mn^{III} atom and the other P atom .2. symmetry and two O atoms are located on mirror planes. The crystal structure contains two types of chains running parallel to [010]. One chain is linear and is composed of alternating $Mn^{III}O_6$ octahedra and PO_4 tetrahedra sharing vertices; the other chain has a zigzag arrangement and is built up from two edge-sharing $Mn^{II}O_6$ octahedra connected to PO_4 tetrahedra by edges and vertices. The two types of chains are linked through PO_4 tetrahedra into an open three-dimensional framework which contains channels parallel to [100] and [010] in which the Ba^{II} ions are located. The alkaline earth cation is surrounded by eight O atoms in the form of a slightly distorted bicapped trigonal prism.

Related literature

For the isotypic lead and strontium analogues, see: Alhakmi *et al.* (2013*a*) and (2013*b*), respectively. For related structures, see: Adam *et al.* (2009); Assani *et al.* (2011*a*,*b*). For bond-valence analysis, see: Brown & Altermatt (1985). For the by-product phase, see: Moore & Araki (1973).

Experimental

Crystal data

$BaMn_3(PO_4)_3$
M_r = 587.07
Orthorhombic, *Imma*
a = 10.3038 (7) Å
b = 14.0163 (11) Å
c = 6.7126 (4) Å
V = 969.44 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.39 mm^{-1}
T = 296 K
0.29 × 0.17 × 0.13 mm

Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.164, T_{max} = 0.376
3968 measured reflections
811 independent reflections
732 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.055
S = 1.09
811 reflections
53 parameters
$\Delta\rho_{max}$ = 1.86 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2767).

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$BaMn^{II}_2Mn^{III}(PO_4)_3$

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S1. Comment

Investigating functional compounds by means of the hydrothermal process, particularly phosphates, we have succeeded to synthesize and structurally characterize new mixed-cation orthophosphates with open frameworks, e.g. the isotypic pair $Ag_2M_3(HPO_4)(PO_4)_2$ (M = Co, Ni) (Assani *et al.*, 2011*a,b*) that is closely related to the alluaudite structure. Others investigated phosphates include compounds crystallizing in the $AMn^{II}_2Mn^{III}(PO_4)_3$ (A = Pb, Sr) structure type (Alhakmi *et al.* (2013*a,b*) with rarely observed mixed-valent $Mn^{II/III}$ cations (Adam *et al.*, 2009). The present article reports on synthesis and crystal structure of the isotypic barium analogue, $BaMn^{II}_2Mn^{III}(PO_4)_3$.

All atoms of this structure are in special positions, except two oxygen atoms (O3, O4) in general position of space group *Imma*. The connection of the metal-oxygen polyhedra, *viz*. BaO_8 polyhedra, MnO_6 octahedra and PO_4 tetrahedra is shown in Fig. 1. The framework of the crystal structure consists of two isolated PO_4 tetrahedra linked to MnO_6 octahedra, building two types of chains running along [010]. The first chain is formed by alternating $Mn^{III}O_6$ octahedra and PO_4 tetrahedra sharing vertices. The second chain is built up from two edge-sharing $Mn^{II}O_6$ octahedra leading to the formation of $Mn^{II}_2O_{10}$ dimers that are connected to two PO_4 tetrahedra by a common edge. These two types of chains are linked together by common vertices of PO_4 tetrahedra to form an open three-dimensional framework that delimits two types of tunnels parallel to [100] and [010] where the Ba^{II} ions are located (Fig. 2). The coordination sphere of the Ba^{II} ion is that of a bicapped trigonal prism.

