



# Synthesis and crystal structure of cerium(IV) bis(phosphite)

Stefano H. Byer and Eric M. Villa\*

Department of Chemistry, Creighton University, 2500 California Plaza, Omaha, Nebraska 68178, USA. \*Correspondence e-mail: ericvilla@creighton.edu

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The structure of cerium(IV) bis(phosphite),  $\text{Ce}(\text{HPO}_3)_2$ , has been solved by single-crystal X-ray diffraction and has trigonal ( $P\bar{3}m1$ ) symmetry. The cerium(IV) cation exhibits site symmetry  $\bar{3}m$  and is octahedrally coordinated by O atoms of the phosphite ligands (point group symmetry  $3m$ ). The highly symmetrical compound has a layered structure parallel to the  $ab$  plane, and is closely related to zirconium(IV) bis(phosphite) solved *via* powder X-ray diffraction with trigonal ( $P\bar{3}$ ) symmetry. Structural details of the two compounds are comparatively discussed.

## 1. Chemical context

Phosphonates are commonly employed within the petroleum industry as antioxidants. Interactions between these antioxidants and possible metal impurities could potentially have unintended consequences in the processing of petroleum products. We are currently studying these interactions by exploring the crystalline materials formed *via* solvothermal syntheses of lanthanides with phosphorous acid.

Phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is a powerful reducing agent and is exceedingly water soluble. The anion  $\text{HPO}_3^{2-}$  has many different names in the literature, including (but not limited to) phosphite, phosphonate, phosphorus(III) oxoanion, oxophosphate(III) and hydridotrioxidophosphate(2-). According to IUPAC, when the hydrogen atom is directly bonded to the phosphorus atom, it is to be named phosphonate; whereas when the anion tautomerizes to the  $\text{PO}_2(\text{OH})^{2-}$  anion, it is named as phosphite. However, the latter ion is rarely identified in the solid state. While IUPAC prefers  $\text{HPO}_3^{2-}$  to be named phosphonate, this name is also used for organophosphorus compounds with the general formula  $R\text{-PO}(\text{OH})_2$  or  $R\text{-PO}(\text{OR})_2$ , where  $R$  = alkyl or aryl groups. To eliminate any confusion with organophosphorus compounds and to be consistent with the recent literature, we will herein refer to the  $\text{HPO}_3^{2-}$  anion as phosphite.

The phosphite anion has many structural similarities to both phosphates and organophosphonates. In the phosphite anion, a hydrogen atom has replaced one of the oxygen atoms, which would be found in phosphate; also, the phosphite anion contains no P—C bonds that are found in phosphonates. Phosphite itself can be used as a precursor for making a vast array of phosphonates. In phosphite, the central phosphorus atom is  $\text{P}^{\text{III}}$  instead of the more air-stable  $\text{P}^{\text{V}}$ , which provides the opportunity for redox chemistry. This ability to act as a reducing agent has led to several mixed-valent uranium compounds (Villa *et al.*, 2012; Villa, Marr *et al.*, 2013; Villa,

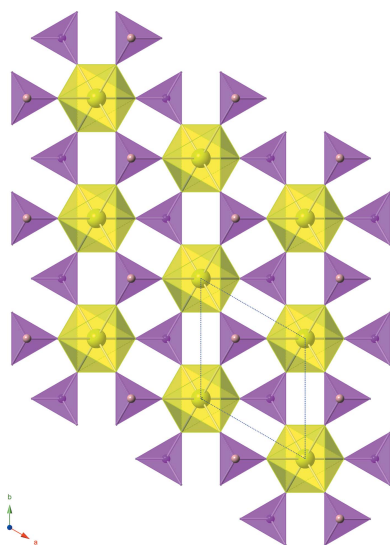


Table 1

Comparison of bond lengths and angles ( $\text{\AA}$ ,  $^\circ$ ) in  $\text{Ce}(\text{HPO}_3)_2$  ( $P\bar{3}m1$ ) and  $\text{Zr}(\text{HPO}_3)_2$  ( $P\bar{3}$ ).

