

were not refined. The structure solution and refinement were carried out on a Compaq Prolinear 4/50 computer using the *MolEN* (Fair, 1990) program package, including *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1271). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aquatris(2,6-difluorobenzoato)praseodymium(III)

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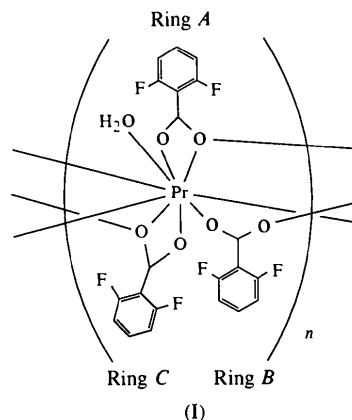
Abstract

The title compound, *catena*-poly[aquapraseodymium(III)-tris(μ -2,6-difluorobenzoato)-*O*:*O'*:*O*:*O'*:*O*:*O'*:*O*], [Pr(C₇H₃F₂O₂)₃(H₂O)], is a single-strand polymer. The Pr atoms are ninefold coordinated by three bridging 2,6-difluorobenzoate ligands and one water mol-

ecule. The 2,6-difluorobenzoate ligands bind in two unique modes, with one ligand forming a common μ -*O*:*O'* bridge and the other two forming less common μ -*O*:*O'*:*O* bridges. One of the F atoms of a benzoate ligand forms a three-center hydrogen bond.

Comment

In the title complex, (I), the 2,6-difluorobenzoate ions are arbitrarily called rings A, B and C.



Praseodymium(III), [Xe]4f², forms a nine-coordinate complex with three 2,6-difluorobenzoate ions and a water molecule (Fig. 1). The coordination sphere of the Pr atom is a square-face-capped trigonal prism; atoms O1A, O2B' and O1C' form the top triangle, and O1C, O1W and O1A'' form the bottom triangle, with O1B, O2A and O2C as the caps [symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$] (Fig. 2). The Pr atom receives 14 electrons from nine ligand atoms (two electrons from each, except for two O1C atoms and two O1A atoms which donate one electron each due to the bridging represented in the scheme above).

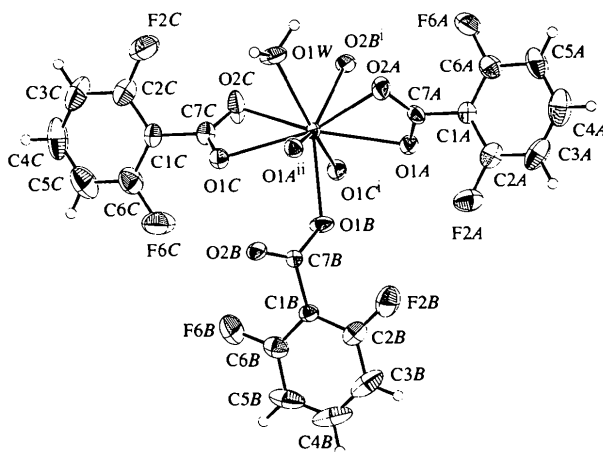


Fig. 1. The crystal structure of the asymmetric unit of the title polymer. Displacement ellipsoids are plotted at the 50% probability level.

† Deceased (1994).

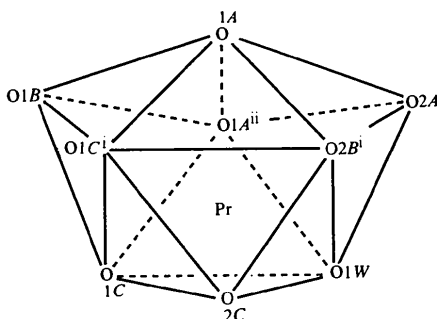


Fig. 2. The square-face-capped trigonal prismatic coordination of the Pr atom.

