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# The iron phosphate $NaBaFe_2(PO_4)_3$

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Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(Fe–O) = 0.005 Å; disorder in main residue; $R$ factor = 0.025; $wR$ factor = 0.060; data-to-parameter ratio = 9.4.

A new iron phosphate, sodium barium diiron tris(phosphate), $NaBaFe_2(PO_4)_3$, has been synthesized by the flux method and shown to exhibit the well known langbeinite type structure. The Na, Ba and Fe atoms all lie on threefold axes, while the P and O atoms occupy general positions, one of the O atoms being disordered over two positions, with site occupancy factors of *ca* 0.7 and 0.3. The $[Fe_2(PO_4)_3]_\infty$ framework consists of $FeO_6$ octahedra sharing all their corners with the $PO_4$ tetrahedra. The $Na^+$ and $Ba^{2+}$ cations are almost equally distributed over two distinct cavities, in which they occupy slightly different positions.

## Related literature

For related literature, see: Baur (1974); Moffat (1978); Padhi *et al.* (1997); Shannon (1976). For the structure of langbeinite, see Zemann & Zemann (1957); Battle *et al.* (1986, 1988).

## Experimental

### *Crystal data*

$NaBaFe_2(PO_4)_3$
$M_r$ = 556.94
Cubic, $P2_13$
$a$ = 9.796 (1) Å
$V$ = 940.1 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 7.82 mm$^{-1}$
$T$ = 293 (2) K
0.1 × 0.1 × 0.1 mm

### *Data collection*

Enraf–Nonius CAD4 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.35, $T_{max}$ = 0.46
2114 measured reflections
657 independent reflections
644 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.082
2 standard reflections
frequency: 120 min
intensity decay: 1%

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
$S$ = 0.92
657 reflections
70 parameters
4 restraints
$\Delta\rho_{max}$ = 0.57 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$
Absolute structure: Flack (1983), 123 Friedel pairs
Flack parameter: −0.03 (3)

**Table 1**
Selected bond angles (°).

| | | | |
|---|---|---|---|
| O4$B^{i}$—Fe2—O1$^{ii}$ | 89.8 (8) | O3—P—O4$A$ | 115.1 (3) |

Symmetry codes: (i) $z, x, y$; (ii) $-z+\frac{3}{2}, -x+1, y-\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2076).

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# supporting information

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## The iron phosphate $NaBaFe_2(PO_4)_3$

**Mourad Hidouri, Hasna Jerbi and Mongi Ben Amara**

### S1. Comment

Iron phosphates are of increasing interst because of their potential applications in various fields ranging from catalysis (Moffat, 1978) to ionic conductivity (Padhi *et al.*, 1997). Moreover, these materials are very attractive in terms of basic reasearch because they exhibit a rich structural chemistry owing to the possible (+2/+3) mixed valence of iron and its tendency to exhibit various coordination polyhedra.

The title cmpound, sodium barium diiron phosphate $NaBaFe_2(PO_4)_3$ was isolated during a systematic investigation of the $Na_2O$–*M*O–$Fe_2O_3$–$P_2O_5$ systems where *M* is a divalent cation. Its structure (Fig. 1) exhibits a three-dimensional $[Fe_2(PO_4)_3]_\infty$ framework built up from corner-sharing $FeO_6$ octahedra and $PO_4$ tetrahedra. Each octahedron is linked to six adjacent tetrahedra and reciprocally each tetrahedron is connected to four neighboring octahedra. This framework delimits two sorts of large cavities, statistically occupied by the $Na^+$ and $Ba^{2+}$ cations.

The two symmetry distinct $FeO_6$ octahedra contained in this structure are somewhat distorted as indicated by the Fe—O distances ranging from 1.963 (5) to 1.991 (4) Å. The average <Fe—O> distances of 1.986 Å for Fe(1) and 1.973 Å for Fe(2) are slightly lower than the value 2.03 Å predicted by Shannon for octahedral $Fe^{3+}$ ions (Shannon, 1976).

The $PO_4$ tetrahedron is strongly distorted with P—O distances scattering from 1.47 (2) to 1.547 (7) Å. Corresponding average value of 1.511 Å agrees with those frequently observed in anhydrous monophosphates (Baur, 1974).

The $Na^+$ and $Ba^{2+}$ cations are statistically distributed over two distinct cavities in which they occupy slightly different positions and have partial occupancies of 0.47, 0.53, 0.53 and 0.47 for Na(1), Ba(1), Na(2) and Ba(2), respectively. The environments of these cations (Fig. 2) were determined assuming all cation-oxygen distances are shorter than the shortest to next cationic site. Each of the Na(1), Ba(1) and Ba(2) environments consists of nine O atoms with cation-oxygen distances in the ranges 2.76 (2)–3.04 (2) Å, 2.753 (7)–2.950 (6) Å and 2.722 (5)–3.047 (7) Å for Na(1), Ba(1) and Ba(2), respectively. The Na(2) environment consists of six O atoms with Na—O distances varying from 2.604 (8) and 3.004 (6) Å.