| Bond lengths | $\text{Ce}(\text{HPO}_3)_2$ | $\text{Zr}(\text{HPO}_3)_2$ | bond angles | $\text{Ce}(\text{HPO}_3)_2$ | $\text{Zr}(\text{HPO}_3)_2$ |
|--------------|-----------------------------|-----------------------------|-------------|-----------------------------|-----------------------------|
| Metal—O      | 2.2193 (19)                 | 2.05 (2)                    | O—metal—O   | 88.85 (8), 91.15 (8)        | 89.2 (4), 90.8 (4)          |
| P—O          | 1.5168 (19)                 | 1.52 (1)                    | metal—O—P   | 162.28 (14)                 | 162.1 (3)                   |
| P—H          | 1.44 (6)                    | 1.43 (fixed)                | O—P—O       | 112.07 (8)                  | 111.2 (5)                   |
|              |                             |                             | O—P—H       | 106.73 (9)                  | 107.6 (6)                   |

$\text{Zr}(\text{HPO}_3)_2$  data from Millini *et al.* (1993).

Alekseev *et al.*, 2013). Moving towards the lanthanides, lanthanide phosphite compounds have been synthesized in one of two main ways: hydrothermally (Cross *et al.*, 2012; Ewald *et al.*, 2003, 2005; Foulon *et al.*, 1993*a,b*, 1995; Loukili *et al.*, 1988, 1991; Tijani *et al.*, 1988; Xiong *et al.*, 2006, 2009; Zhang *et al.*, 1992) and phosphite flux reactions (Zakharova *et al.*, 2003). We have expanded this chemistry by exploring solvothermal syntheses of lanthanide phosphites. Herein we will discuss the crystal structure of the title compound, a new cerium(IV) bis(phosphite).

## 2. Structural commentary

The title compound  $\text{Ce}(\text{HPO}_3)_2$  crystallizes in the space group  $P\bar{3}m1$ . The smallest repeating unit contains one cerium(IV), one oxygen, one phosphorus(III) and one hydrogen atom. This simple structure contains slightly distorted octahedrally coordinated cerium(IV) cations (site symmetry  $\bar{3}m$ ; Fig. 1), which are linked together by corner-sharing phosphite ligands. These phosphite ligands have a slightly distorted tetrahedral

configuration (point group symmetry  $3m$ ). Each phosphorus(III) atom in the phosphite ligand is bonded to three oxygen atoms, comprising the bottom of the tetrahedron, and one hydrogen atom. The sheets of  $\text{Ce}(\text{HPO}_3)_2$ , which are located in the  $ab$  plane, contain alternating up-down phosphite ligands around the cerium(IV) metal cation, as indicated by the different directions of the hydrogen atoms (Figs. 2, 3). These sheets are layered down the  $c$  axis, where each cerium(IV) atom resides directly below the cerium above it at a distance of 5.6099 (3)  $\text{\AA}$ , which corresponds to the length of

