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Redetermination of Fe₂[BP₃O₁₂]

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P}-\text{O}) = 0.004$ Å; R factor = 0.035; wR factor = 0.072; data-to-parameter ratio = 10.5.

Explorations of phases in the quaternary Fe^{III}-B^{III}-P^V-O system prepared by the high temperature solution growth (HTSG) method led to single-crystal growth of anhydrous diiron(III) borotriphosphate, Fe₂[BP₃O₁₂]. This phase has been synthesized previously as a microcrystalline material and its structure refined in space group $P3$ from powder X-ray diffraction data using the Rietveld method [Chen *et al.* (2004). *J. Inorg. Mater.* **19**, 429-432]. In the current single-crystal study, it was shown that the correct space group is $P6_3/m$. The three-dimensional structure of the title compound is built up from FeO₆ octahedra (3.. symmetry), trigonal-planar BO₃ groups ($\bar{6}$ symmetry) and PO₄ tetrahedra ($m..$ symmetry). Two FeO₆ octahedra form Fe₂O₉ dimers *via* face-sharing, while the anionic BO₃ and PO₄ groups are connected *via* corner-sharing to build up the [BP₃O₁₂]⁶⁻ anion. Both units are interconnected *via* corner-sharing.

Related literature

Reviews on the crystal chemistry of borophosphates were given by Kniep *et al.* (1998) and Ewald *et al.* (2007). For the previous powder study of Fe₂[BP₃O₁₂], see: Chen *et al.* (2004). For the structure of a related borophosphate, see: Zhao *et al.* (2009). Meisel *et al.* (2004) have reported the structure of V₂[BP₃O₁₂] and Mi *et al.* (2000) that of Cr₂[BP₃O₁₂].

Experimental

Crystal data

Fe ₂ [BP ₃ O ₁₂]	$a = 8.0347$ (8) Å
$M_r = 407.42$	$c = 7.4163$ (13) Å
Hexagonal, $P6_3/m$	$V = 414.63$ (9) Å ³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 4.15$ mm⁻¹

$T = 293$ K
 $0.15 \times 0.05 \times 0.05$ mm

Data collection

Rigaku Mercury70 CCD diffractometer	3247 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	345 independent reflections
$T_{\min} = 0.575$, $T_{\max} = 0.819$	338 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	33 parameters
$wR(F^2) = 0.072$	$\Delta\rho_{\max} = 0.58$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{\min} = -0.78$ e Å ⁻³
345 reflections	

Table 1

Selected bond lengths (Å).

Fe1—O3 ⁱ	1.929 (2)	P1—O2	1.538 (3)
Fe1—O2	2.103 (2)	P1—O1	1.586 (3)
P1—O3	1.507 (3)	O1—B1	1.357 (3)

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Data collection: *CrystalClear* (Rigaku, 2004); 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: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2377).

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Redetermination of Fe₂[BP₃O₁₂]

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Comment

The systematic development of borophosphates has led to a broad spectrum of new borophosphate compounds with quite different anionic partial structures, such as oligomeric units, chains, ribbons, layers, and three-dimensional frameworks. (Kniep *et al.*, 1998; Ewald *et al.*, 2007; Zhao *et al.*, 2009).

Most of the borophosphate compounds were synthesized under hydrothermal conditions; hence, their structures usually incorporate water molecules, hydroxy groups or organic templates. There are considerably less anhydrous borophosphate compounds known, which might have better chemical and thermal stability than the hydrous or templated phases to ensure the feasibility of industrial applications. Herein, we report the redetermined structure of the anhydrous diiron(III) borotriphosphate, Fe₂[BP₃O₁₂].