The as-described structure is closely related to the langbeinite-like phosphates $KBaM_2(PO_4)_3$ (*M* = Fe, Cr) (Battle *et al.*, 1986, 1988). However, it differs by the fact that the atom O4, which occupies a single site in the potassium phosphates, is, in the title compound, statistically occupying two distinct positions, O4A and O4B which exhibit partial occupancies of 0.7 and 0.3, respectively. These different values can be explained by the fact that the O4A site is occupied if it is bonded to Na(1), Ba(1) or Ba(2) whereas the O4B site is occupied if it is bonded to Na(1) or Ba(1).

### S2. Experimental

Single crystals of the title compund were grown in a flux of sodium dimolybdate $Na_2Mo_2O_7$ with an atomic ratio P:Mo = 6:1. A starting mixture of 1.071 g of $Na_2CO_3$, 1.993 g of $BaCO_3$, 8.162 g of $Fe(NO_3)_3.9H_2O$, 4.002 g of $(NH_4)_2HPO_4$ and 1.454 g of $MoO_3$ was dissolved in nitric acid and the obtained solution was evaporated to dryness. The dry residue was transferred into a platinum crucible and then heated up 600°C to decompose $H_2O$ and $NH_3$. In a second step, the sample

was melted for 1 h at 900°C and then cooled down to room temperature with a 10° $h^{-1}$ rate. The final product, obtained after washing with warm water to dissolve the flux is essentially composed of pink and prismatic shaped crystals. Their qualitative elemental analysis using electron microprobe analysis indicated the presence of Na, Ba, Fe and P and no impurity elements have been detected.

### S3. Refinement

The Ba and Fe atoms were located by direct methods and the remaining atoms were found by successive difference Fourier maps. All atomic positions were refined anisotropically.

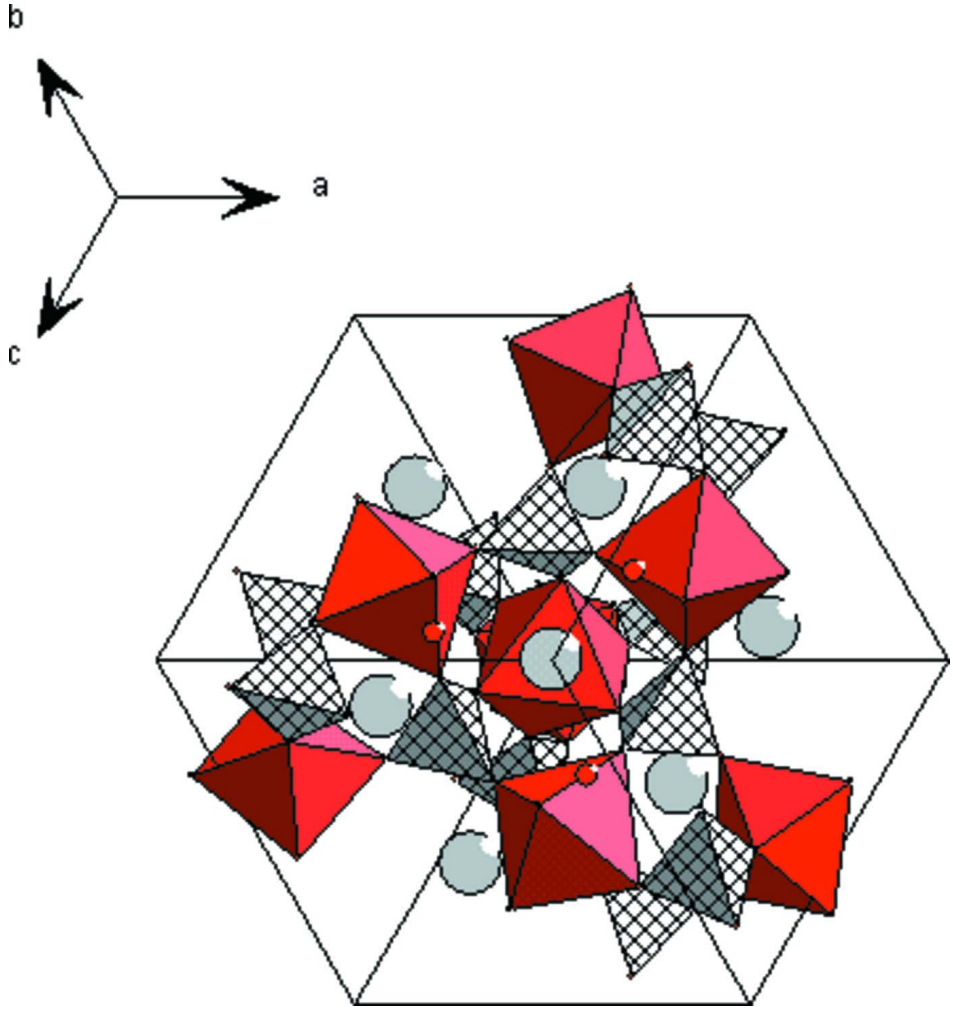


**Figure 1**

A projection of the structure along the [111] direction.