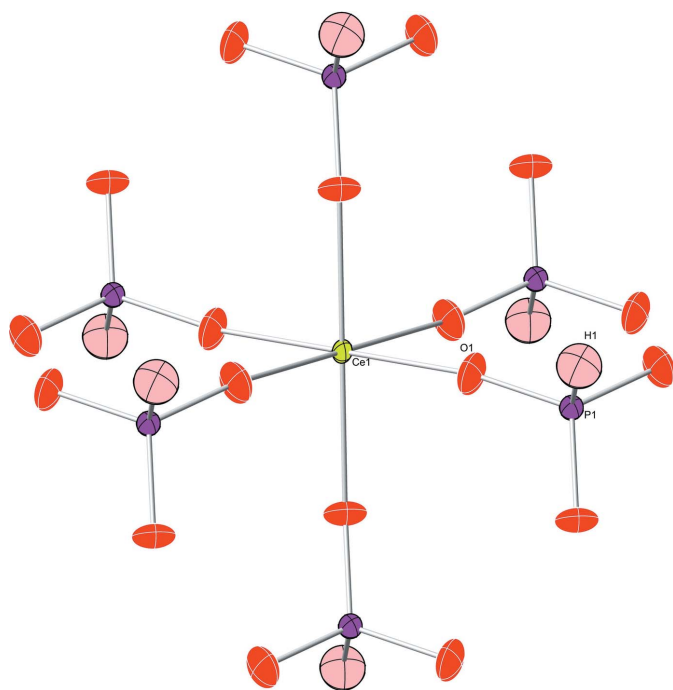


Figure 1

The coordination sphere of the cerium(IV) atom with atoms of the asymmetric unit labelled. Displacement ellipsoids are drawn at the 50% probability level. Bond lengths and angles can be found in Table 1.

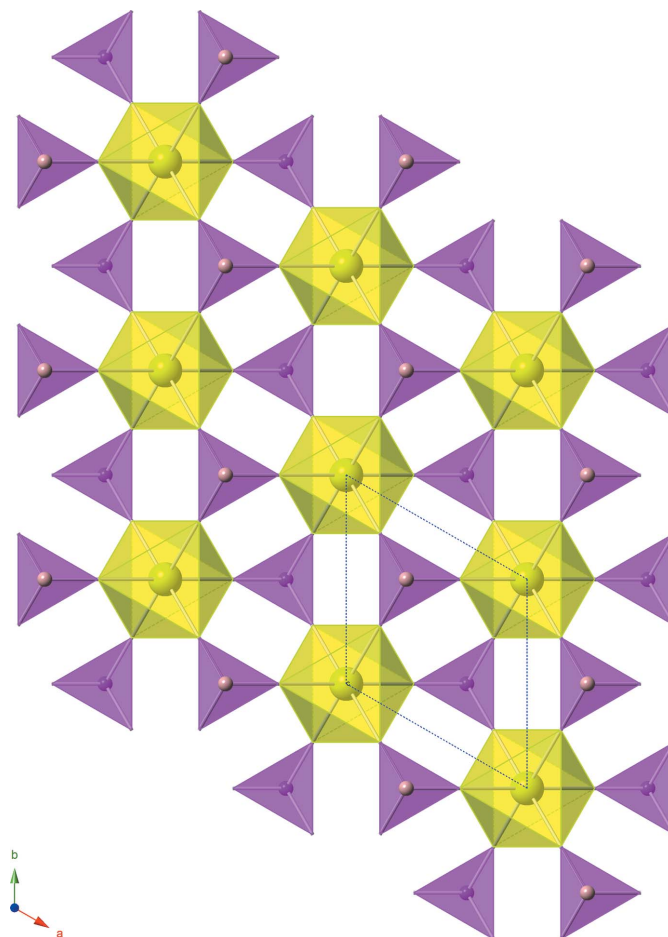
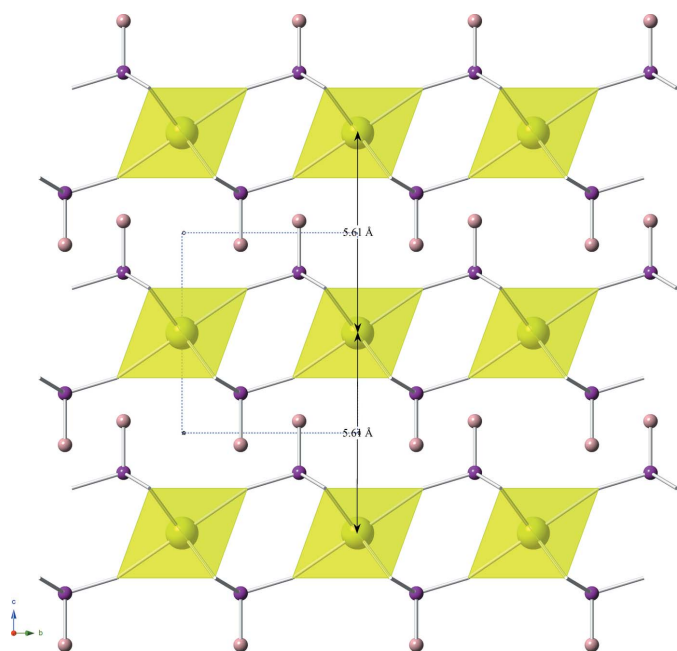


