Dicaesium tetrachloridodioxido-plutonate(VI)

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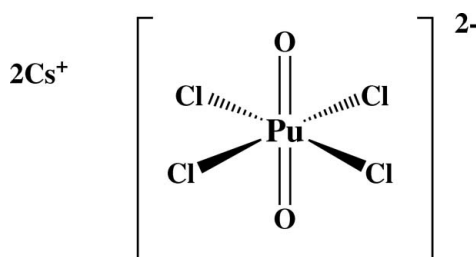Correspondence e-mail: mpw@lanl.gov

The anion of the title complex, $Cs_2[PuCl_4O_2]$, adopts a pseudo-octahedral geometry ($2/m$ crystallographic site symmetry) with two plutonyl oxide ligands in axial sites and four chloride ligands occupying the equatorial plane. Charge balance is maintained by two caesium cations per tetrachloridodioxidoplutonate(VI) anion. Principal bond lengths include Pu—O = 1.752 (3) Å and Pu—Cl = 2.6648 (8) Å.

Related literature

For related literature, see: Hall *et al.* (1966); Watkin *et al.* (1991); Wilkerson *et al.* (2004); Wilkerson *et al.* (2007); Bean *et al.* (2004, 2005); Grenthe *et al.* (2006); Grigoriev *et al.* (2004); Runde *et al.* (2003); Sessler *et al.* (2002).

Experimental

Crystal data

$Cs_2[PuCl_4O_2]$	$V = 530.91$ (6) Å^3
$M_r = 678.67$	$Z = 2$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 11.9489$ (7) Å	$\mu = 13.92$ mm^{-1}
$b = 7.7286$ (5) Å	$T = 141$ (2) K
$c = 5.7855$ (4) Å	$0.22 \times 0.18 \times 0.12$ mm
$\beta = 96.439$ (1)°	

Data collection

Bruker APEXII CCD diffractometer	3212 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	711 independent reflections
$T_{min} = 0.150$, $T_{max} = 0.286$ (expected range = 0.099–0.188)	659 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.015$	27 parameters
$wR(F^2) = 0.037$	$\Delta\rho_{max} = 0.78$ e Å^{-3}
$S = 1.26$	$\Delta\rho_{min} = -0.64$ e Å^{-3}
711 reflections	

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2048).

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supporting information

Dicaesium tetrachloridodioxidoplutonate(VI)

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S1. Comment

The title compound, (1), is isostructural with the uranium analogue Cs2U(VI)O2Cl4 and the neptunium analogue Cs2Np(VI)O2Cl4, which crystallize in the space group C2/m (Hall *et al.*, 1966; Watkin *et al.*, 1991; Wilkerson *et al.*, 2007). The Pu atom sits on a site of 2/m crystallographic symmetry; the twofold rotation axis bisects the Cl—U—Cl angle, and the plutonyl axis lies in the mirror plane. The plutonium metal is coordinated in a pseudo-octahedral fashion by two oxo groups and four chloride ligands. The oxo groups of the plutonyl ion lie *trans* to one another with a bond angle of 180.0 (3). This angle is equivalent within 3 σ to those reported for the limited number of plutonyl structures published (range 178.0 (4)–179.4 (2)) (Bean *et al.*, 2004; Bean *et al.*, 2005; Grigoriev *et al.*, 2004; Runde *et al.*, 2003). This value is within the range reported for the majority of actinyl compounds (Grenthe *et al.*, 2006). The Pu—O(oxo) distances are 1.752 (3) Å. Although there are no reported six coordinate plutonyl structures with which to compare, this value is within range of Pu—O(oxo) bond lengths reported for seven coordinate plutonyl structures (1.727 (4)–1.771 (11) Å) (Bean *et al.*, 2004; Bean *et al.*, 2005; Grigoriev *et al.*, 2004; Runde *et al.*, 2003). The chloride ligands lie in the equatorial plane of the plutonyl ion, and the Pu—Cl bond distances are 2.6648 (8) Å. Although there are no plutonyl chloride structures reported, these values are longer than Np—Cl bond lengths reported for six-coordinate $Cs_2NpO_2Cl_4$ (2.653 (3) Å) (Wilkerson *et al.*, 2004).