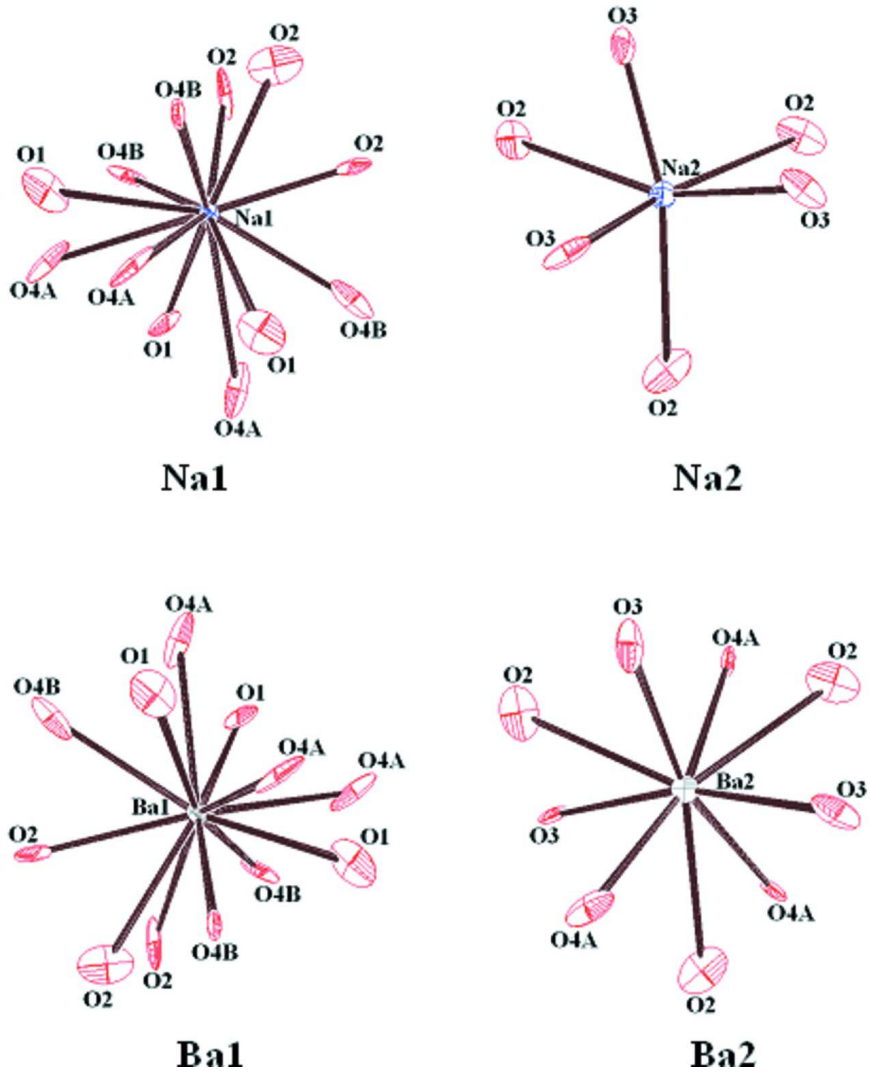


**Figure 2**

The environments of the Na and Ba sites showing the anisotropic atomic displacements at the 50% level.

