inorganic compounds

Praseodymium(III) sulfate hydroxide, Pr(SO$_4$)(OH)

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The title compound, Pr(SO$_4$)(OH), obtained under hydrothermal conditions, consists of Pr^{III} ions coordinated by nine O atoms from six sulfate groups and three hydroxide anions. The bridging mode of the O atoms results in the formation of a three-dimensional framework, stabilized by two O—H···O hydrogen-bonding interactions.

Related literature

Lanthanide sulfate hydroxides exhibit a variety of architectures, see: Xu *et al.* (2007); Zhang *et al.* (2004). For related structures, see: Yang *et al.* (2005); Ding *et al.* (2006); Zhang *et al.* (2004); Zhang & Lu (2008).

Experimental

Crystal data

Pr(SO$_4$)(OH)
M_r = 253.98
Monoclinic, $P2_1/n$
a = 4.4891 (18) Å
b = 12.484 (5) Å
c = 6.894 (3) Å
β = 106.310 (7)°

V = 370.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.59 mm^{-1}
T = 293 K
$0.20 \times 0.10 \times 0.10$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.213, T_{max} = 0.257

2849 measured reflections
840 independent reflections
813 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.080
S = 1.09
840 reflections

65 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.73 e Å^{-3}
$\Delta\rho_{min}$ = −2.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O3^i	0.85	2.20	2.630 (7)	111
O5—H5A···O2^{ii}	0.85	2.31	3.082 (7)	152

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

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supporting information

Praseodymium(III) sulfate hydroxide, Pr(SO₄)(OH)

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S1. Comment

Lanthanide sulfate hydroxides exhibit a variety of architectures (Xu *et al.*, 2007; Zhang *et al.*, 2004). We report here the compound $Pr(SO_4)(OH)$, which is isostructural to $Ln(SO_4)(OH)$ (Ln = La, Ce, Eu, Nd) (Zhang *et al.*, 2004; Yang *et al.*, 2005; Ding *et al.*, 2006; Zhang *et al.*, 2008). The Pr^{III} ion is coordinated in a distorted tricapped trigonal prismatic geometry by the oxygen atoms from six sulfate groups and three hydroxide anions (Fig. 1). All oxygen atoms of the sulfate groups take part in the coordination. The S atom makes four S–O–La linkages through two 2-coordinated oxygen atoms [S–O–La] and two 3-coordinated oxygen atoms [S–(μ_3-O)–La₂]. The oxygen atoms of the hydroxide groups are four-coordinate, [HO—μ_3-La₃], linking three different Pr ions. The bridging mode of the oxygen atoms results in a three-dimensional framework, with the H atom of hydroxide anions forming weak O—H···O hydrogen bonds with two O atoms of sulfate groups (Fig. 2).

S2. Experimental

A mixture of $Pr(NO_3)_3.6H_2O$ (0.25 mmol, 0.1088 g), $MnSO_4.H_2O$ (0.2 mmol, 0.0338 g), and H_2O (15 mL) was sealed in a 25-mL Teflon-lined stainless steel reactor and heated at 443 K for 72 h, and then cooled to room temperature over 3 days. Light-green prismatic crystals were obtained (yield: 32% based on $Pr(NO_3)_3.6H_2O$).