Figure 2

The sheet-like arrangement of the polyhedra parallel to the  $ab$  plane in the crystal structure of  $\text{Ce}(\text{HPO}_3)_2$ . The unit cell is shown with blue dashed lines. This polyhedral representation contains the same color scheme as Fig. 1.


**Figure 3**

The stacking of the cerium(IV) phosphite sheets are shown in a projection along the *a* axis. Again, the unit cell is shown with blue dashed lines and the color scheme is the same as the above images.

the *c* axis; between the layers, the Ce—Ce—Ce angle is 180.0° (Fig. 3).

This structure is closely related to a known zirconium(IV) bis(phosphite),  $Zr(HPO_3)_2$ , which was isolated *via* a very different synthesis route involving refluxing in concentrated phosphorous acid and using HF to precipitate the desired compound (Millini *et al.*, 1993). The structure was elucidated from powder X-ray diffraction data and has many similarities to the title structure shown above (Table 1). The main difference between the two is the metal–oxygen bond length, where the Ce—O bond length is unsurprisingly slightly longer. The zirconium coordination appears to be a bit closer to being octahedral than the cerium, but they are nearly the same after comparing the error of refinement.

### 3. Synthesis and crystallization

Cerium(IV) bis(phosphite) was synthesized solvothermally in acetonitrile ( $CH_3CN$ ). A stock solution of 1.00 M  $H_3PO_3$  was prepared in acetonitrile. 0.0572 grams of ceric ammonium nitrate,  $(NH_4)_2Ce(NO_3)_6$ , was placed into a PTFE liner along with 2 ml of the 1.00 M phosphorous acid solution, yielding a solution 0.0522 M ceric ammonium nitrate. This gives an approximate molar ratio of cerium(IV) to phosphite of 1:20. After the cerium was completely dissolved, the PTFE liner was capped and sealed inside of a stainless steel autoclave. This was then placed into a programmable box furnace and heated to 363 K over a period of 30 minutes, held at 363 K for four h and then cooled for 975 minutes down to 298 K (or a rate of 4 K per hour).

**Table 2**

Experimental details.

|  |   |
|--|---|
| <b>Crystal data</b>  |   |
| Chemical formula   | $Ce(HPO_3)_2$                                       |
| $M_r$  | 300.08  |
| Crystal system, space group  | Trigonal, $P\bar{3}m1$                              |
| Temperature (K)  | 293   |
| <i>a</i> , <i>c</i> (Å)  | 5.6859 (3), 5.6099 (3)                              |
| <i>V</i> (Å <sup>3</sup> )   | 157.07 (2)  |
| <i>Z</i>   | 1   |
| Radiation type   | Mo $K\alpha$  |
| $\mu$ (mm <sup>-1</sup> )  | 7.71  |
| Crystal size (mm)  | 0.21 × 0.09 × 0.08                                  |
| <b>Data collection</b>   |   |
| Diffractometer   | Rigaku SCX-Mini                                     |
| Absorption correction  | Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015) |
| $T_{min}$ , $T_{max}$  | 0.799, 1.000  |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 1852, 197, 197                                      |
| $R_{int}$  | 0.018   |
| $(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )                           | 0.713   |
| <b>Refinement</b>  |   |
| $R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>                             | 0.010, 0.029, 1.26                                  |
| No. of reflections   | 197   |
| No. of parameters  | 13  |
| H-atom treatment   | Only H-atom coordinates refined                     |
| $\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )               | 0.51, -0.35   |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009) and *CrystalMaker* (Palmer, 2014).