Bond valence sum calculation (Brown & Altermatt, 1985) of $BaMn^{II}_2Mn^{III}(PO_4)_3$ resulted in expected values (in valence units) for the ions $Ba1^{II}$ (2.26), $Mn1^{III}$ (3.01), $Mn2^{II}$ (2.09), $P1^{V}$ (4.99), and $P2^{V}$ (4.87). The three-dimensional framework of $BaMn^{II}_2Mn^{III}(PO_4)_3$ and its isotypic $AMn^{II}_2Mn^{III}(PO_4)_3$ (A = Pb, Sr) analogues, resemble that of the $Ag_2M_3(HPO_4)(PO_4)_2$ type with M = Ni or Co, whereby the two Ag^+ cations in the channels are replaced by Ba^{II}, Pb^{II} or Sr^{II}.

S2. Experimental

The hydrothermal treatment of a reaction mixture of barium, manganese and phosphate precursors in a proportion corresponding to the molar ratio Ba: Mn: P = 1: 3: 3 has allowed to isolate brown block-shaped crystals corresponding to the title compound as well as a parallelepipedic colourless crystals which were identified to be the known manganese phosphate $Mn_5(HPO_4)_2(PO_4)_2{\cdot}4H_2O$ (Moore & Araki, 1973). The hydrothermal reaction was conducted in a 23 ml Teflon-lined autoclave, filled to 50% with distilled water and under autogeneous pressure at 463 K for five days.

S3. Refinement

The highest peak and the deepest hole in the final Fourier map are at 0.82 Å and 1.00 Å away from Ba1.

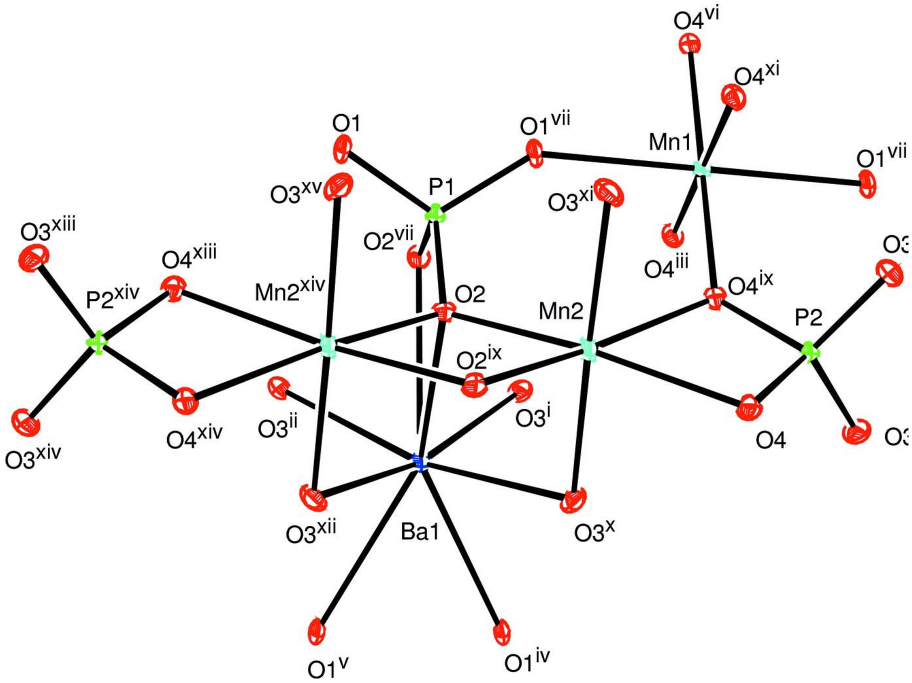

Figure 1

The main building units of the crystal structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) *x*, -*y* + 1, -*z*; (ii) -*x*, *y* - 1/2, -*z*; (iii) *x*, *y* - 1/2, -*z*; (iv) -*x*, -*y* + 1, -*z*; (v) *x*, *y*, *z* - 1; (vi) -*x*, -*y* + 1/2, *z* - 1; (vii) -*x*, -*y* + 1/2, *z*; (viii) -*x* + 1/2, *y* - 1/2, *z* + 1/2; (ix) *x* - 1/2, -*y* + 1/2, -*z* + 1/2; (*x*) -*x* + 1/2, -*y* + 1/2, -*z* + 1/2; (xi) *x* - 1/2, *y* - 1/2, *z* + 1/2; (xii) -*x*, -*y*, -*z* + 1; (xiii) -*x* + 1/2, -*y* + 1, *z* + 1/2; (xiv) -*x* + 1/2, *y*, -*z* + 1/2.]