The basic building units of the three-dimensional structure of the title compound are FeO₆ octahedra (3.. symmetry), trigonal-planar BO₃ groups ($\bar{6}$ symmetry) and PO₄ tetrahedra (*m.* symmetry) (Fig. 1). Two neighboring FeO₆ octahedra are connected *via* their faces to form Fe₂O₉ dimers. Trigonal-planar BO₃ units and PO₄ tetrahedra are isolated. Each BO₃ triangle connects three PO₄ tetrahedra *via* corner-sharing O atoms and each PO₄ connects three Fe₂O₉ groups and one BO₃ group also *via* corner sharing. As shown in Fig. 2, the aforementioned groups are interconnected to form the three-dimensional framework of the title compound. Chen *et al.* (2004) have previously refined the structure of Fe₂[BP₃O₁₂] in space group *P3* using the Rietveld method. The analogous chromium compound Cr₂[BP₃O₁₂] (Mi *et al.*, 2000) is isotopic to this structure model. The differences between the previous and the current model are discussed in the *Refinement Section*. The three-dimensional frameworks of Cr₂[BP₃O₁₂] (space group *P3*) and our model of Fe₂[BP₃O₁₂] (space group *P6₃/m*) are very similar, and the differences mainly lie in the distortion of the MO₆ octahedra (*M* = Cr, Fe). The asymmetric unit of Cr₂[BP₃O₁₂] consists of four Cr atoms, and the Cr–O bond distances range from 1.88 (2) to 2.07 (2) Å, while there is only one Fe site in the asymmetric unit of Fe₂[BP₃O₁₂] with Fe–O bond distances ranging from 1.929 (2) to 2.103 (2) Å. Based on the current findings, a space group change from *P3* to *P6₃/m* seems to be most likely for the Cr compound but has to be evidenced experimentally. Meisel *et al.* (2004) have reported the analogous vanadium(III) compound V₂[BP₃O₁₂] in space group *P6₃/m*, but with a tripled unit cell (*a* of the V compound $\approx 3^{1/2} \times a$ of the Fe and Cr compounds). However, a comparison of the three structures shows very similar frameworks.

Experimental

Single crystals of Fe₂[BP₃O₁₂] have been prepared by the high temperature solution growth (HTSG) method in air. A powder mixture of Fe₂O₃, B₂O₃ and NaPO₃ at the molar ratio of Fe: B: Na: P = 1:5:10:10 was first ground in an agate mortar and then transferred to a platinum crucible. The sample was gradually heated in air at 1173 K for 24 h. In this stage, the reagents were completely melted. After that, the intermediate product was slowly cooled to 673 K at the rate of 2 K h⁻¹

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and then quenched to room temperature. The obtained crystals were light-red and of prismatic shape. The dimensions of the used sample were typical for the grown crystals in this batch.

Refinement

Chen *et al.* (2004) have refined the structure of $\text{Fe}_2[\text{BP}_3\text{O}_{12}]$ using the Rietved method from powder X-ray data and determined the space group to be $P3$, in analogy with the chromium compound $\text{Cr}_2[\text{BP}_3\text{O}_{12}]$ (Mi *et al.*, 2000). However, in our study we determined the structure from single-crystal X-ray diffraction data in the centrosymmetric space group $P6_3/m$. In the progress of the space group determination using *XPREP* (Sheldrick, 2008), the mean $|E^*E-1|$ statistics gave a value of 0.948 revealing that the structure is centrosymmetric; the CFOM (combined figure-of-merit) value for each space group determination were $P3$ (16.06), $P\bar{3}$ (7.16), $P6_3$ (7.56), $P6_3/m$ (1.75). So we selected the latter space group to solve the structure. The final refinement converged with satisfactory results ($R_1(\text{gt}) = 0.0348$). Furthermore, the final refined model was checked with the ADDSYM algorithm using the program *PLATON* (Spek, 2009), and no higher symmetry was found. Hence, our final structure model is considered to be reasonable and corrects the previous model by Chen *et al.* (2004).

The highest peak in the difference electron density map is located at a distance of 1.41 Å from the Fe1 site while the deepest hole is at a distance of 0.83 Å from the same site.