**sodium barium diiron tris(phosphate)**

*Crystal data*

$NaBaFe_2(PO_4)_3$
$M_r = 556.94$
Cubic, $P2_13$
Hall symbol: P 2ac 2ab 3
$a = 9.796$ (1) Å
$V = 940.1$ (3) Å$^3$
$Z = 4$
$F(000) = 1040$
$D_x = 3.935$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.0$–$13.0°$
$\mu = 7.82$ mm$^{-1}$
$T = 293$ K
Prism, pink
0.1 × 0.1 × 0.1 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.35, $T_{max}$ = 0.46
2114 measured reflections
657 independent reflections
644 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.082
$\theta_{max}$ = 29.9°, $\theta_{min}$ = 2.9°
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 13$
2 standard reflections every 120 min
intensity decay: 1%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
$S$ = 0.92
657 reflections
70 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + 5.7579P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.57 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0145 (15)
Absolute structure: Flack (1983), with how many Friedel pairs?
Absolute structure parameter: −0.03 (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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Na1 | 0.9427 (12) | 0.9427 (12) | 0.9427 (12) | 0.0144 (3) | 0.4738 (16) |
| Ba1 | 0.92953 (9) | 0.92953 (9) | 0.92953 (9) | 0.0144 (3) | 0.5262 (16) |
| Na2 | 0.6862 (8) | 0.6862 (8) | 0.6862 (8) | 0.0232 (4) | 0.5262 (16) |
| Ba2 | 0.70555 (8) | 0.70555 (8) | 0.70555 (8) | 0.0232 (4) | 0.4738 (16) |
| Fe1 | 0.35313 (6) | 0.85313 (6) | 0.64687 (6) | 0.0104 (2) | |
| Fe2 | 0.91362 (6) | 0.08638 (6) | 0.58638 (6) | 0.0101 (2) | |
| P | 0.03742 (10) | 0.77099 (11) | 0.62578 (10) | 0.0068 (2) | |
| O1 | 0.9926 (5) | 0.9134 (4) | 0.6562 (7) | 0.0461 (14) | |
| O2 | 0.9463 (5) | 0.6999 (6) | 0.5243 (5) | 0.0440 (13) | |
| O3 | 0.1846 (4) | 0.7653 (6) | 0.5752 (5) | 0.0368 (12) | |
| O4A | 0.0112 (7) | 0.6985 (10) | 0.7629 (8) | 0.0389 (18) | 0.701 (4) |
| O4B | 0.0527 (17) | 0.672 (2) | 0.738 (2) | 0.0389 (18) | 0.299 (4) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Na1 | 0.0144 (3) | 0.0144 (3) | 0.0144 (3) | −0.0019 (3) | −0.0019 (3) | −0.0019 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ba1 | 0.0144 (3) | 0.0144 (3) | 0.0144 (3) | −0.0019 (3) | −0.0019 (3) | −0.0019 (3) |
| Na2 | 0.0232 (4) | 0.0232 (4) | 0.0232 (4) | 0.0016 (3) | 0.0016 (3) | 0.0016 (3) |
| Ba2 | 0.0232 (4) | 0.0232 (4) | 0.0232 (4) | 0.0016 (3) | 0.0016 (3) | 0.0016 (3) |
| Fe1 | 0.0104 (2) | 0.0104 (2) | 0.0104 (2) | 0.0001 (2) | −0.0001 (2) | −0.0001 (2) |
| Fe2 | 0.0101 (2) | 0.0101 (2) | 0.0101 (2) | 0.0024 (2) | 0.0024 (2) | −0.0024 (2) |
| P | 0.0066 (4) | 0.0073 (4) | 0.0064 (4) | −0.0005 (3) | −0.0028 (3) | 0.0010 (3) |
| O1 | 0.045 (3) | 0.0170 (19) | 0.076 (4) | 0.0191 (19) | −0.015 (3) | −0.015 (2) |
| O2 | 0.029 (2) | 0.061 (3) | 0.042 (3) | 0.003 (2) | −0.025 (2) | −0.031 (2) |
| O3 | 0.0120 (16) | 0.063 (3) | 0.035 (2) | −0.0091 (18) | 0.0085 (16) | −0.023 (2) |
| O4A | 0.020 (4) | 0.066 (5) | 0.031 (3) | 0.020 (3) | 0.015 (3) | 0.040 (3) |
| O4B | 0.020 (4) | 0.066 (5) | 0.031 (3) | 0.020 (3) | 0.015 (3) | 0.040 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Na1—O1$^{i}$ | 2.864 (12) | Ba2—O3$^{xiii}$ | 2.772 (5) |
| Na1—O1 | 2.864 (12) | Ba2—O3$^{xiv}$ | 2.772 (5) |
| Na1—O1$^{ii}$ | 2.864 (12) | Ba2—O2$^{ii}$ | 2.952 (5) |
| Na1—O4B$^{iii}$ | 2.86 (3) | Ba2—O2 | 2.952 (5) |
| Na1—O4B$^{iv}$ | 2.86 (3) | Ba2—O2$^{i}$ | 2.952 (5) |
| Na1—O4B$^{v}$ | 2.86 (3) | Ba2—O4A$^{vi}$ | 3.047 (7) |
| Na1—O4A$^{vi}$ | 3.045 (17) | Ba2—O4A$^{vii}$ | 3.047 (7) |
| Na1—O4A$^{vii}$ | 3.045 (17) | Ba2—O4A$^{viii}$ | 3.047 (7) |
| Na1—O4A$^{viii}$ | 3.045 (17) | Fe1—O2$^{ii}$ | 1.979 (4) |
| Na1—O2$^{ix}$ | 2.763 (17) | Fe1—O2$^{xv}$ | 1.979 (4) |
| Na1—O2$^{x}$ | 2.763 (17) | Fe1—O2$^{xvi}$ | 1.979 (4) |
| Na1—O2$^{xi}$ | 2.763 (17) | Fe1—O3$^{xiii}$ | 1.990 (4) |
| Ba1—O1$^{i}$ | 2.753 (7) | Fe1—O3 | 1.990 (4) |
| Ba1—O1 | 2.753 (7) | Fe1—O3$^{xvii}$ | 1.990 (4) |
| Ba1—O1$^{ii}$ | 2.753 (7) | Fe1—Ba1$^{xviii}$ | 3.6878 (19) |
| Ba1—O4B$^{iii}$ | 2.89 (3) | Fe1—Ba2$^{iv}$ | 3.7867 (6) |
| Ba1—O4B$^{iv}$ | 2.89 (3) | Fe1—Ba2$^{xv}$ | 3.7867 (6) |
| Ba1—O4B$^{v}$ | 2.89 (3) | Fe2—O4B$^{xix}$ | 1.946 (18) |
| Ba1—O4A$^{vi}$ | 2.902 (10) | Fe2—O4B$^{ii}$ | 1.946 (18) |
| Ba1—O4A$^{vii}$ | 2.902 (10) | Fe2—O4B$^{xii}$ | 1.946 (18) |
| Ba1—O4A$^{viii}$ | 2.902 (10) | Fe2—O1$^{xx}$ | 1.984 (5) |
| Ba1—O2$^{ix}$ | 2.950 (6) | Fe2—O1$^{xxi}$ | 1.984 (5) |
| Ba1—O2$^{x}$ | 2.950 (6) | Fe2—O1$^{xxii}$ | 1.984 (5) |
| Ba1—O2$^{xi}$ | 2.950 (6) | Fe2—O4A$^{xix}$ | 1.982 (7) |
| Na2—O3$^{xii}$ | 2.604 (8) | Fe2—O4A$^{ii}$ | 1.982 (7) |
| Na2—O3$^{xiii}$ | 2.604 (8) | Fe2—O4A$^{xii}$ | 1.982 (7) |
| Na2—O3$^{xiv}$ | 2.604 (8) | P—O4B | 1.470 (18) |
| Na2—O2 | 3.004 (6) | P—O1$^{xxiii}$ | 1.493 (4) |
| Na2—O2$^{i}$ | 3.004 (6) | P—O2$^{xxiii}$ | 1.506 (4) |
| Na2—O2$^{ii}$ | 3.004 (6) | P—O3 | 1.526 (4) |
| Ba2—O3$^{xii}$ | 2.772 (5) | P—O4A | 1.541 (7) |
| | | | |
| O1$^{i}$—Na1—O1 | 94.9 (5) | O2$^{ix}$—Ba1—O2$^{xi}$ | 55.17 (13) |
| O1$^{i}$—Na1—O1$^{ii}$ | 94.9 (5) | O2$^{x}$—Ba1—O2$^{xi}$ | 55.17 (13) |