The resulting mixture was washed with cold water and then placed into a plastic petri dish. The excess water was removed and the crystals were dispersed with acetonitrile. The large, hexagonal prisms of the title compound were light yellow in color. Many suitable crystals were present. A large crystal was isolated in immersion oil and broken perpendicular to the hexagonal face to yield a clean crystal for single-crystal X-ray diffraction.

### 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen-atom position was placed as a riding atom on the phosphorus position. The maximum electron density peaks are  $0.330 e^- \text{ \AA}^{-3}$  (located between P1 and O1 at 0.686 and 0.838 Å, respectively),  $0.320 e^- \text{ \AA}^{-3}$  (located adjacent to O1 at 0.608 Å) and  $0.250 e^- \text{ \AA}^{-3}$  (located adjacent to Ce1 at 0.692 Å), which lead to nothing reasonable. All other maximum density peaks are under  $0.2 e^- \text{ \AA}^{-3}$ . The minimum electron density is a very minimal at  $-0.609 e^- \text{ \AA}^{-3}$ . Two electron density holes of about the same magnitude reside around the phosphorus atom.

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## supporting information

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## Synthesis and crystal structure of cerium(IV) bis(phosphite)

Stefano H. Byer and Eric M. Villa

## Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009) and *CrystalMaker* (Palmer, 2014); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

## Cerium(IV) bis(phosphite)

## Crystal data

|                                    |   |
|------------------------------------|---|
| Ce(HPO <sub>3</sub> ) <sub>2</sub> | $D_x = 3.172 \text{ Mg m}^{-3}$                         |
| $M_r = 300.08$                     | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Trigonal, $P\bar{3}m1$             | Cell parameters from 1912 reflections                   |
| $a = 5.6859 (3) \text{ \AA}$       | $\theta = 4.0\text{--}32.7^\circ$                       |
| $c = 5.6099 (3) \text{ \AA}$       | $\mu = 7.71 \text{ mm}^{-1}$                            |
| $V = 157.07 (2) \text{ \AA}^3$     | $T = 293 \text{ K}$                                     |
| $Z = 1$                            | Hexagonal, clear light yellow                           |
| $F(000) = 138$                     | $0.21 \times 0.09 \times 0.08 \text{ mm}$               |

## Data collection

|  |  |
|--|--|
| Rigaku SCX-Mini diffractometer   | 1852 measured reflections  |
| Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source  | 197 independent reflections  |
| Graphite monochromator   | 197 reflections with $I > 2\sigma(I)$                                  |
| $\omega$ scans   | $R_{\text{int}} = 0.018$   |
| Absorption correction: multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015) | $\theta_{\text{max}} = 30.5^\circ$ , $\theta_{\text{min}} = 5.5^\circ$ |
| $T_{\text{min}} = 0.799$ , $T_{\text{max}} = 1.000$                        | $h = -8 \rightarrow 8$   |
|  | $k = -8 \rightarrow 8$   |
|  | $l = -7 \rightarrow 8$   |

## Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | Primary atom site location: dual                     |
| Least-squares matrix: full      | Hydrogen site location: difference Fourier map       |
| $R[F^2 > 2\sigma(F^2)] = 0.010$ | Only H-atom coordinates refined                      |
| $wR(F^2) = 0.029$               | $w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 0.0962P]$    |
| $S = 1.26$                      | where $P = (F_o^2 + 2F_c^2)/3$                       |
| 197 reflections                 | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| 13 parameters                   | $\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$  |
| 0 restraints                    | $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$ |

*Special details*

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

**Refinement.** The structure was refined using SHELXT (Sheldrick, 2015) Intrinsic Phasing and SHELXL (Sheldrick, 2015). Olex2 (Dolomanov *et al.*, 2009) was used as a graphical interface. Images of the above compound were made using CrystalMaker for Windows, version 9.2.8 (CrystalMaker, 2017). The refinement proceeded without any incidents and without any need for modelling disorder or twinning or restraints.

