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C-type CeP_3O_9

Jacqueline M. Cole[a]* and Dora Ilieva[b]‡

[a]Cavendish Laboratory, Department of Physics, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, England, and [b]Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 11, Sofia 1113, Bulgaria

‡ Present address: Center for Functional Genomics, Michael DeGroote School of Medicine, McMaster University, 1200 Main Street West, Hamilton, ON, Canada L8N 3Z5

Correspondence e-mail: jmc61@cam.ac.uk

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(P–O) = 0.003 Å
R factor = 0.025
wR factor = 0.055
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of cerium *catena*-polyphosphate, CeP_3O_9, is isotypic with the previously reported structures of La, Pr, Nd and Gd C-type polyphosphates. The absolute configuration of CeP_3O_9 was determined reliably. The structure contains helical polyphosphate chains with a period of six tetrahedra running along the *c* axis, and the Ce cation is in an eightfold coordination by terminal O atoms of the polyphosphate chains. Ce, one P and one O atom are located on twofold rotation axes.

Comment

The crystal structure of CeP_3O_9 is of interest since polymorphs and phase transitions are prevalent in crystalline metal polyphosphates (Durif, 1995). There are six structural forms of $M(PO_3)_3$ (M = trivalent metal) *catena*-polyphosphates known (d'Yvoire, 1962; Rémy & Boullé, 1972; Bagieu-Beucher, 1978), called types *A*–*F*. Type *C* has been shown to be the most stable form by far, and therefore the most common (d'Yvoire, 1962; Durif, 1995). Such structures crystallize with monoclinic or orthorhombic symmetry.

The title compound, CeP_3O_9, crystallizes in the orthorhombic *C*-form and is isotypic with other REP_3O_9 compounds, where *RE* = La, Pr, Nd and Gd (Matuszewski *et al.*, 1988; Jouini *et al.*, 2003; Hong, 1974; Naili *et al.*, 2006). The rare earth ion is eightfold coordinated by O atoms in a distorted dodecahedral configuration, in which two Ce—O bonds are substantially longer (Table 1). These polyhedra lie in a zigzag arrangement and are joined together in infinite

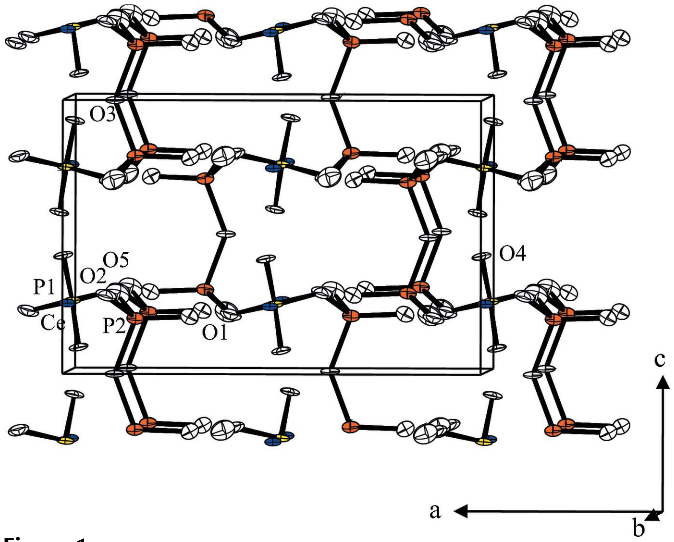

Figure 1
The structure of CeP_3O_9, projected approximately along the *b* axis. Displacement parameters are given at the 74% probability level.

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phosphate chains with a repeating unit of six tetrahedra. The helical polyphosphate chains run along the *c* axis, as imposed by the 2_1 screw-axis symmetry (Fig. 1). There are two crystallographically independent PO_4 tetrahedra in this chain. In each, there are two longer and two shorter bonds (Table 1); the O atoms of the shorter ones coordinate to Ce, whilst the longer bonds are involved in P—O—P bridging along the phosphate chain. The minimum Ce⋯Ce separation is 4.281 (1) Å.