| | | | |
|---|---|---|---|
| O1—Na1—O1$^{ii}$ | 94.9 (5) | O3$^{xii}$—Na2—O3$^{xiii}$ | 100.1 (3) |
| O1$^{i}$—Na1—O4B$^{iii}$ | 58.0 (4) | O3$^{xii}$—Na2—O3$^{xiv}$ | 100.1 (3) |
| O1—Na1—O4B$^{iii}$ | 79.6 (4) | O3$^{xiii}$—Na2—O3$^{xiv}$ | 100.1 (3) |
| O1$^{ii}$—Na1—O4B$^{iii}$ | 151.3 (7) | O3$^{xii}$—Na2—O2 | 83.46 (16) |
| O1$^{i}$—Na1—O4B$^{iv}$ | 151.3 (7) | O3$^{xiii}$—Na2—O2 | 158.5 (4) |
| O1—Na1—O4B$^{iv}$ | 58.0 (4) | O3$^{xiv}$—Na2—O2 | 58.53 (12) |
| O1$^{ii}$—Na1—O4B$^{iv}$ | 79.6 (4) | O3$^{xii}$—Na2—O2$^{i}$ | 58.53 (12) |
| O4B$^{iii}$—Na1—O4B$^{iv}$ | 118.89 (19) | O3$^{xiii}$—Na2—O2$^{i}$ | 83.46 (16) |
| O1$^{i}$—Na1—O4B$^{v}$ | 79.6 (4) | O3$^{xiv}$—Na2—O2$^{i}$ | 158.5 (4) |
| O1—Na1—O4B$^{v}$ | 151.3 (7) | O2—Na2—O2$^{i}$ | 115.68 (18) |
| O1$^{ii}$—Na1—O4B$^{v}$ | 58.0 (4) | O3$^{xii}$—Na2—O2$^{ii}$ | 158.5 (4) |
| O4B$^{iii}$—Na1—O4B$^{v}$ | 118.89 (19) | O3$^{xiii}$—Na2—O2$^{ii}$ | 58.53 (12) |
| O4B$^{iv}$—Na1—O4B$^{v}$ | 118.89 (19) | O3$^{xiv}$—Na2—O2$^{ii}$ | 83.46 (16) |
| O1$^{i}$—Na1—O4A$^{vi}$ | 46.9 (2) | O2—Na2—O2$^{ii}$ | 115.68 (18) |
| O1—Na1—O4A$^{vi}$ | 107.0 (6) | O2$^{i}$—Na2—O2$^{ii}$ | 115.68 (18) |
| O1$^{ii}$—Na1—O4A$^{vi}$ | 49.5 (3) | O3$^{xii}$—Ba2—O3$^{xiii}$ | 92.09 (15) |
| O1$^{i}$—Na1—O4A$^{vii}$ | 49.5 (3) | O3$^{xii}$—Ba2—O3$^{xiv}$ | 92.09 (15) |
| O1—Na1—O4A$^{vii}$ | 46.9 (2) | O3$^{xiii}$—Ba2—O3$^{xiv}$ | 92.09 (15) |
| O1$^{ii}$—Na1—O4A$^{vii}$ | 107.0 (6) | O3$^{xii}$—Ba2—O2$^{ii}$ | 148.54 (14) |
| O1$^{i}$—Na1—O4A$^{viii}$ | 107.0 (6) | O3$^{xiii}$—Ba2—O2$^{ii}$ | 57.63 (12) |
| O1—Na1—O4A$^{viii}$ | 49.5 (3) | O3$^{xiv}$—Ba2—O2$^{ii}$ | 81.64 (14) |
| O1$^{ii}$—Na1—O4A$^{viii}$ | 46.9 (2) | O3$^{xii}$—Ba2—O2 | 81.64 (14) |
| O4A$^{vi}$—Na1—O4A$^{viii}$ | 81.1 (5) | O3$^{xiii}$—Ba2—O2 | 148.54 (14) |
| O4A$^{vii}$—Na1—O4A$^{viii}$ | 81.1 (5) | O3$^{xiv}$—Ba2—O2 | 57.63 (12) |
| O1$^{i}$—Na1—O2$^{ix}$ | 97.97 (19) | O2$^{ii}$—Ba2—O2 | 118.95 (3) |
| O1—Na1—O2$^{ix}$ | 104.0 (2) | O3$^{xii}$—Ba2—O2$^{i}$ | 57.63 (12) |
| O1$^{ii}$—Na1—O2$^{ix}$ | 156.0 (6) | O3$^{xiii}$—Ba2—O2$^{i}$ | 81.64 (14) |
| O4B$^{iv}$—Na1—O2$^{ix}$ | 97.9 (6) | O3$^{xiv}$—Ba2—O2$^{i}$ | 148.54 (14) |
| O4B$^{v}$—Na1—O2$^{ix}$ | 104.6 (6) | O2$^{ii}$—Ba2—O2$^{i}$ | 118.95 (3) |
| O4A$^{vi}$—Na1—O2$^{ix}$ | 134.2 (2) | O2—Ba2—O2$^{i}$ | 118.95 (3) |
| O4A$^{vii}$—Na1—O2$^{ix}$ | 96.81 (16) | O3$^{xii}$—Ba2—O4A$^{vi}$ | 104.95 (16) |
| O4A$^{viii}$—Na1—O2$^{ix}$ | 144.2 (3) | O3$^{xiii}$—Ba2—O4A$^{vi}$ | 83.7 (2) |
| O1$^{i}$—Na1—O2$^{x}$ | 156.0 (6) | O3$^{xiv}$—Ba2—O4A$^{vi}$ | 162.54 (16) |
| O1—Na1—O2$^{x}$ | 97.97 (19) | O2$^{ii}$—Ba2—O4A$^{vi}$ | 81.80 (17) |
| O1$^{ii}$—Na1—O2$^{x}$ | 104.0 (2) | O2—Ba2—O4A$^{vi}$ | 127.8 (2) |
| O4B$^{iii}$—Na1—O2$^{x}$ | 104.6 (6) | O2$^{i}$—Ba2—O4A$^{vi}$ | 47.59 (16) |
| O4B$^{iv}$—Na1—O2$^{x}$ | 49.4 (4) | O3$^{xii}$—Ba2—O4A$^{vii}$ | 83.7 (2) |
| O4B$^{v}$—Na1—O2$^{x}$ | 97.9 (6) | O3$^{xiii}$—Ba2—O4A$^{vii}$ | 162.54 (16) |
| O4A$^{vi}$—Na1—O2$^{x}$ | 144.2 (3) | O3$^{xiv}$—Ba2—O4A$^{vii}$ | 104.95 (16) |
| O4A$^{vii}$—Na1—O2$^{x}$ | 134.2 (2) | O2$^{ii}$—Ba2—O4A$^{vii}$ | 127.8 (2) |
| O4A$^{viii}$—Na1—O2$^{x}$ | 96.81 (16) | O2—Ba2—O4A$^{vii}$ | 47.59 (16) |
| O2$^{ix}$—Na1—O2$^{x}$ | 59.2 (4) | O2$^{i}$—Ba2—O4A$^{vii}$ | 81.80 (17) |
| O1$^{i}$—Na1—O2$^{xi}$ | 104.0 (2) | O4A$^{vi}$—Ba2—O4A$^{vii}$ | 81.1 (3) |
| O1—Na1—O2$^{xi}$ | 156.0 (6) | O3$^{xii}$—Ba2—O4A$^{viii}$ | 162.54 (17) |
| O1$^{ii}$—Na1—O2$^{xi}$ | 97.97 (19) | O3$^{xiii}$—Ba2—O4A$^{viii}$ | 104.95 (16) |
| O4B$^{iii}$—Na1—O2$^{xi}$ | 97.9 (6) | O3$^{xiv}$—Ba2—O4A$^{viii}$ | 83.7 (2) |
| O4B$^{iv}$—Na1—O2$^{xi}$ | 104.6 (6) | O2$^{ii}$—Ba2—O4A$^{viii}$ | 47.59 (16) |
| O4A$^{vi}$—Na1—O2$^{xi}$ | 96.81 (16) | O2—Ba2—O4A$^{viii}$ | 81.80 (17) |