S2. Experimental

Caesium chloride (0.021 g, 0.12 mmol; Aldrich, 99.999%) was dissolved in 2*M* HCl (0.5 ml; Aldrich, ACS reagent, 37%), and this solution was added to a stock solution of 0.063 *M* $Pu(VI)O_2^{2+}$ in 2*M* HCl (1 ml, 0.063 mmol; Fisher, Certified ACS Plus) (Sessler *et al.*, 2002). The vial containing the solution was covered loosely with parafilm and allowed to stand for 2 weeks at room temperature. Following evaporation of the solvent, dark golden-brown blocks formed. A dark golden-brown block of 0.22 *x* 0.18 *x* 0.12 mm was cut from a larger crystal, and then thinly coated with epoxy and placed in a capillary. The capillary was coated with a thin film of acrylic dissolved in ethyl acetate. (Note: this triple containment was necessitated by the health hazards of transuranic materials.)
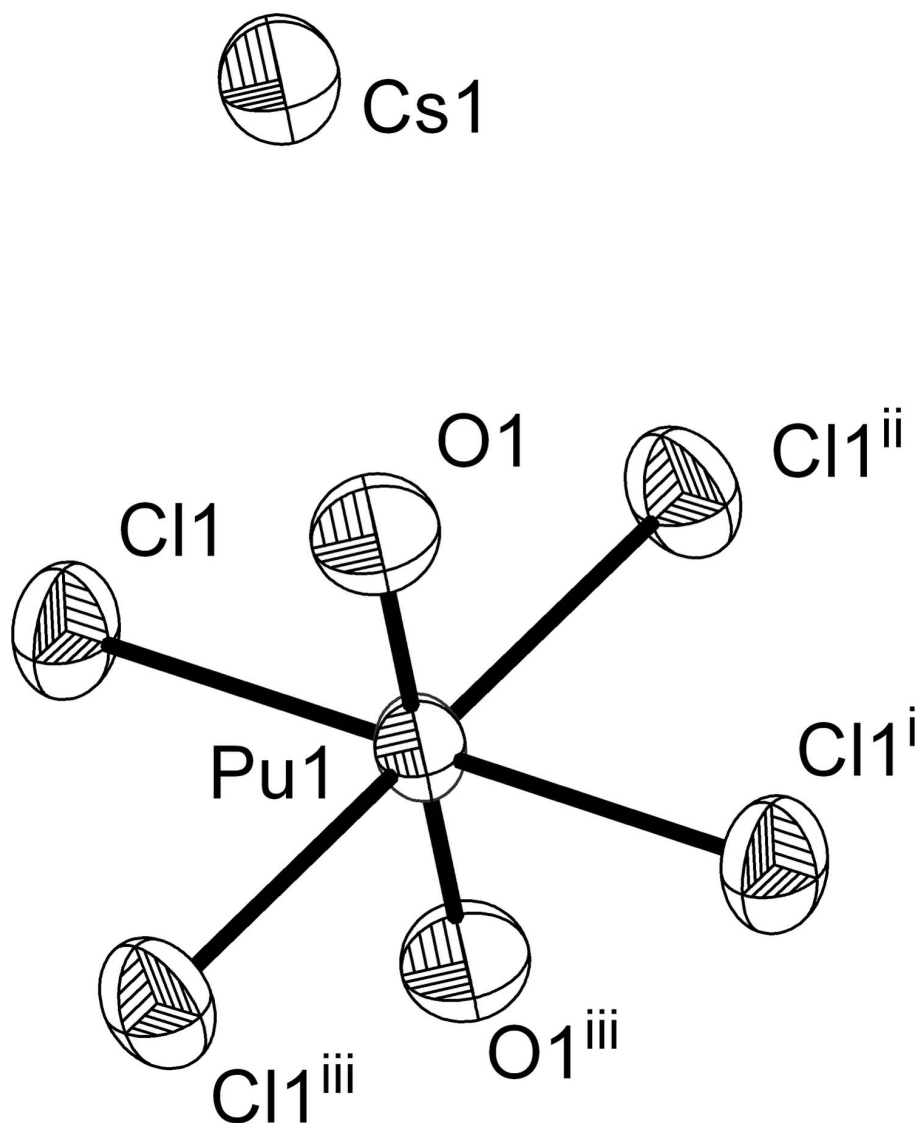
Figure 1

Molecular structure (70% probability displacement ellipsoids) of $Cs_2PuO_2Cl_4$ and the atom-numbering scheme used in Table 1. Symmetry codes as in Table 1.

