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

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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**^aDepartment of Chemistry, University of Ioannina, Gr-451 10 Ioannina, Greece,^bDepartment of Physics, University of Thessaloniki, Gr-540 06 Thessaloniki, Greece,and ^cDepartment of Chemistry, University of Reading, Whiteknights, Reading RG4 9BB, EnglandCorrespondence e-mail: iplakatu@cc.uoi.gr**Key indicators**

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

Disorder in main residue

R factor = 0.035

wR factor = 0.086

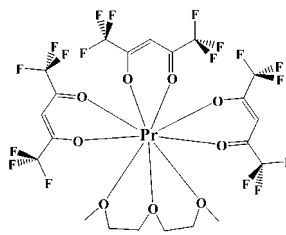
Data-to-parameter ratio = 8.6

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

The title compound, $[\text{Pr}(\text{C}_5\text{HF}_6\text{O}_2)_3(\text{C}_6\text{H}_{14}\text{O}_3)]$ or $[\text{Pr}(\text{hfpd})_3(2\text{g})]$, was prepared by the reaction of $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ 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-hexafluoropentane-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 = triethyleneglycol 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 $[\text{La}(\text{hfpd})_3(2\text{g})]$. 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

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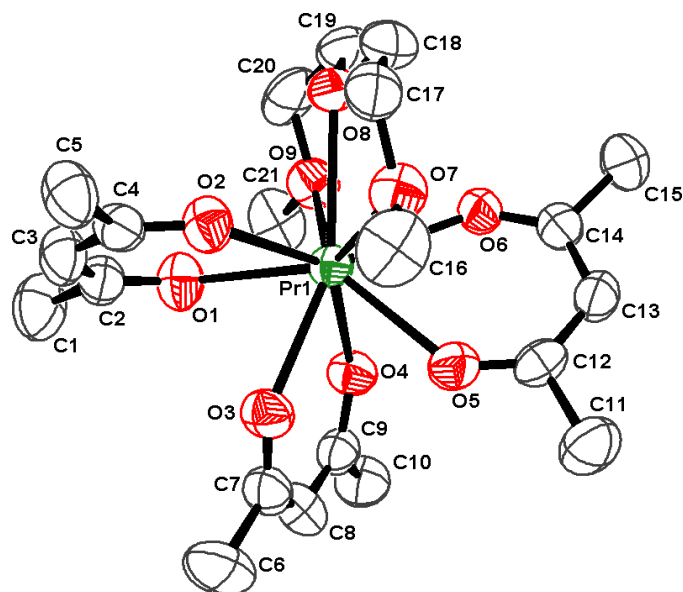


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. H and F atoms have been omitted for clarity.

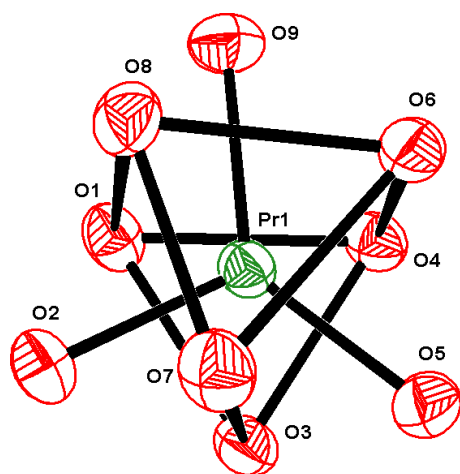


Figure 2
The coordination sphere of (I), showing the tricapped trigonal prismatic geometry.

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 $_{\beta}$ -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 $_{\text{glyme}}$ bond lengths span the range 2.599–2.617 Å, and they are longer than the Pr–O $_{\beta}$ -diketonate bonds, as expected.

Experimental

Aqueous ammonia was added to a methanolic solution containing PrCl $_3$ ·7H $_2$ O 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 $_2$ O) $_3$. 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 $_6$ H $_{14}$ O $_3$)(C $_5$ HF $_6$ O $_2$) $_3$]
 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) $^\circ$
 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 $^\circ$
 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 $^\circ$
 h = –11 → 11
 k = 0 → 18
 l = –24 → 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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.010
 $\Delta\rho_{\text{max}}$ = 0.84 e Å $^{-3}$
 $\Delta\rho_{\text{min}}$ = –0.71 e Å $^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00417 (8)

Table 1

Selected geometric parameters (Å, $^\circ$).

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 F1A/B–F3A/B, 0.175/0.825 (2) for F7A/B–F9A/B, 0.518/0.482 (2) for F10A/B–F12A/B and 0.514/0.486 (2) for F13A/B–F15A/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: *SIR97* (Altomare *et al.*, 1999) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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