S3. Refinement

The oxygen-bound H-atoms were located in the difference Fourier map and refined with the O—H distance restrained to 0.85 Å [$U_{iso}(H) = 1.2U_{eq}(O)$].
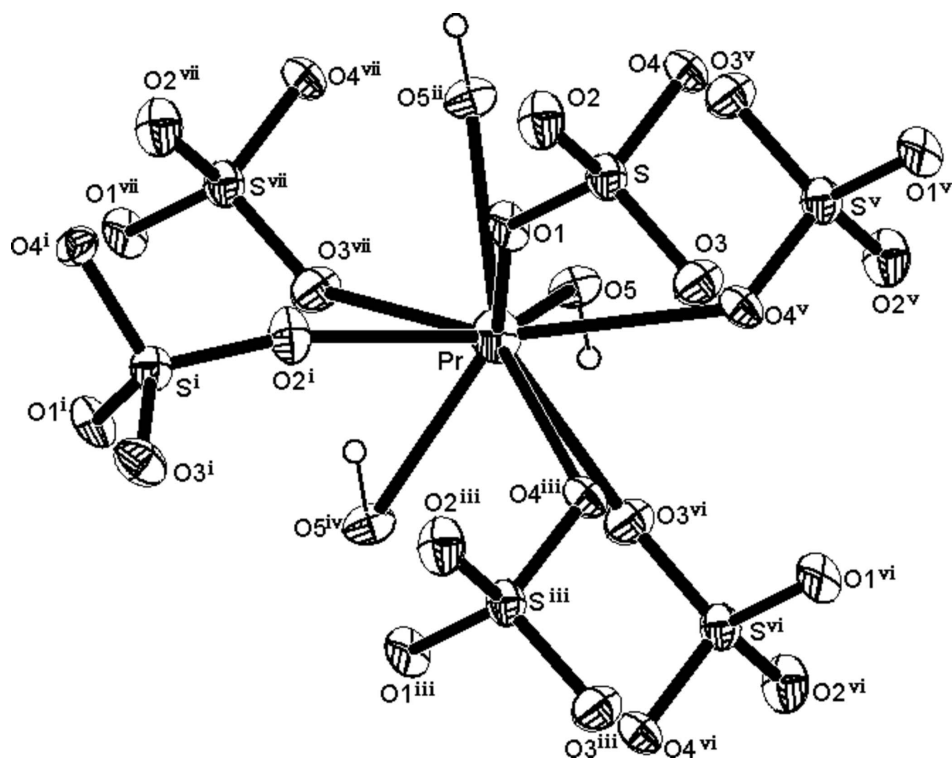
Figure 1

Coordination of Pr in Pr(SO₄)(OH). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) x-1/2, -y+3/2, z+1/2; (ii) -x+1, -y+2, -z+1; (iii) x-1, y, z; (iv) -x, -y+2, -z+1; (v) -x+1, -y+2, -z; (vi) -x, -y+2, -z; (vii) x, y, z+1.]
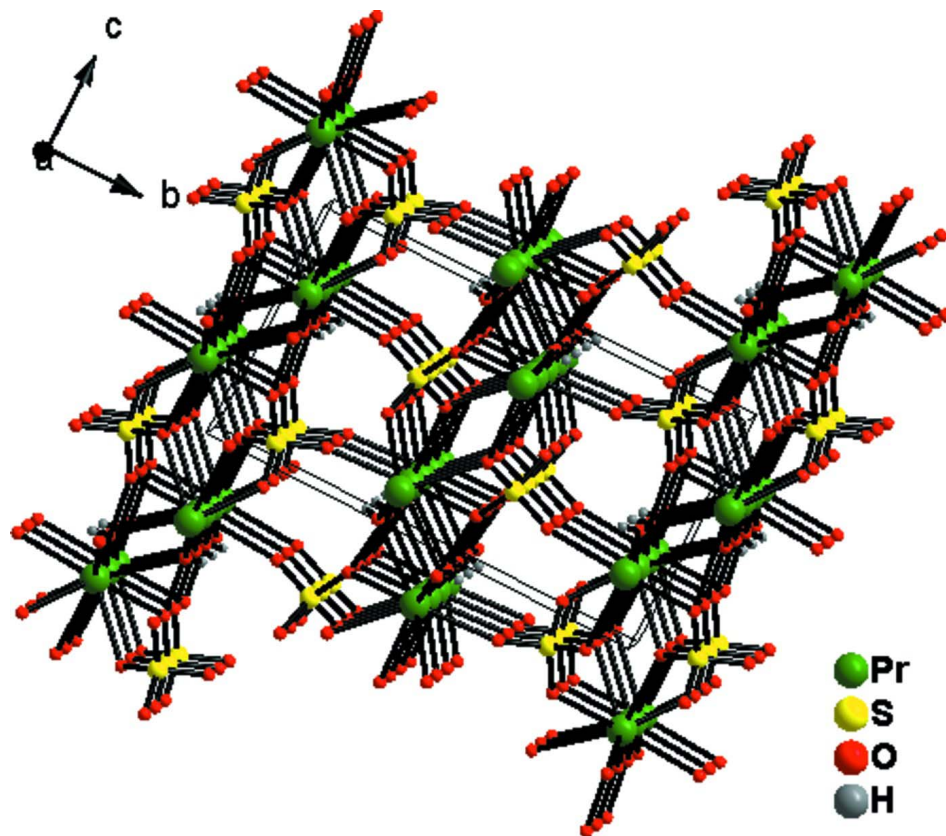
Figure 2

Three-dimensional network in Pr(SO₄)(OH).