Dicaesium tetrachloridodioxidoplutonium(VI)

Crystal data

$Cs_2[PuCl_4O_2]$	$Z = 2$
$M_r = 678.67$	$F(000) = 576$
Monoclinic, $C2/m$	$D_x = 4.245$ Mg m^{-3}
Hall symbol: -C 2y	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.9489$ (7) Å	$\theta = 3.2–28.7°$
$b = 7.7286$ (5) Å	$\mu = 13.92$ mm^{-1}
$c = 5.7855$ (4) Å	$T = 141$ K
$\beta = 96.439$ (1)°	Irregular, golden brown
$V = 530.91$ (6) Å^3	$0.22 \times 0.18 \times 0.12$ mm

Data collection

Bruker D8 with APEXII CCD diffractometer	3212 measured reflections
Radiation source: fine-focus sealed tube	711 independent reflections
Graphite monochromator	659 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	$\theta_{max} = 28.7°$, $\theta_{min} = 3.2°$
	$h = -15 \rightarrow 15$
	$k = -10 \rightarrow 10$
$T_{min} = 0.150$, $T_{max} = 0.286$	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.015$	$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2]$
$wR(F^2) = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.26$	$(\Delta/\sigma)_{max} = 0.001$
711 reflections	$\Delta\rho_{max} = 0.78$ e Å^{-3}
27 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0050 (2)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pu1	0.0000	0.0000	0.0000	0.02605 (11)
Cs1	0.34147 (2)	0.0000	0.69601 (6)	0.03801 (11)
Cl1	−0.10351 (7)	−0.24889 (10)	0.21367 (16)	0.0390 (2)
O1	0.1124 (3)	0.0000	0.2222 (6)	0.0395 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pu1	0.02849 (15)	0.02078 (14)	0.02946 (15)	0.000	0.00583 (9)	0.000
Cs1	0.03790 (19)	0.03608 (19)	0.0419 (2)	0.000	0.01250 (15)	0.000
Cl1	0.0436 (4)	0.0305 (4)	0.0454 (5)	−0.0015 (3)	0.0162 (4)	0.0058 (3)
O1	0.0381 (19)	0.0424 (19)	0.0371 (19)	0.000	0.0002 (16)	0.000

Geometric parameters (Å, º)

Pu1—O1^i	1.752 (3)	Cs1—Cl1^{xii}	3.5201 (8)
Pu1—O1	1.752 (3)	Cs1—Cl1^{viii}	3.5201 (8)