The O atoms in the fluorobenzoate ions form bridges in the structure. The two O atoms of ring A are coordinated to the same Pr atom and one of the two O atoms is also bonded to another Pr atom. This is also true for ring C, except that the bridging O atom in ring C is not bonded to the Pr atom to which the O atom of ring A is bonded. The two O atoms of ring B, however, are bonded to different Pr atoms, forming an *O:O'* bridge. The overall crystal structure is a single-strand polymer of Pr^{III} and 2,6-difluorobenzoate ions. The structure of this complex is similar to those of other praseodymium complexes which tend to form polymeric structures (Xuye & Kezhen, 1985). The reason for this might lie in the large atomic radius of the Pr atom (2.67 Å) and the accessibility of the *f* atomic orbitals to the difluorobenzoate ligands. Comparison may be made with the crystal structures of the complexes of the hydroxybenzoate ion with erbium (2.45 Å), neodymium (2.64 Å) and cerium (2.70 Å); in these, hydroxybenzoate ions bridge the metal centres to form single-strand polymers (Koizumi *et al.*, 1984).

The F2B atom participates in hydrogen bonding with the H1W and O1B atoms of the neighboring unit (Fig. 3); H1W...O1Bⁱⁱ 2.181, O1W...O1Bⁱⁱ 2.847, H1W...F2Bⁱⁱ 2.170, O1W...F2Bⁱⁱ 2.990, F2Bⁱⁱ...O1Bⁱⁱ 2.982 Å; O1W—H1W...O1Bⁱⁱ 124.7, O1W—H1W...O1Bⁱⁱ 141.3, O1Bⁱⁱ...H1W...F2Bⁱⁱ 86.5°; the sum of the angles about the three-center hydrogen bond (Jeffrey & Saenger, 1991) is 352.5°.

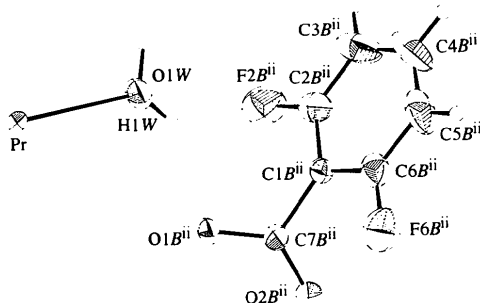


Fig. 3. Three-center hydrogen bonding.

Experimental

A solution of praseodymium carbonate [Pr₂(CO₃)₃; 0.5 mmol] in water was added to 2,6-difluorobenzoic acid (1.5 mmol). The mixture was stirred at room temperature and allowed to crystallize (Koizumi *et al.*, 1984)

Crystal data

[Pr(C₇H₃F₂O₂)₃(H₂O)]

M_r = 630.21

Monoclinic

*P*2₁/*c*

a = 21.803 (2) Å

b = 12.319 (2) Å

c = 7.898 (2) Å

β = 92.11 (2)°

V = 2119.8 (7) Å³

Z = 4

D_x = 1.975 Mg m⁻³

D_m = 1.98 Mg m⁻³

D_m measured by flotation in CHBr₃/CHCl₃

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 15.09–19.45°

μ = 2.394 mm⁻¹

T = 293 (2) K

Prism

0.4 × 0.2 × 0.2 mm

Light green

Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

ψ scan (*SDP/IDP*; Enraf–Nonius, 1985)

T_{min} = 0.55, *T_{max}* = 0.62

3666 measured reflections

3666 independent reflections

3245 observed reflections

[*I* > 2σ(*I*)]

θ_{max} = 25.97°

h = -26 → 26

k = 0 → 15

l = 0 → 9

3 standard reflections

frequency: 240 min

intensity decay: 0.2%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0316

wR(*F*²) = 0.0834

S = 1.148

3666 reflections

318 parameters

H atoms riding

w = 1/[σ²(*F_o*²) + (0.0291*P*)² + 8.3061*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.003

Δρ_{max} = 0.525 e Å⁻³

Δρ_{min} = -0.990 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Pr	0.24732 (2)	0.19688 (2)	0.24139 (3)	0.02051 (9)
O1W	0.2210 (2)	0.0354 (3)	0.4217 (5)	0.0427 (11)
O1A	0.1799 (2)	0.2551 (3)	-0.0178 (4)	0.0282 (8)
C7A	0.1344 (3)	0.2011 (5)	0.0318 (6)	0.0264 (11)
O2A	0.1395 (2)	0.1390 (3)	0.1556 (5)	0.0345 (9)
C1A	0.0722 (3)	0.2175 (5)	-0.0546 (7)	0.0278 (12)
C2A	0.0468 (3)	0.3182 (5)	-0.0777 (8)	0.0393 (15)
F2A	0.0779 (2)	0.4055 (3)	-0.0179 (5)	0.0543 (10)
C3A	-0.0103 (3)	0.3343 (7)	-0.1523 (9)	0.053 (2)
C4A	-0.0425 (3)	0.2445 (8)	-0.2085 (10)	0.061 (2)
C6A	0.0378 (3)	0.1301 (5)	-0.1113 (8)	0.0382 (14)
F6A	0.0619 (2)	0.0299 (3)	-0.0927 (5)	0.0555 (11)