The crystal was then mounted on MiTeGen Microloop with non-drying immersion oil. The crystal was then optically aligned on the Rigaku SCX-Mini diffractometer using a digital camera. Initial matrix images were collected to determine the unit cell, validity and proper exposure time. Three hemispheres (where  $\varphi = 0.0, 120.0$  and  $240.0$ ) of data were collected with each consisting 180 images each with  $1.00^\circ$  widths and a  $1.00^\circ$  step. Refinement of the structure was based on F2 against all reflections. The R-factor R is based on  $F2 > 2\sigma(F2)$ , but is not relevant to the choice of reflections for refinement; whereas the weighted R-factor wR and goodness of fit S are based on F2. Due to the presence of exclusively intense diffraction peaks, there is no observable difference between the R factors for all versus gt.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | x            | y          | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|------------|--------------|----------------------------------|
| Ce1 | 1.0000       | 1.0000     | 0.5000       | 0.01612 (11)                     |
| P1  | 0.6667       | 0.3333     | 0.19839 (17) | 0.01440 (18)                     |
| O1  | 0.81417 (19) | 0.6283 (4) | 0.2762 (4)   | 0.0330 (4)                       |
| H1  | 0.6667       | 0.3333     | -0.059 (11)  | 0.040*                           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$    | $U^{23}$    |
|-----|--------------|--------------|--------------|--------------|-------------|-------------|
| Ce1 | 0.00810 (11) | 0.00810 (11) | 0.03215 (17) | 0.00405 (6)  | 0.000       | 0.000       |
| P1  | 0.0114 (3)   | 0.0114 (3)   | 0.0204 (4)   | 0.00569 (13) | 0.000       | 0.000       |
| O1  | 0.0330 (8)   | 0.0141 (8)   | 0.0456 (9)   | 0.0071 (4)   | -0.0037 (4) | -0.0074 (7) |

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

|   |             |  |             |
|---|-------------|--|-------------|
| Ce1—O1                                  | 2.2193 (19) | P1—H1                                  | 1.44 (6)    |
| P1—O1                                   | 1.5168 (19) |  |             |
| O1 <sup>i</sup> —Ce1—O1 <sup>ii</sup>   | 180.0       | O1 <sup>ii</sup> —Ce1—O1               | 91.15 (8)   |
| O1 <sup>iii</sup> —Ce1—O1 <sup>iv</sup> | 88.85 (8)   | O1 <sup>i</sup> —Ce1—O1 <sup>v</sup>   | 91.15 (8)   |
| O1 <sup>i</sup> —Ce1—O1 <sup>iv</sup>   | 88.85 (8)   | O1 <sup>ii</sup> —Ce1—O1 <sup>iv</sup> | 91.15 (8)   |
| O1—Ce1—O1 <sup>iv</sup>                 | 91.15 (8)   | O1—Ce1—O1 <sup>v</sup>                 | 88.85 (8)   |
| O1—Ce1—O1 <sup>iii</sup>                | 180.00 (9)  | O1 <sup>vi</sup> —P1—O1 <sup>vii</sup> | 112.07 (8)  |
| O1 <sup>iii</sup> —Ce1—O1 <sup>v</sup>  | 91.15 (8)   | O1 <sup>vi</sup> —P1—O1                | 112.07 (8)  |
| O1 <sup>i</sup> —Ce1—O1 <sup>iii</sup>  | 91.15 (8)   | O1 <sup>vii</sup> —P1—O1               | 112.07 (8)  |
| O1 <sup>i</sup> —Ce1—O1                 | 88.85 (8)   | O1—P1—H1                               | 106.73 (9)  |
| O1 <sup>ii</sup> —Ce1—O1 <sup>iii</sup> | 88.85 (8)   | O1 <sup>vi</sup> —P1—H1                | 106.73 (9)  |
| O1 <sup>ii</sup> —Ce1—O1 <sup>v</sup>   | 88.85 (8)   | O1 <sup>vii</sup> —P1—H1               | 106.73 (9)  |
| O1 <sup>iv</sup> —Ce1—O1 <sup>v</sup>   | 180.0       | P1—O1—Ce1                              | 162.28 (14) |

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