Pu1—Cl1ii	2.6648 (8)	Cs1—Cl1xiii	3.5674 (10)
Pu1—Cl1	2.6648 (8)	Cs1—Cl1xiv	3.5674 (10)
Pu1—Cl1iii	2.6648 (8)	Cs1—O1	3.650 (4)
Pu1—Cl1i	2.6648 (8)	Cs1—Cl1xv	3.6710 (9)
Pu1—Cs1iv	4.5680 (3)	Cs1—Cl1vi	3.6710 (9)
Pu1—Cs1v	4.5680 (3)	Cs1—Pu1xiii	4.5680 (3)
Pu1—Cs1vi	4.5680 (3)	Cs1—Pu1xvi	4.5680 (3)
Pu1—Cs1vii	4.5680 (3)	Cs1—Pu1xvii	4.6207 (3)
Pu1—Cs1viii	4.6207 (3)	Cl1—Cs1xviii	3.5209 (9)
Pu1—Cs1ix	4.6207 (3)	Cl1—Cs1viii	3.5201 (8)
Cs1—Cl1x	3.5209 (9)	Cl1—Cs1iv	3.5674 (10)
Cs1—Cl1xi	3.5209 (9)	Cl1—Cs1vi	3.6710 (9)
O1i—Pu1—O1	180.0 (3)	Cl1x—Cs1—Cl1xiii	158.75 (3)
O1i—Pu1—Cl1ii	90.98 (8)	Cl1xi—Cs1—Cl1xiii	109.41 (2)
O1—Pu1—Cl1ii	89.02 (8)	Cl1xii—Cs1—Cl1xiii	104.390 (15)
O1i—Pu1—Cl1	89.02 (8)	Cl1viii—Cs1—Cl1xiii	69.76 (2)
O1—Pu1—Cl1	90.98 (8)	Cl1x—Cs1—Cl1xiv	109.41 (2)
Cl1ii—Pu1—Cl1	87.58 (3)	Cl1xi—Cs1—Cl1xiv	158.75 (3)
O1i—Pu1—Cl1iii	89.02 (8)	Cl1xii—Cs1—Cl1xiv	69.76 (2)
O1—Pu1—Cl1iii	90.98 (8)	Cl1viii—Cs1—Cl1xiv	104.390 (15)
Cl1ii—Pu1—Cl1iii	180.00 (5)	Cl1xiii—Cs1—Cl1xiv	65.91 (3)
Cl1—Pu1—Cl1iii	92.42 (3)	Cl1x—Cs1—O1	66.15 (5)
O1i—Pu1—Cl1i	90.98 (8)	Cl1xi—Cs1—O1	66.15 (5)
O1—Pu1—Cl1i	89.02 (8)	Cl1xii—Cs1—O1	63.98 (5)
Cl1ii—Pu1—Cl1i	92.42 (3)	Cl1viii—Cs1—O1	63.98 (5)
Cl1—Pu1—Cl1i	180.00 (4)	Cl1xiii—Cs1—O1	133.04 (4)
Cl1iii—Pu1—Cl1i	87.58 (3)	Cl1xiv—Cs1—O1	133.04 (4)
O1i—Pu1—Cs1iv	57.778 (4)	Cl1x—Cs1—Cl1xv	99.912 (18)
O1—Pu1—Cs1iv	122.222 (4)	Cl1xi—Cs1—Cl1xv	65.75 (3)
Cl1ii—Pu1—Cs1iv	53.469 (18)	Cl1xii—Cs1—Cl1xv	163.34 (3)
Cl1—Pu1—Cs1iv	51.24 (2)	Cl1viii—Cs1—Cl1xv	112.348 (8)
Cl1iii—Pu1—Cs1iv	126.531 (18)	Cl1xiii—Cs1—Cl1xv	61.25 (2)
Cl1i—Pu1—Cs1iv	128.76 (2)	Cl1xiv—Cs1—Cl1xv	95.403 (19)
O1i—Pu1—Cs1v	122.222 (4)	O1—Cs1—Cl1xv	131.50 (4)
O1—Pu1—Cs1v	57.778 (4)	Cl1x—Cs1—Cl1vi	65.75 (3)
Cl1ii—Pu1—Cs1v	126.531 (18)	Cl1xi—Cs1—Cl1vi	99.912 (18)
Cl1—Pu1—Cs1v	128.76 (2)	Cl1xii—Cs1—Cl1vi	112.348 (8)
Cl1iii—Pu1—Cs1v	53.469 (18)	Cl1viii—Cs1—Cl1vi	163.34 (3)
Cl1i—Pu1—Cs1v	51.24 (2)	Cl1xiii—Cs1—Cl1vi	95.403 (19)
Cs1iv—Pu1—Cs1v	180.000 (8)	Cl1xiv—Cs1—Cl1vi	61.25 (2)
O1i—Pu1—Cs1vi	122.222 (4)	O1—Cs1—Cl1vi	131.50 (4)
O1—Pu1—Cs1vi	57.778 (4)	Cl1xv—Cs1—Cl1vi	63.83 (3)
Cl1ii—Pu1—Cs1vi	51.24 (2)	Cl1x—Cs1—Pu1xiii	131.698 (14)
Cl1—Pu1—Cs1vi	53.469 (18)	Cl1xi—Cs1—Pu1xiii	74.494 (15)
Cl1iii—Pu1—Cs1vi	128.76 (2)	Cl1xii—Cs1—Pu1xiii	135.406 (14)
Cl1i—Pu1—Cs1vi	126.531 (18)	Cl1viii—Cs1—Pu1xiii	77.734 (14)
Cs1iv—Pu1—Cs1vi	64.454 (8)	Cl1xiii—Cs1—Pu1xiii	35.626 (12)