| | | | |
|---|---|---|---|
| O4A$^{vii}$—Na1—O2$^{xi}$ | 144.2 (3) | O2$^{i}$—Ba2—O4A$^{viii}$ | 127.8 (2) |
| O4A$^{viii}$—Na1—O2$^{xi}$ | 134.2 (2) | O4A$^{vi}$—Ba2—O4A$^{viii}$ | 81.1 (3) |
| O2$^{ix}$—Na1—O2$^{xi}$ | 59.2 (4) | O4A$^{vii}$—Ba2—O4A$^{viii}$ | 81.1 (3) |
| O2$^{x}$—Na1—O2$^{xi}$ | 59.2 (4) | O2$^{ii}$—Fe1—O2$^{xv}$ | 87.3 (2) |
| O1$^{i}$—Ba1—O1 | 100.10 (14) | O2$^{ii}$—Fe1—O2$^{xvi}$ | 87.3 (2) |
| O1$^{i}$—Ba1—O1$^{ii}$ | 100.10 (14) | O2$^{xv}$—Fe1—O2$^{xvi}$ | 87.3 (2) |
| O1—Ba1—O1$^{ii}$ | 100.10 (14) | O2$^{ii}$—Fe1—O3$^{xiii}$ | 88.26 (18) |
| O1$^{i}$—Ba1—O4B$^{iii}$ | 58.8 (4) | O2$^{xv}$—Fe1—O3$^{xiii}$ | 89.2 (2) |
| O1—Ba1—O4B$^{iii}$ | 80.9 (4) | O2$^{xvi}$—Fe1—O3$^{xiii}$ | 174.5 (2) |
| O1$^{ii}$—Ba1—O4B$^{iii}$ | 158.5 (4) | O2$^{ii}$—Fe1—O3 | 174.5 (2) |
| O1$^{i}$—Ba1—O4B$^{iv}$ | 158.5 (4) | O2$^{xv}$—Fe1—O3 | 88.26 (18) |
| O1—Ba1—O4B$^{iv}$ | 58.8 (4) | O2$^{xvi}$—Fe1—O3 | 89.2 (2) |
| O1$^{ii}$—Ba1—O4B$^{iv}$ | 80.9 (4) | O3$^{xiii}$—Fe1—O3 | 95.0 (2) |
| O4B$^{iii}$—Ba1—O4B$^{iv}$ | 116.8 (2) | O2$^{ii}$—Fe1—O3$^{xvii}$ | 89.2 (2) |
| O1$^{i}$—Ba1—O4B$^{v}$ | 80.9 (4) | O2$^{xv}$—Fe1—O3$^{xvii}$ | 174.5 (2) |
| O1—Ba1—O4B$^{v}$ | 158.5 (4) | O2$^{xvi}$—Fe1—O3$^{xvii}$ | 88.26 (18) |
| O1$^{ii}$—Ba1—O4B$^{v}$ | 58.8 (4) | O3$^{xiii}$—Fe1—O3$^{xvii}$ | 95.0 (2) |
| O4B$^{iii}$—Ba1—O4B$^{v}$ | 116.8 (2) | O3—Fe1—O3$^{xvii}$ | 95.0 (2) |
| O4B$^{iv}$—Ba1—O4B$^{v}$ | 116.8 (2) | O4B$^{xix}$—Fe2—O4B$^{ii}$ | 80.8 (9) |
| O1$^{i}$—Ba1—O4A$^{vi}$ | 49.19 (16) | O4B$^{xix}$—Fe2—O4B$^{xii}$ | 80.8 (9) |
| O1—Ba1—O4A$^{vi}$ | 114.25 (19) | O4B$^{ii}$—Fe2—O4B$^{xii}$ | 80.8 (9) |
| O1$^{ii}$—Ba1—O4A$^{vi}$ | 51.94 (17) | O4B$^{xix}$—Fe2—O1$^{xx}$ | 169.5 (6) |
| O1$^{i}$—Ba1—O4A$^{vii}$ | 51.94 (17) | O4B$^{ii}$—Fe2—O1$^{xx}$ | 89.8 (8) |
| O1—Ba1—O4A$^{vii}$ | 49.19 (16) | O4B$^{xii}$—Fe2—O1$^{xx}$ | 93.0 (5) |
| O1$^{ii}$—Ba1—O4A$^{vii}$ | 114.25 (19) | O4B$^{xix}$—Fe2—O1$^{xxi}$ | 93.0 (5) |
| O1$^{i}$—Ba1—O4A$^{viii}$ | 114.25 (19) | O4B$^{ii}$—Fe2—O1$^{xxi}$ | 169.5 (6) |
| O1—Ba1—O4A$^{viii}$ | 51.94 (17) | O4B$^{xii}$—Fe2—O1$^{xxi}$ | 89.8 (8) |
| O1$^{ii}$—Ba1—O4A$^{viii}$ | 49.19 (16) | O1$^{xx}$—Fe2—O1$^{xxi}$ | 95.5 (3) |
| O4A$^{vi}$—Ba1—O4A$^{viii}$ | 86.1 (2) | O4B$^{xix}$—Fe2—O1$^{xxii}$ | 89.8 (8) |
| O4A$^{vii}$—Ba1—O4A$^{viii}$ | 86.1 (2) | O4B$^{ii}$—Fe2—O1$^{xxii}$ | 93.0 (5) |
| O1$^{i}$—Ba1—O2$^{ix}$ | 96.20 (14) | O4B$^{xii}$—Fe2—O1$^{xxii}$ | 169.5 (6) |
| O1—Ba1—O2$^{ix}$ | 102.04 (15) | O1$^{xx}$—Fe2—O1$^{xxii}$ | 95.5 (3) |
| O1$^{ii}$—Ba1—O2$^{ix}$ | 149.64 (14) | O1$^{xxi}$—Fe2—O1$^{xxii}$ | 95.5 (3) |
| O4B$^{iii}$—Ba1—O2$^{ix}$ | 47.5 (4) | O1$^{xx}$—Fe2—O4A$^{xix}$ | 168.6 (3) |
| O4B$^{iv}$—Ba1—O2$^{ix}$ | 93.1 (4) | O1$^{xxi}$—Fe2—O4A$^{xix}$ | 77.4 (3) |
| O4B$^{v}$—Ba1—O2$^{ix}$ | 99.2 (4) | O1$^{xxii}$—Fe2—O4A$^{xix}$ | 94.1 (3) |
| O4A$^{vi}$—Ba1—O2$^{ix}$ | 132.27 (18) | O4B$^{xix}$—Fe2—O4A$^{ii}$ | 78.2 (6) |
| O4A$^{vii}$—Ba1—O2$^{ix}$ | 95.97 (17) | O4B$^{ii}$—Fe2—O4A$^{ii}$ | 15.9 (5) |
| O4A$^{viii}$—Ba1—O2$^{ix}$ | 141.66 (18) | O4B$^{xii}$—Fe2—O4A$^{ii}$ | 95.9 (8) |
| O1$^{i}$—Ba1—O2$^{x}$ | 149.64 (14) | O1$^{xx}$—Fe2—O4A$^{ii}$ | 94.1 (3) |
| O1—Ba1—O2$^{x}$ | 96.20 (14) | O1$^{xxi}$—Fe2—O4A$^{ii}$ | 168.6 (3) |
| O1$^{ii}$—Ba1—O2$^{x}$ | 102.04 (15) | O1$^{xxii}$—Fe2—O4A$^{ii}$ | 77.4 (3) |
| O4B$^{iii}$—Ba1—O2$^{x}$ | 99.2 (4) | O4A$^{xix}$—Fe2—O4A$^{ii}$ | 94.0 (3) |
| O4B$^{iv}$—Ba1—O2$^{x}$ | 47.5 (4) | O1$^{xx}$—Fe2—O4A$^{xii}$ | 77.4 (3) |
| O4B$^{v}$—Ba1—O2$^{x}$ | 93.1 (4) | O1$^{xxi}$—Fe2—O4A$^{xii}$ | 94.1 (3) |
| O4A$^{vi}$—Ba1—O2$^{x}$ | 141.66 (18) | O1$^{xxii}$—Fe2—O4A$^{xii}$ | 168.6 (3) |
| O4A$^{vii}$—Ba1—O2$^{x}$ | 132.27 (18) | O4A$^{xix}$—Fe2—O4A$^{xii}$ | 94.0 (3) |
| O4A$^{viii}$—Ba1—O2$^{x}$ | 95.97 (17) | O4A$^{ii}$—Fe2—O4A$^{xii}$ | 94.0 (3) |