Figures



Fig. 1. Section of the structure of $\text{Fe}_2[\text{BP}_3\text{O}_{12}]$ with the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $x - y, -1 + x, 1 - z$; (iii) $y, 1 - x + y, 1 - z$; (iv) $1 - x + y, 1 - x, 0.5 - z$; (v) $1 - y, x - y, z$; (vi) $x, y, 0.5 - z$; (vii) $2 - y, 1 + x - y, z$; (viii) $1 - x + y, 2 - x, 0.5 - z$.]

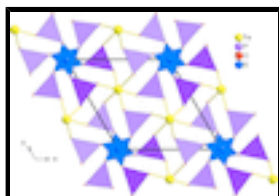


Fig. 2. View of the crystal structure of $\text{Fe}_2[\text{BP}_3\text{O}_{12}]$ in a projection along $[001]$.

diiron(III) borotriphosphate

Crystal data

$\text{Fe}_2[\text{BP}_3\text{O}_{12}]$

$M_r = 407.42$

Hexagonal, $P6_3/m$

Hall symbol: $-P\ 6c$

$a = 8.0347$ (8) Å

$c = 7.4163$ (13) Å

$V = 414.63$ (9) Å³

$Z = 2$

$F(000) = 396$

$D_x = 3.263$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1049 reflections

$\theta = 4.0\text{--}27.4^\circ$

$\mu = 4.15$ mm⁻¹

$T = 293$ K

Prism, light-red

$0.15 \times 0.05 \times 0.05$ mm

Data collection

Rigaku Mercury70 CCD diffractometer	345 independent reflections
Radiation source: fine-focus sealed tube	338 reflections with $I > 2\sigma(I)$
Graphite Monochromator	$R_{\text{int}} = 0.042$
Detector resolution: 14.6306 pixels mm^{-1}	$\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 2.9^\circ$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -10 \rightarrow 10$
$T_{\text{min}} = 0.575$, $T_{\text{max}} = 0.819$	$l = -9 \rightarrow 6$
3247 measured reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.035$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 3.P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
345 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
33 parameters	$\Delta\rho_{\text{max}} = 0.58 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.78 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.6667	0.3333	0.45190 (12)	0.0072 (3)
P1	1.04513 (17)	0.68473 (17)	0.2500	0.0064 (3)
O2	0.8735 (5)	0.4782 (5)	0.2500	0.0080 (7)
O1	0.9428 (5)	0.8099 (5)	0.2500	0.0097 (8)
B1	1.0000	1.0000	0.2500	0.0101 (19)
O3	1.1626 (3)	0.7289 (3)	0.4200 (4)	0.0115 (6)

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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0076 (3)	0.0076 (3)	0.0063 (5)	0.00381 (15)	0.000	0.000
P1	0.0055 (6)	0.0057 (6)	0.0077 (7)	0.0025 (5)	0.000	0.000
O2	0.0067 (15)	0.0059 (16)	0.0099 (19)	0.0021 (13)	0.000	0.000
O1	0.0060 (16)	0.0056 (16)	0.017 (2)	0.0022 (13)	0.000	0.000
B1	0.008 (2)	0.008 (2)	0.014 (5)	0.0040 (12)	0.000	0.000
O3	0.0116 (12)	0.0115 (12)	0.0127 (15)	0.0066 (10)	-0.0045 (11)	-0.0019 (10)

Geometric parameters (\AA , $^\circ$)