Cs1[v]—Pu1—Cs1[vi]	115.546 (8)	Cl1[xiv]—Cs1—Pu1[xiii]	96.174 (16)
O1[i]—Pu1—Cs1[vii]	57.778 (4)	O1—Cs1—Pu1[xiii]	122.194 (5)
O1—Pu1—Cs1[vii]	122.222 (4)	Cl1[xv]—Cs1—Pu1[xiii]	35.683 (12)
Cl1[ii]—Pu1—Cs1[vii]	128.76 (2)	Cl1[vi]—Cs1—Pu1[xiii]	94.713 (15)
Cl1—Pu1—Cs1[vii]	126.531 (18)	Cl1[x]—Cs1—Pu1[xvi]	74.494 (15)
Cl1[iii]—Pu1—Cs1[vii]	51.24 (2)	Cl1[xi]—Cs1—Pu1[xvi]	131.698 (14)
Cl1[i]—Pu1—Cs1[vii]	53.469 (18)	Cl1[xii]—Cs1—Pu1[xvi]	77.734 (14)
Cs1[iv]—Pu1—Cs1[vii]	115.546 (8)	Cl1[viii]—Cs1—Pu1[xvi]	135.406 (14)
Cs1[v]—Pu1—Cs1[vii]	64.454 (8)	Cl1[xiii]—Cs1—Pu1[xvi]	96.174 (16)
Cs1[vi]—Pu1—Cs1[vii]	180.000 (7)	Cl1[xiv]—Cs1—Pu1[xvi]	35.626 (12)
O1[i]—Pu1—Cs1[viii]	69.04 (11)	O1—Cs1—Pu1[xvi]	122.194 (5)
O1—Pu1—Cs1[viii]	110.96 (11)	Cl1[xv]—Cs1—Pu1[xvi]	94.713 (15)
Cl1[ii]—Pu1—Cs1[viii]	130.706 (17)	Cl1[vi]—Cs1—Pu1[xvi]	35.683 (12)
Cl1—Pu1—Cs1[viii]	49.294 (17)	Pu1[xiii]—Cs1—Pu1[xvi]	115.546 (8)
Cl1[iii]—Pu1—Cs1[viii]	49.294 (17)	Cl1[x]—Cs1—Pu1[xvii]	123.572 (15)
Cl1[i]—Pu1—Cs1[viii]	130.706 (17)	Cl1[xi]—Cs1—Pu1[xvii]	123.572 (15)
Cs1[iv]—Pu1—Cs1[viii]	78.510 (5)	Cl1[xii]—Cs1—Pu1[xvii]	35.021 (13)
Cs1[v]—Pu1—Cs1[viii]	101.490 (5)	Cl1[viii]—Cs1—Pu1[xvii]	35.021 (13)
Cs1[vi]—Pu1—Cs1[viii]	101.490 (5)	Cl1[xiii]—Cs1—Pu1[xvii]	76.579 (13)
Cs1[vii]—Pu1—Cs1[viii]	78.510 (5)	Cl1[xiv]—Cs1—Pu1[xvii]	76.579 (13)
O1[i]—Pu1—Cs1[ix]	110.96 (11)	O1—Cs1—Pu1[xvii]	70.49 (5)
O1—Pu1—Cs1[ix]	69.04 (11)	Cl1[xv]—Cs1—Pu1[xvii]	136.161 (13)
Cl1[ii]—Pu1—Cs1[ix]	49.294 (17)	Cl1[vi]—Cs1—Pu1[xvii]	136.161 (13)
Cl1—Pu1—Cs1[ix]	130.706 (17)	Pu1[xiii]—Cs1—Pu1[xvii]	101.490 (5)
Cl1[iii]—Pu1—Cs1[ix]	130.706 (17)	Pu1[xvi]—Cs1—Pu1[xvii]	101.490 (5)
Cl1[i]—Pu1—Cs1[ix]	49.294 (17)	Pu1—Cl1—Cs1[xviii]	154.58 (3)
Cs1[iv]—Pu1—Cs1[ix]	101.490 (5)	Pu1—Cl1—Cs1[viii]	95.68 (2)
Cs1[v]—Pu1—Cs1[ix]	78.510 (5)	Cs1[xviii]—Cl1—Cs1[viii]	87.583 (18)
Cs1[vi]—Pu1—Cs1[ix]	78.510 (5)	Pu1—Cl1—Cs1[iv]	93.13 (2)
Cs1[vii]—Pu1—Cs1[ix]	101.490 (5)	Cs1[xviii]—Cl1—Cs1[iv]	109.41 (2)
Cs1[viii]—Pu1—Cs1[ix]	180.000 (3)	Cs1[viii]—Cl1—Cs1[iv]	110.24 (2)
Cl1[x]—Cs1—Cl1[xi]	66.90 (3)	Pu1—Cl1—Cs1[vi]	90.85 (2)
Cl1[x]—Cs1—Cl1[xii]	92.417 (18)	Cs1[xviii]—Cl1—Cs1[vi]	80.088 (18)
Cl1[xi]—Cs1—Cl1[xii]	130.133 (13)	Cs1[viii]—Cl1—Cs1[vi]	163.34 (3)
Cl1[x]—Cs1—Cl1[viii]	130.133 (13)	Cs1[iv]—Cl1—Cs1[vi]	84.597 (19)
Cl1[xi]—Cs1—Cl1[viii]	92.417 (18)	Pu1—O1—Cs1	178.55 (16)
Cl1[xii]—Cs1—Cl1[viii]	66.25 (3)		

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