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|---|---|---|---|
| O2$^{ix}$—Ba1—O2$^{x}$ | 55.17 (13) | O4B—P—O1$^{xxiii}$ | 119.9 (10) |
| O1$^{i}$—Ba1—O2$^{xi}$ | 102.04 (15) | O4B—P—O2$^{xxiii}$ | 104.3 (11) |
| O1—Ba1—O2$^{xi}$ | 149.64 (14) | O1$^{xxiii}$—P—O2$^{xxiii}$ | 112.9 (3) |
| O1$^{ii}$—Ba1—O2$^{xi}$ | 96.20 (14) | O4B—P—O3 | 97.0 (6) |
| O4B$^{iii}$—Ba1—O2$^{xi}$ | 93.1 (4) | O1$^{xxiii}$—P—O3 | 112.2 (3) |
| O4B$^{iv}$—Ba1—O2$^{xi}$ | 99.2 (4) | O2$^{xxiii}$—P—O3 | 109.2 (3) |
| O4B$^{v}$—Ba1—O2$^{xi}$ | 47.5 (4) | O4B—P—O4A | 20.6 (6) |
| O4A$^{vi}$—Ba1—O2$^{xi}$ | 95.97 (16) | O1$^{xxiii}$—P—O4A | 102.0 (4) |
| O4A$^{vii}$—Ba1—O2$^{xi}$ | 141.66 (18) | O2$^{xxiii}$—P—O4A | 105.3 (4) |
| O4A$^{viii}$—Ba1—O2$^{xi}$ | 132.27 (18) | O3—P—O4A | 115.1 (3) |