C5A	-0.0193 (3)	0.1411 (7)	-0.1885 (9)	0.054 (2)
O1B	0.2474 (2)	0.3995 (3)	0.2618 (5)	0.0405 (10)
O2B	0.2578 (2)	0.4444 (3)	0.5343 (4)	0.0337 (9)
C7B	0.2563 (2)	0.4663 (4)	0.3818 (6)	0.0248 (11)
C1B	0.2638 (3)	0.5840 (4)	0.3365 (6)	0.0264 (11)
C2B	0.2178 (3)	0.6436 (5)	0.2512 (7)	0.0362 (14)
F2B	0.1661 (2)	0.5908 (4)	0.2015 (5)	0.0590 (11)
C3B	0.2222 (4)	0.7515 (6)	0.2189 (10)	0.058 (2)
C4B	0.2750 (5)	0.8052 (6)	0.2742 (10)	0.063 (2)
C5B	0.3214 (4)	0.7513 (6)	0.3572 (10)	0.059 (2)
C6B	0.3149 (3)	0.6415 (5)	0.3866 (7)	0.0383 (14)
F6B	0.3601 (2)	0.5875 (4)	0.4671 (5)	0.0625 (12)
O1C	0.3123 (2)	0.2287 (3)	0.5214 (5)	0.0297 (9)
O2C	0.3470 (2)	0.1136 (4)	0.3384 (5)	0.0548 (11)
C7C	0.3537 (3)	0.1639 (5)	0.4723 (7)	0.0316 (13)
C1C	0.4109 (3)	0.1484 (5)	0.5767 (7)	0.0308 (12)
C2C	0.4302 (3)	0.0478 (6)	0.6316 (9)	0.048 (2)
F2C	0.3934 (2)	-0.0377 (4)	0.5988 (6)	0.0695 (13)
C3C	0.4851 (4)	0.0325 (8)	0.7167 (11)	0.071 (3)
C4C	0.5237 (4)	0.1180 (10)	0.7459 (11)	0.079 (3)
C5C	0.5070 (4)	0.2196 (8)	0.6940 (11)	0.068 (2)
C6C	0.4509 (3)	0.2344 (6)	0.6148 (9)	0.047 (2)
F6C	0.4343 (2)	0.3331 (3)	0.5574 (7)	0.0680 (13)

Table 2. Selected geometric parameters (Å, °)