Fe1—O3 ⁱ	1.929 (2)	P1—O2	1.538 (3)
Fe1—O3 ⁱⁱ	1.929 (2)	P1—O1	1.586 (3)
Fe1—O3 ⁱⁱⁱ	1.929 (2)	O2—Fe1 ^{iv}	2.103 (2)
Fe1—O2 ^{iv}	2.103 (2)	O1—B1	1.357 (3)
Fe1—O2	2.103 (2)	B1—O1 ^{vii}	1.357 (3)
Fe1—O2 ^v	2.103 (2)	B1—O1 ^{viii}	1.357 (3)
P1—O3	1.507 (3)	O3—Fe1 ⁱ	1.929 (2)
P1—O3 ^{vi}	1.507 (3)		
O3 ⁱ —Fe1—O3 ⁱⁱ	97.83 (11)	O3—P1—O3 ^{vi}	113.6 (2)
O3 ⁱ —Fe1—O3 ⁱⁱⁱ	97.83 (11)	O3—P1—O2	111.85 (12)
O3 ⁱⁱ —Fe1—O3 ⁱⁱⁱ	97.83 (11)	O3 ^{vi} —P1—O2	111.85 (12)
O3 ⁱ —Fe1—O2 ^{iv}	93.65 (11)	O3—P1—O1	108.24 (12)
O3 ⁱⁱ —Fe1—O2 ^{iv}	91.53 (11)	O3 ^{vi} —P1—O1	108.24 (12)
O3 ⁱⁱⁱ —Fe1—O2 ^{iv}	164.04 (11)	O2—P1—O1	102.37 (18)
O3 ⁱ —Fe1—O2	91.53 (11)	P1—O2—Fe1	129.13 (10)
O3 ⁱⁱ —Fe1—O2	164.04 (11)	P1—O2—Fe1 ^{iv}	129.14 (10)
O3 ⁱⁱⁱ —Fe1—O2	93.65 (11)	Fe1—O2—Fe1 ^{iv}	90.78 (13)
O2 ^{iv} —Fe1—O2	74.92 (10)	B1—O1—P1	136.3 (3)
O3 ⁱ —Fe1—O2 ^v	164.04 (11)	O1 ^{vii} —B1—O1 ^{viii}	120.000 (1)
O3 ⁱⁱ —Fe1—O2 ^v	93.65 (11)	O1 ^{vii} —B1—O1	120.000 (1)
O3 ⁱⁱⁱ —Fe1—O2 ^v	91.53 (11)	O1 ^{viii} —B1—O1	120.000 (1)
O2 ^{iv} —Fe1—O2 ^v	74.92 (10)	P1—O3—Fe1 ⁱ	142.54 (17)
O2—Fe1—O2 ^v	74.92 (10)		

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

Fig. 1

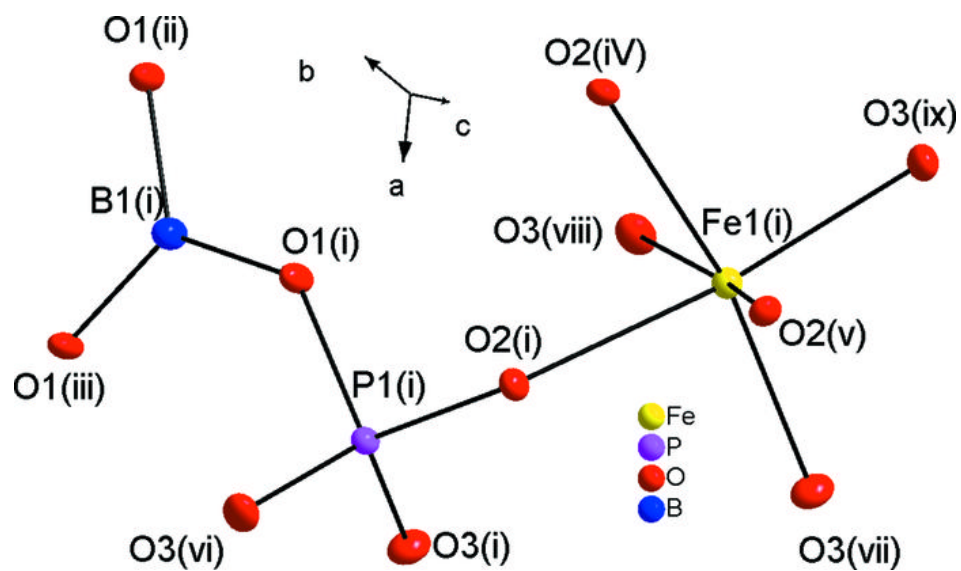


Fig. 2