Experimental

A mixture composed of CeO_2 and NaH_2PO_4 (1:10 molar ratio) was melted in an aluminium crucible by heating from room temperature to 1473 K at a rate of 7 K min^{-1}. The liquid was held at 1473 K for 3 h and then quenched to 1073 K at a rate of 3 K min^{-1}. Single crystals of CeP_3O_9 leached out from the melt. This yielded rectangular crystals of a size typical of that used in this X-ray diffraction experiment.

Crystal data

CeP_3O_9
$M_r = 377.03$
Orthorhombic, $C222_1$
$a = 11.236$ (2) Å
$b = 8.6110$ (17) Å
$c = 7.3458$ (15) Å
$V = 710.7$ (2) $Å^3$
$Z = 4$
Mo *Kα* radiation
$\mu = 7.10$ mm^{-1}
$T = 180$ (2) K
0.15 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.461$, $T_{max} = 0.700$
1045 measured reflections
686 independent reflections
658 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.055$
$S = 1.05$
686 reflections
61 parameters
$\Delta\rho_{max} = 0.78$ e $Å^{-3}$
$\Delta\rho_{min} = -1.38$ e $Å^{-3}$
Absolute structure: Flack (1983), 198 Friedel pairs
Flack parameter: −0.06 (3)

Table 1
Selected bond lengths (Å).

Ce1—O1^{i}	2.390 (4)	P1—O4^{vii}	1.500 (3)
Ce1—O1^{ii}	2.390 (4)	P1—O4^{vi}	1.500 (3)
Ce1—O2^{iii}	2.406 (4)	P1—O5	1.573 (4)
Ce1—O2	2.406 (4)	P1—O5^{iii}	1.573 (4)
Ce1—O4^{iv}	2.462 (3)	P2—O2	1.475 (4)
Ce1—O4^{v}	2.462 (3)	P2—O1^{viii}	1.483 (4)
Ce1—O4^{vi}	2.735 (3)	P2—O3^{ix}	1.592 (2)
Ce1—O4^{vii}	2.735 (3)	P2—O5^{viii}	1.593 (4)

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $-x+2, y, -z+\frac{1}{2}$; (iv) $-x+1, -y+1, z-\frac{1}{2}$; (v) $x+1, -y+1, -z+1$; (vi) $-x+1, y, -z+\frac{1}{2}$; (vii) $x+1, y, z$; (viii) $x, y+1, z$; (ix) $x, y, z-1$.

The unit-cell parameters are almost identical to those obtained previously from a CeP_3O_9 room-temperature powder X-ray diffraction measurement [$a = 11.236$ (4), $b = 8.602$ (1) Å, $c = 7.349$ (2) Å; Deichman *et al.*, 1984]. The anisotropic displacement parameters (ADP) of Ce1, P2 and O3, are rather prolate or oblate. Since a refinement with monoclinic crystal symmetry was not stable at all, and there is no evidence of twinning, this observation seems to reflect a symmetry constraint given that these atoms all lie on special positions (twofold axes). Inspection of the ADPs in isotypic REP_3O_9 structures, where *RE* = La, Pr, Nd, Gd shows that this trend is echoed, and it may indicate the incipient transition from the orthorhombic to monoclinic *C*-form that occurs in heavier rare-earth *catena*-polyphosphates [see REP_3O_9 unit-cell parameters collated by Durif (1995)]. The absolute configuration of CeP_3O_9 was determined by refinement of the Flack (1983) parameter, which is very close to 0, thus indicating the correct sense of the refined configuration. Pseudo-symmetry can also manifest itself in a bias of the Flack parameter and pseudo-symmetry is prevalent in this class of phosphate materials due to the dominant rare earth scatterer. That said, all searches for pseudosymmetry in this compound failed, using the program *PSEUDO* (Igartua *et al.*, 1996, 1999). The deepest hole observed in the final Fourier map lies 0.91 Å from Ce1.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

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