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(Diethyleneglycol dimethyl ether)tris-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)praseodymium(III)

John Plakatouras,[a]* Constantin Kavounis[b] and Christine Cardin[c]

[a]Department of Chemistry, University of Ioannina, Gr-451 10 Ioannina, Greece, [b]Department of Physics, University of Thessaloniki, Gr-540 06 Thessaloniki, Greece, and [c]Department of Chemistry, University of Reading, Whiteknights, Reading RG4 9BB, England

Correspondence e-mail: iplakatu@cc.uoi.gr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.035
wR factor = 0.086
Data-to-parameter ratio = 8.6

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

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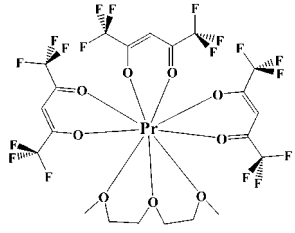
The title compound, $[Pr(C_5HF_6O_2)_3(C_6H_{14}O_3)]$ or $[Pr(hfpd)_3(2g)]$, was prepared by the reaction of $PrCl_3{\cdot}7H_2O$ and hfpd-H (1,1,1,5,5,5-hexafluoropentane-2,4-dione) in the presence of aqueous ammonia and recrystallization of the product from *n*-hexane in the presence of diglyme (2g). The metal atom is nine-coordinate, bonded to three bidentate β-diketonato ligands and the polyether molecule.

Comment

Volatile compounds of rare earths have been the subject of great interest because they are needed for the preparation of many technologically interesting thin films by metal-organic chemical vapor deposition (MOCVD). Particular attention has recently been devoted to the preparation of new lanthanide β-diketonate adducts with polyethers (Drake *et al.*, 1993; Bradley *et al.*, 1994; Baxter *et al.*, 1995). Some of them exhibit improved properties in terms of thermal stability and volatility, of potential interest for application as precursors in the MOCVD fabrication of electroceramics. In a previous study, we have shown that water in the reaction mixture of lanthanide halides with hfpd-H (1,1,1,5,5,5-hexafluropentane-2,4-dione) strongly affects the identity of the products (Plakatouras *et al.*, 1994), leading to non-volatile aggregates when present. The reaction of lanthanum oxide with hfpd-H in the presence of a glyme (1g = ethyleneglycol dimethyl ether, 2g = diethyleneglycol dimethyl ether and 3g = triethyl-eneglycol dimethyl ether) in hexane leads, after heating, to volatile lanthanum(III)-β-diketonate adducts with the abovementioned glymes (Malandrino *et al.*, 1998). The diglyme adduct was used for the fabrication of LaF_3 films by means of atmospheric pressure MOCVD and for $LaAlO_3$ with low pressure MOCVD.



(I)

The title compound, (I), was synthesized utilizing mild conditions (see *Experimental*) and is isostructural with $[La(hfpd)_3(2g)]$. The Pr atom is nine-coordinate and is located at the center of a tricapped trigonal prism defined by six O atoms belonging to three bidentate chelating hfpd ligands and three O atoms belonging to one diethyleneglycol dimethyl

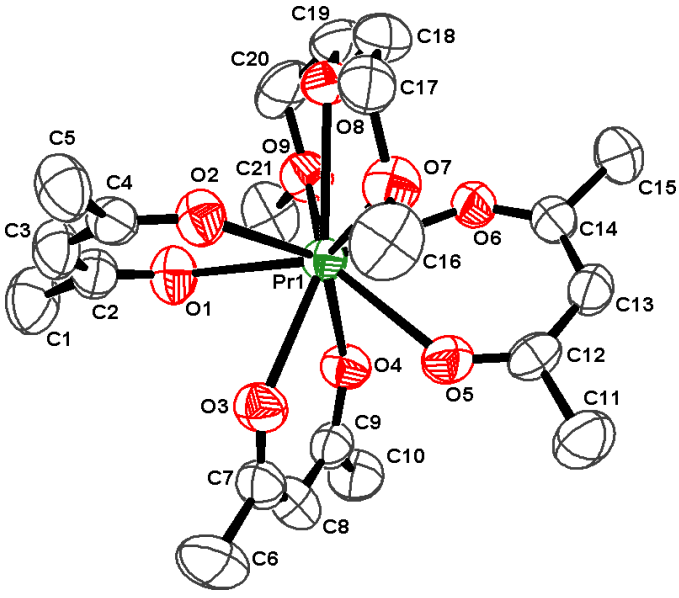


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H and F atoms have been omitted for clarity.