Pr—O2B ⁱ	2.405 (4)	O1B—C7B	1.265 (6)
Pr—O1C ⁱ	2.459 (4)	O2B—C7B	1.234 (6)
Pr—O2C	2.497 (4)	O2B—Pr ⁱⁱ	2.405 (4)
Pr—O1B	2.501 (4)	C7B—C1B	1.503 (7)
Pr—O1A ⁱⁱ	2.517 (4)	C2B—F2B	1.347 (8)
Pr—O1W	2.525 (4)	C6B—F6B	1.331 (8)
Pr—O2A	2.526 (4)	O1C—C7C	1.277 (7)
Pr—O1A	2.578 (4)	O1C—Pr ⁱⁱ	2.459 (4)
Pr—O1C	2.612 (4)	O2C—C7C	1.231 (7)
O1A—C7A	1.268 (6)	C7C—C1C	1.480 (7)
O1A—Pr ⁱ	2.517 (4)	C2C—F2C	1.344 (8)
C7A—O2A	1.243 (6)	C6C—F6C	1.343 (8)
C7A—C1A	1.508 (7)		
O2B ⁱ —Pr—O1C ⁱ	73.60 (13)	C7A—O1A—Pr ⁱ	147.3 (3)
O2B ⁱ —Pr—O2C	78.91 (14)	C7A—O1A—Pr	92.2 (3)
O1C ⁱ —Pr—O2C	81.5 (2)	Pr ⁱ —O1A—Pr	109.47 (14)
O2B ⁱ —Pr—O1B	140.01 (13)	O2A—C7A—O1A	121.1 (5)
O1C ⁱ —Pr—O1B	71.00 (14)	O2A—C7A—C1A	119.4 (5)
O2C—Pr—O1B	113.1 (2)	O1A—C7A—C1A	119.4 (5)
O2B ⁱ —Pr—O1A ⁱⁱ	139.19 (14)	C7A—O2A—Pr	95.3 (3)
O1C ⁱ —Pr—O1A ⁱⁱ	144.48 (13)	F2A—C2A—C1A	118.7 (5)
O2C—Pr—O1A ⁱⁱ	113.00 (13)	F2A—C2A—C3A	118.2 (6)
O1B—Pr—O1A ⁱⁱ	73.48 (14)	F6A—C6A—C5A	118.9 (6)
O2B ⁱ —Pr—O1W	80.95 (13)	F6A—C6A—C1A	118.3 (5)
O1C ⁱ —Pr—O1W	147.25 (14)	C7B—O1B—Pr	134.2 (3)
O2C—Pr—O1W	73.5 (2)	C7B—O2B—Pr ⁱⁱ	145.4 (4)
O1B—Pr—O1W	138.54 (13)	O2B—C7B—O1B	125.9 (5)
O1A ⁱⁱ —Pr—O1W	66.91 (13)	O2B—C7B—C1B	116.4 (4)
O2B ⁱ —Pr—O2A	73.99 (14)	O1B—C7B—C1B	117.7 (4)
O1C ⁱ —Pr—O2A	118.07 (12)	C6B—C1B—C2B	115.5 (6)
O2C—Pr—O2A	139.2 (2)	C6B—C1B—C7B	121.7 (5)
O1B—Pr—O2A	107.3 (2)	C2B—C1B—C7B	122.6 (5)
O1A ⁱⁱ —Pr—O2A	72.85 (12)	F2B—C2B—C3B	118.8 (6)
O1W—Pr—O2A	72.56 (14)	F2B—C2B—C1B	117.8 (6)
O2B ⁱ —Pr—O1A	74.17 (13)	F6B—C6B—C1B	117.4 (5)
O1C ⁱ —Pr—O1A	70.24 (12)	F6B—C6B—C5B	119.4 (7)
O2C—Pr—O1A	145.31 (14)	C1B—C6B—C5B	123.2 (7)
O1B—Pr—O1A	76.85 (13)	C7C—O1C—Pr ⁱⁱ	151.7 (3)
O1A ⁱⁱ —Pr—O1A	101.68 (12)	C7C—O1C—Pr	91.0 (3)
O1W—Pr—O1A	122.16 (14)	Pr ⁱⁱ —O1C—Pr	110.23 (14)
O2A—Pr—O1A	50.74 (12)	C7C—O2C—Pr	97.6 (4)
O2B ⁱ —Pr—O1C	128.48 (13)	O2C—C7C—O1C	120.8 (5)
O1C ⁱ —Pr—O1C	103.52 (13)	O2C—C7C—C1C	119.1 (5)
O2C—Pr—O1C	50.46 (13)	O1C—C7C—C1C	120.1 (5)
O1B—Pr—O1C	78.27 (13)	F2C—C2C—C3C	119.6 (7)
O1A ⁱⁱ —Pr—O1C	68.81 (12)	F2C—C2C—C1C	118.1 (6)
O1W—Pr—O1C	76.58 (14)	F6C—C6C—C5C	120.1 (7)
O2A—Pr—O1C	137.74 (12)	F6C—C6C—C1C	117.0 (5)
O1A—Pr—O1C	155.03 (12)		

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XPLA* and *ZORTEP* (Zsolnai, 1995).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dichloro[*N,N'*-ethylenebis(3-*tert*-butyl-5-methylsalicylideneiminato)-*N,N',O,O'*]-titanium(IV), [TiCl₂(C₂₆H₃₄N₂O₂)]

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Abstract

The synthetic route to obtain single crystals of dichloro{6,6'-di-*tert*-butyl-2,2'-[1,2-ethanediylbis(nitrilomethylidyne-*N*)]-4,4'-dimethyldiphenolato-*O,O'*}titanium(IV) is described. The X-ray analysis reveals that the title compound is a monomer with four molecules in the unit cell. There are only weak van der Waals-type forces between neighboring molecules. The compound