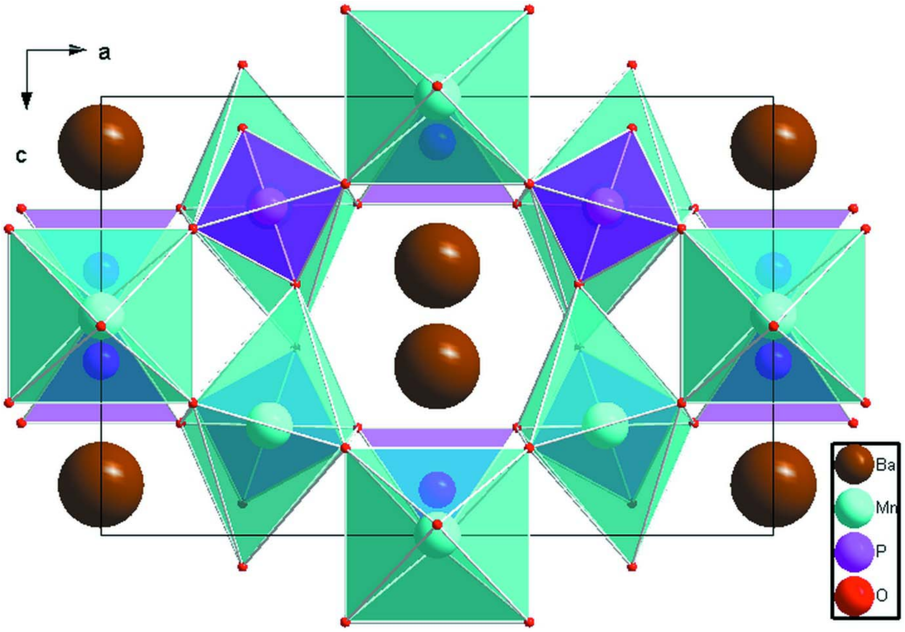

Figure 2

Polyhedral representation of $BaMn_3(PO_4)_3$ with channels running parallel to [010].

Barium trimanganese tris(orthophosphate)

Crystal data

$BaMn_3(PO_4)_3$	$F(000) = 1088$
$M_r = 587.07$	$D_x = 4.022$ Mg m^{-3}
Orthorhombic, *Imma*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -I 2b 2	Cell parameters from 811 reflections
$a = 10.3038$ (7) Å	$\theta = 3.4–30.5°$
$b = 14.0163$ (11) Å	$\mu = 8.39$ mm^{-1}
$c = 6.7126$ (4) Å	$T = 296$ K
$V = 969.44$ (12) Å^3	Block, brown
$Z = 4$	0.29 × 0.17 × 0.13 mm

Data collection

Bruker X8 APEX diffractometer	3968 measured reflections
Radiation source: fine-focus sealed tube	811 independent reflections
Graphite monochromator	732 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$\theta_{max} = 30.5°$, $\theta_{min} = 3.4°$
$T_{min} = 0.164$, $T_{max} = 0.376$	$h = -14 \rightarrow 13$
	$k = -19 \rightarrow 20$
	$l = -9 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.020$	$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.09$	$\Delta\rho_{max} = 1.86$ e Å^{-3}
811 reflections	$\Delta\rho_{min} = -0.78$ e Å^{-3}
53 parameters	
0 restraints	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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}
Ba1	0.0000	0.2500	−0.11499 (4)	0.01125 (10)
Mn1	0.0000	0.5000	0.5000	0.00794 (15)
Mn2	0.2500	0.36758 (4)	0.2500	0.01092 (13)
P1	0.0000	0.2500	0.39677 (16)	0.0078 (2)
P2	0.2500	0.57094 (6)	0.2500	0.00851 (17)
O1	0.0000	0.15998 (16)	0.5237 (4)	0.0115 (5)