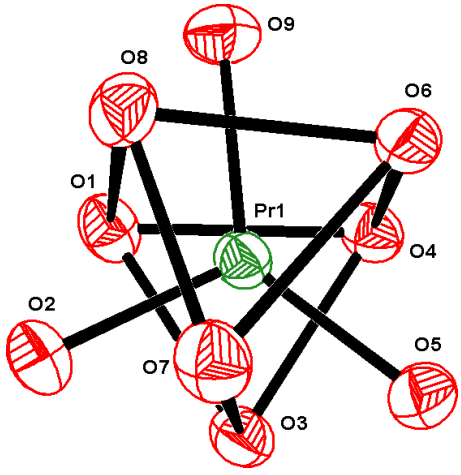


Figure 2
The coordination sphere of (I), showing the tricapped trigonal prismatic geometry.

ether molecule (Fig. 1). The trigonal bases of the prism are defined by O1/O3/O4 and O6/O7/O8. Atoms O2, O5 and O9 cap rectangular faces O1/O3/O7/O8, O3/O4/O6/O7, and O1/O4/O6/O8, respectively (Fig. 2). The Pr—$O_{\beta\text{-diketonate}}$ bond distances span the range 2.423–2.493 Å, and they are in agreement with similar complexes. The difference in C—O bond lengths within the same hfpd molecule is reflected in the difference of the corresponding Pr—O bond lengths, *i.e.* the longer Pr—O bond is associated with a short C—O bond. This is the case for the two hfpd molecules. The Pr—O_{glyme} bond lengths span the range 2.599–2.617 Å, and they are longer than the Pr—$O_{\beta\text{-diketonate}}$ bonds, as expected.

Experimental

Aqueous ammonia was added to a methanolic solution containing $PrCl_3{\cdot}7H_2O$ and hfpd-H in a 1:3.1 molar ratio until the pH was *ca* 4.5. The resulting precipitate was isolated and characterized as $Pr(hfpd)_3(H_2O)_3$. Recrystallization of this compound from *n*-hexane in the presence of one equivalent of diglyme led to the formation of the title compound in the form of large green prisms suitable for X-ray studies.

Crystal data

$[Pr(C_6H_{14}O_3)(C_5HF_6O_2)_3]$
M_r = 896.26
Monoclinic, $P2_1/c$
a = 10.013 (3) Å
b = 15.656 (4) Å
c = 21.133 (5) Å
β = 103.48 (4)°
V = 3221.7 (15) Å^3
Z = 4
D_x = 1.848 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4409 reflections
θ = 2.5–24.0°
μ = 1.66 mm^{-1}
T = 293 (2) K
Prism, green
0.45 × 0.30 × 0.20 mm

Data collection

Mar Research Image Plate Scanner diffractometer
Arndt–Wonacott oscillation method
Absorption correction: multi-scan (*XDS*; Kabsch, 1993)
T_{min} = 0.542, T_{max} = 0.741
9202 measured reflections
4785 independent reflections
4219 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 24.9°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.086
S = 1.09
4785 reflections
555 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 8.0994P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.010
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00417 (8)

Table 1
Selected geometric parameters (Å, °).

Pr1—O4	2.4225 (17)	Pr1—O1	2.4927 (17)
Pr1—O2	2.4517 (16)	Pr1—O9	2.5995 (16)
Pr1—O3	2.4576 (15)	Pr1—O8	2.6072 (15)
Pr1—O5	2.4629 (15)	Pr1—O7	2.6176 (17)
Pr1—O6	2.4891 (17)		
O4—Pr1—O3	71.48 (5)	O9—Pr1—O8	63.52 (5)
O5—Pr1—O6	68.67 (5)	O9—Pr1—O7	124.82 (5)
O2—Pr1—O1	67.64 (6)	O8—Pr1—O7	63.39 (5)

All H atoms were placed at idealized positions and refined using a riding model; their isotropic displacement factors, U_{iso}, were fixed at 1.2 or 1.5 times U_{eq} of the parent C atom. The F atoms on C1, C6, C10 and C11 are disordered between two orientations; the relevant fluorines were assigned partial occupancies [0.513/0.487 (2) for F1*A*/*B*–F3*A*/*B*, 0.175/0.825 (2) for F7*A*/*B*–F9*A*/*B*, 0.518/0.482 (2) for F10*A*/*B*–F12*A*/*B* and 0.514/0.486 (2) for F13*A*/*B*–F15*A*/*B*] and refined anisotropically along with the other non-H atoms.

Data collection: *Mar Research Image-Plate Scanner Software* (Mar Research, 2002); cell refinement: *XDS* (Kabsch, 1993); data reduction: *XDS*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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