Praseodymium(III) sulfate hydroxide

Crystal data

Pr(SO₄)(OH)	$F(000) = 464$
$M_r = 253.98$	$D_x = 4.550$ Mg m⁻³
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 1066 reflections
$a = 4.4891$ (18) Å	$\theta = 3.3$–27.4°
$b = 12.484$ (5) Å	$\mu = 13.59$ mm⁻¹
$c = 6.894$ (3) Å	$T = 293$ K
$\beta = 106.310$ (7)°	Prism, light green
$V = 370.8$ (3) Å³	$0.20 \times 0.10 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	2849 measured reflections
Radiation source: fine-focus sealed tube	840 independent reflections
Graphite monochromator	813 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.053$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.4°$, $\theta_{min} = 3.3°$
	$h = -5 \rightarrow 5$
	$k = -14 \rightarrow 16$
$T_{min} = 0.213$, $T_{max} = 0.257$	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.080$	$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 1.2539P]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
840 reflections	$(\Delta/\sigma)_{max} = 0.001$
65 parameters	$\Delta\rho_{max} = 1.73$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -2.15$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0303 (17)

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}
Pr	0.14215 (8)	0.93511 (2)	0.30120 (5)	0.0103 (2)
S	0.4863 (3)	0.85448 (11)	−0.1115 (2)	0.0100 (3)
O1	0.3690 (11)	0.8345 (4)	0.0615 (6)	0.0156 (9)
O2	0.5908 (12)	0.7551 (4)	−0.1798 (7)	0.0189 (10)
O3	0.2507 (11)	0.9045 (4)	−0.2785 (7)	0.0179 (10)
O4	0.7557 (12)	0.9298 (3)	−0.0482 (8)	0.0137 (10)
O5	0.3035 (11)	1.0859 (4)	0.5390 (7)	0.0141 (9)
H5A	0.1434	1.1193	0.5488	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pr	0.0129 (3)	0.0104 (3)	0.0083 (3)	0.00025 (10)	0.00418 (19)	−0.00100 (9)
S	0.0118 (7)	0.0098 (7)	0.0091 (7)	−0.0002 (5)	0.0041 (6)	0.0002 (5)
O1	0.020 (2)	0.020 (2)	0.012 (2)	0.002 (2)	0.0142 (19)	0.0010 (17)
O2	0.027 (2)	0.014 (2)	0.020 (2)	0.001 (2)	0.011 (2)	−0.0016 (17)
O3	0.017 (2)	0.023 (2)	0.015 (2)	0.005 (2)	0.0060 (19)	0.0030 (19)
O4	0.013 (2)	0.013 (2)	0.016 (2)	−0.0039 (15)	0.005 (2)	−0.0022 (14)
O5	0.014 (2)	0.017 (2)	0.012 (2)	0.0037 (18)	0.0044 (18)	−0.0042 (17)

Geometric parameters (Å, º)

Pr—O2^i	2.393 (5)	S—O1	1.455 (5)
Pr—O5^{ii}	2.436 (5)	S—O3	1.466 (5)