O2	0.1185 (2)	0.2500	0.2553 (3)	0.0107 (4)
O3	0.21046 (19)	0.63040 (12)	0.0721 (3)	0.0133 (3)
O4	0.36337 (16)	0.49927 (12)	0.1983 (2)	0.0103 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01480 (16)	0.01187 (15)	0.00707 (14)	0.000	0.000	0.000
Mn1	0.0102 (3)	0.0081 (3)	0.0056 (3)	0.000	0.000	−0.0001 (2)
Mn2	0.0154 (3)	0.0063 (2)	0.0110 (2)	0.000	−0.00074 (18)	0.000
P1	0.0104 (5)	0.0065 (5)	0.0066 (5)	0.000	0.000	0.000
P2	0.0121 (4)	0.0064 (4)	0.0071 (3)	0.000	0.0010 (3)	0.000
O1	0.0166 (12)	0.0049 (9)	0.0129 (11)	0.000	0.000	0.0014 (8)
O2	0.0121 (11)	0.0103 (11)	0.0098 (10)	0.000	0.0035 (8)	0.000
O3	0.0183 (8)	0.0114 (8)	0.0100 (7)	0.0027 (6)	0.0006 (7)	0.0033 (6)
O4	0.0123 (8)	0.0087 (7)	0.0100 (7)	0.0014 (6)	0.0016 (6)	0.0009 (5)

Geometric parameters (Å, º)

Ba1—O1^{i}	2.734 (2)	Mn2—O2	2.1337 (16)
Ba1—O1^{ii}	2.734 (2)	Mn2—O2^{xiii}	2.1337 (16)
Ba1—O3^{iii}	2.7560 (18)	Mn2—O3^{iii}	2.2006 (17)
Ba1—O3^{iv}	2.7560 (18)	Mn2—O3^{ix}	2.2006 (17)
Ba1—O3^{v}	2.7560 (18)	Mn2—O4	2.2117 (17)
Ba1—O3^{vi}	2.7560 (18)	Mn2—O4^{x}	2.2117 (17)
Ba1—O2	2.769 (2)	P1—O1	1.523 (2)
Ba1—O2^{vii}	2.769 (2)	P1—O1^{vii}	1.523 (2)
Mn1—O4^{viii}	1.9377 (17)	P1—O2^{vii}	1.547 (2)
Mn1—O4^{ix}	1.9377 (17)	P1—O2	1.547 (2)
Mn1—O4^{x}	1.9377 (17)	P2—O3^{x}	1.5119 (17)
Mn1—O4^{xi}	1.9377 (17)	P2—O3	1.5119 (17)
Mn1—O1^{vii}	2.248 (2)	P2—O4^{x}	1.5792 (17)
Mn1—O1^{xii}	2.248 (2)	P2—O4	1.5792 (17)
O1^{i}—Ba1—O1^{ii}	54.97 (9)	O4^{ix}—Mn1—O1^{vii}	87.51 (6)
O1^{i}—Ba1—O3^{iii}	111.92 (5)	O4^{x}—Mn1—O1^{vii}	92.49 (6)
O1^{ii}—Ba1—O3^{iii}	79.16 (5)	O4^{xi}—Mn1—O1^{vii}	87.51 (6)
O1^{i}—Ba1—O3^{iv}	79.16 (5)	O4^{viii}—Mn1—O1^{xii}	87.51 (6)
O1^{ii}—Ba1—O3^{iv}	111.92 (5)	O4^{ix}—Mn1—O1^{xii}	92.49 (6)
O3^{iii}—Ba1—O3^{iv}	168.02 (7)	O4^{x}—Mn1—O1^{xii}	87.51 (6)
O1^{i}—Ba1—O3^{v}	79.16 (5)	O4^{xi}—Mn1—O1^{xii}	92.49 (6)
O1^{ii}—Ba1—O3^{v}	111.92 (5)	O1^{vii}—Mn1—O1^{xii}	180.0
O3^{iii}—Ba1—O3^{v}	74.93 (8)	O2—Mn2—O2^{xiii}	78.86 (10)
O3^{iv}—Ba1—O3^{v}	103.78 (8)	O2—Mn2—O3^{iii}	84.77 (8)
O1^{i}—Ba1—O3^{vi}	111.92 (5)	O2^{xiii}—Mn2—O3^{iii}	96.38 (8)
O1^{ii}—Ba1—O3^{vi}	79.16 (5)	O2—Mn2—O3^{ix}	96.38 (8)
O3^{iii}—Ba1—O3^{vi}	103.78 (8)	O2^{xiii}—Mn2—O3^{ix}	84.77 (8)
O3^{iv}—Ba1—O3^{vi}	74.93 (8)	O3^{iii}—Mn2—O3^{ix}	178.52 (9)