Symmetry codes: (i) *y*, *z*, *x*; (ii) *z*, *x*, *y*; (iii) *y*+1/2, −*z*+3/2, −*x*+1; (iv) −*x*+1, *y*+1/2, −*z*+3/2; (v) −*z*+3/2, −*x*+1, *y*+1/2; (vi) *y*, *z*, *x*+1; (vii) *x*+1, *y*, *z*; (viii) *z*, *x*+1, *y*; (ix) *y*+1/2, −*z*+3/2, −*x*+2; (x) −*x*+2, *y*+1/2, −*z*+3/2; (xi) −*z*+3/2, −*x*+2, *y*+1/2; (xii) −*y*+3/2, −*z*+1, *x*+1/2; (xiii) −*z*+1, *x*+1/2, −*y*+3/2; (xiv) *x*+1/2, −*y*+3/2, −*z*+1; (xv) *x*−1/2, −*y*+3/2, −*z*+1; (xvi) −*y*+1, *z*+1/2, −*x*+3/2; (xvii) *y*−1/2, −*z*+3/2, −*x*+1; (xviii) −*x*+3/2, −*y*+2, *z*−1/2; (xix) −*x*+1, *y*−1/2, −*z*+3/2; (xx) −*z*+3/2, −*x*+1, *y*−1/2; (xxi) −*y*+2, *z*−1/2, −*x*+3/2; (xxii) *x*, *y*−1, *z*; (xxiii) *x*−1, *y*, *z*.