Pr—O5	2.468 (5)	S—O4	1.497 (5)
Pr—O1	2.508 (4)	O2—Pr^{viii}	2.393 (5)
Pr—O4^{iii}	2.543 (5)	O3—Pr^{vi}	2.643 (5)
Pr—O5^{iv}	2.554 (5)	O3—Pr^{ix}	2.826 (5)
Pr—O4^{v}	2.558 (5)	O4—Pr^{x}	2.543 (5)
Pr—O3^{vi}	2.643 (5)	O4—Pr^{v}	2.558 (5)
Pr—O3^{vii}	2.826 (5)	O5—Pr^{ii}	2.436 (5)
Pr—Pr^{iv}	3.7056 (12)	O5—Pr^{iv}	2.554 (5)
Pr—Pr^{ii}	3.9388 (12)	O5—H5A	0.8500
S—O2	1.450 (5)		
O2^{i}—Pr—O5^{ii}	88.30 (16)	O5—Pr—Pr^{iv}	43.35 (12)
O2^{i}—Pr—O5	137.33 (16)	O1—Pr—Pr^{iv}	173.83 (10)
O5^{ii}—Pr—O5	73.13 (18)	O4^{iii}—Pr—Pr^{iv}	115.28 (12)
O2^{i}—Pr—O1	66.58 (17)	O5^{iv}—Pr—Pr^{iv}	41.55 (10)
O5^{ii}—Pr—O1	72.04 (15)	O4^{v}—Pr—Pr^{iv}	112.38 (11)
O5—Pr—O1	136.21 (16)	O3^{vi}—Pr—Pr^{iv}	49.45 (10)
O2^{i}—Pr—O4^{iii}	88.59 (15)	O3^{vii}—Pr—Pr^{iv}	45.31 (10)
O5^{ii}—Pr—O4^{iii}	139.79 (17)	O2^{i}—Pr—Pr^{ii}	116.25 (12)
O5—Pr—O4^{iii}	130.10 (14)	O5^{ii}—Pr—Pr^{ii}	36.83 (11)
O1—Pr—O4^{iii}	70.01 (15)	O5—Pr—Pr^{ii}	36.29 (11)
O2^{i}—Pr—O5^{iv}	77.01 (17)	O1—Pr—Pr^{ii}	105.16 (11)
O5^{ii}—Pr—O5^{iv}	128.20 (19)	O4^{iii}—Pr—Pr^{ii}	151.15 (10)
O5—Pr—O5^{iv}	84.90 (16)	O5^{iv}—Pr—Pr^{ii}	109.08 (11)
O1—Pr—O5^{iv}	138.17 (15)	O4^{v}—Pr—Pr^{ii}	86.32 (11)
O4^{iii}—Pr—O5^{iv}	89.84 (16)	O3^{vi}—Pr—Pr^{ii}	97.46 (11)
O2^{i}—Pr—O4^{v}	136.90 (16)	O3^{vii}—Pr—Pr^{ii}	57.99 (11)
O5^{ii}—Pr—O4^{v}	91.33 (16)	Pr^{iv}—Pr—Pr^{ii}	71.85 (3)
O5—Pr—O4^{v}	82.80 (16)	O2—S—O1	110.1 (3)
O1—Pr—O4^{v}	72.38 (15)	O2—S—O3	109.7 (3)
O4^{iii}—Pr—O4^{v}	64.96 (17)	O1—S—O3	111.7 (3)
O5^{iv}—Pr—O4^{v}	132.35 (15)	O2—S—O4	108.9 (3)
O2^{i}—Pr—O3^{vi}	132.98 (17)	O1—S—O4	108.5 (3)
O5^{ii}—Pr—O3^{vi}	133.47 (15)	O3—S—O4	107.9 (3)
O5—Pr—O3^{vi}	61.84 (16)	S—O1—Pr	139.7 (3)
O1—Pr—O3^{vi}	136.71 (14)	S—O2—Pr^{viii}	155.7 (3)
O4^{iii}—Pr—O3^{vi}	72.40 (15)	S—O3—Pr^{vi}	133.7 (3)
O5^{iv}—Pr—O3^{vi}	60.84 (15)	S—O3—Pr^{ix}	137.8 (3)
O4^{v}—Pr—O3^{vi}	72.83 (16)	Pr^{vi}—O3—Pr^{ix}	85.24 (13)
O2^{i}—Pr—O3^{vii}	78.53 (16)	S—O4—Pr^{x}	125.0 (3)
O5^{ii}—Pr—O3^{vii}	70.23 (15)	S—O4—Pr^{v}	120.0 (3)
O5—Pr—O3^{vii}	59.19 (16)	Pr^{x}—O4—Pr^{v}	115.04 (17)
O1—Pr—O3^{vii}	128.53 (14)	Pr^{ii}—O5—Pr	106.87 (18)
O4^{iii}—Pr—O3^{vii}	147.45 (16)	Pr^{ii}—O5—Pr^{iv}	128.20 (19)
O5^{iv}—Pr—O3^{vii}	58.29 (15)	Pr—O5—Pr^{iv}	95.10 (16)
O4^{v}—Pr—O3^{vii}	140.86 (15)	Pr^{ii}—O5—H5A	142.8
O3^{vi}—Pr—O3^{vii}	94.76 (13)	Pr—O5—H5A	109.3
O2^{i}—Pr—Pr^{iv}	109.56 (13)	Pr^{iv}—O5—H5A	40.0