O3^{v}—Ba1—O3^{vi}	168.02 (7)	O2—Mn2—O4	169.28 (7)
O1^{i}—Ba1—O2	142.77 (4)	O2^{xiii}—Mn2—O4	107.86 (7)
O1^{ii}—Ba1—O2	142.77 (4)	O3^{iii}—Mn2—O4	86.16 (6)
O3^{iii}—Ba1—O2	63.86 (5)	O3^{ix}—Mn2—O4	92.61 (7)
O3^{iv}—Ba1—O2	104.67 (5)	O2—Mn2—O4^{x}	107.86 (7)
O3^{v}—Ba1—O2	63.86 (5)	O2^{xiii}—Mn2—O4^{x}	169.28 (7)
O3^{vi}—Ba1—O2	104.67 (5)	O3^{iii}—Mn2—O4^{x}	92.61 (7)
O1^{i}—Ba1—O2^{vii}	142.77 (4)	O3^{ix}—Mn2—O4^{x}	86.16 (6)
O1^{ii}—Ba1—O2^{vii}	142.77 (4)	O4—Mn2—O4^{x}	66.86 (9)
O3^{iii}—Ba1—O2^{vii}	104.67 (5)	O1—P1—O1^{vii}	111.94 (19)
O3^{iv}—Ba1—O2^{vii}	63.86 (5)	O1—P1—O2^{vii}	110.09 (7)
O3^{v}—Ba1—O2^{vii}	104.67 (5)	O1^{vii}—P1—O2^{vii}	110.09 (7)
O3^{vi}—Ba1—O2^{vii}	63.86 (5)	O1—P1—O2	110.09 (7)
O2—Ba1—O2^{vii}	52.33 (10)	O1^{vii}—P1—O2	110.09 (7)
O4^{viii}—Mn1—O4^{ix}	180.0	O2^{vii}—P1—O2	104.27 (19)
O4^{viii}—Mn1—O4^{x}	93.19 (10)	O3^{x}—P2—O3	113.10 (14)
O4^{ix}—Mn1—O4^{x}	86.81 (10)	O3^{x}—P2—O4^{x}	112.12 (9)
O4^{viii}—Mn1—O4^{xi}	86.81 (10)	O3—P2—O4^{x}	108.95 (10)
O4^{ix}—Mn1—O4^{xi}	93.19 (10)	O3^{x}—P2—O4	108.95 (10)
O4^{x}—Mn1—O4^{xi}	180.0	O3—P2—O4	112.12 (9)
O4^{viii}—Mn1—O1^{vii}	92.49 (6)	O4^{x}—P2—O4	100.99 (13)

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