O5ⁱⁱ—Pr—Prⁱᵛ	103.47 (11)		

O2—S—O1—Pr	179.4 (4)	O1—S—O4—Prˣ	33.7 (4)
O3—S—O1—Pr	−58.5 (5)	O3—S—O4—Prˣ	154.9 (3)
O4—S—O1—Pr	60.3 (5)	O2—S—O4—Prᵛ	93.2 (3)
O2ⁱ—Pr—O1—S	167.8 (5)	O1—S—O4—Prᵛ	−147.0 (3)
O5ⁱⁱ—Pr—O1—S	−96.1 (4)	O3—S—O4—Prᵛ	−25.8 (4)
O5—Pr—O1—S	−57.3 (5)	O2ⁱ—Pr—O5—Prⁱⁱ	68.0 (3)
O4ⁱⁱⁱ—Pr—O1—S	70.4 (4)	O5ⁱⁱ—Pr—O5—Prⁱⁱ	0.0
O5ⁱᵛ—Pr—O1—S	136.1 (4)	O1—Pr—O5—Prⁱⁱ	−38.5 (3)
O4ᵛ—Pr—O1—S	1.3 (4)	O4ⁱⁱⁱ—Pr—O5—Prⁱⁱ	−141.99 (18)
O3ᵛⁱ—Pr—O1—S	39.2 (5)	O5ⁱᵛ—Pr—O5—Prⁱⁱ	132.5 (2)
O3ᵛⁱⁱ—Pr—O1—S	−140.6 (4)	O4ᵛ—Pr—O5—Prⁱⁱ	−93.60 (19)
Prⁱᵛ—Pr—O1—S	−140.0 (7)	O3ᵛⁱ—Pr—O5—Prⁱⁱ	−167.9 (2)
Prⁱⁱ—Pr—O1—S	−79.7 (4)	O3ᵛⁱⁱ—Pr—O5—Prⁱⁱ	76.67 (19)
O1—S—O2—Prᵛⁱⁱⁱ	13.5 (8)	Prⁱᵛ—Pr—O5—Prⁱⁱ	132.5 (2)
O3—S—O2—Prᵛⁱⁱⁱ	−109.8 (7)	O2ⁱ—Pr—O5—Prⁱᵛ	−64.5 (3)
O4—S—O2—Prᵛⁱⁱⁱ	132.3 (7)	O5ⁱⁱ—Pr—O5—Prⁱᵛ	−132.5 (2)
O2—S—O3—Prᵛⁱ	168.4 (4)	O1—Pr—O5—Prⁱᵛ	−171.07 (15)
O1—S—O3—Prᵛⁱ	46.0 (5)	O4ⁱⁱⁱ—Pr—O5—Prⁱᵛ	85.5 (2)
O4—S—O3—Prᵛⁱ	−73.1 (4)	O5ⁱᵛ—Pr—O5—Prⁱᵛ	0.0
O2—S—O3—Prⁱˣ	−39.4 (5)	O4ᵛ—Pr—O5—Prⁱᵛ	133.87 (16)
O1—S—O3—Prⁱˣ	−161.8 (4)	O3ᵛⁱ—Pr—O5—Prⁱᵛ	59.53 (16)
O4—S—O3—Prⁱˣ	79.1 (5)	O3ᵛⁱⁱ—Pr—O5—Prⁱᵛ	−55.86 (15)
O2—S—O4—Prˣ	−86.1 (4)	Prⁱⁱ—Pr—O5—Prⁱᵛ	−132.5 (2)

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

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H5A⋯O3ᵛⁱ	0.85	2.20	2.630 (7)	111
O5—H5A⋯O2ˣⁱ	0.85	2.31	3.082 (7)	152

Symmetry codes: (vi) $-x$, $-y+2$, $-z$; (xi) $-x+1/2$, $y+1/2$, $-z+1/2$.