

(Ethanol-O)tris(nitrato-O,O')bis(triphenylphosphine oxide-O)cerium(III)

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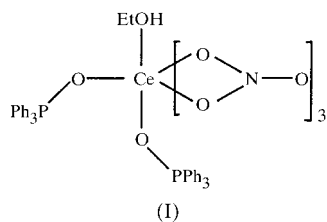
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The title compound, $[\text{Ce}(\text{NO}_3)_3(\text{C}_2\text{H}_6\text{O})(\text{C}_{18}\text{H}_{15}\text{OP})_2]$, contains discrete molecules with nine-coordinate Ce atoms having all nitrate groups bonded as symmetrical bidentate ligands [Ce—O(P) 2.369 (2) and 2.385 (2), Ce—O(N) 2.549 (3)—2.596 (3) and Ce—O(Et) 2.515 (3) Å].

Comment

As part of an ongoing study into the solution equilibria found in lanthanide complexes of phosphine oxides, the compound $[\text{Ce}(\text{Ph}_3\text{PO})_2(\text{EtOH})(\text{NO}_3)_3]$, (I), was isolated (Cousins & Hart, 1967).



The paramagnetic (f^1) species showed a single contact shifted $^{31}\text{P}\{^1\text{H}\}$ NMR resonance (CH_2Cl_2 , 300 K) with a high frequency shift, $\delta = 72.0$ (relative to 85% H_3PO_4), and addition of Ph_3PO showed discrete resonances for the ligand at $\delta = 26.0$, consistent with slow exchange on the NMR timescale. In dichloromethane solution, the complex is a non-electrolyte, the conductivity being only very slightly above that of the pure solvent, and hence the nitrate groups remain coordinated. The crystal structure revealed a nine-coordinate cerium bonded to three bidentate nitrate groups, two phosphine oxides and ethanol. The nitrate ion is bonded as a symmetrical bidentate ligand with the $\text{O}_c\text{—N—O}_c$ angle smaller than the idealized value in the free $D_{3h}\text{NO}_3^-$ anion, where O_c is a coordinated O atom. As noted before (Valle *et al.*, 1986), the uncoordinated O atom (O_t) has shorter N— O_t distances than the N— O_c distances by *ca* 0.05 Å. If the nitrate groups are conceptually replaced by a monodentate ligand, the coordination around Ce may be described as 'mer-octahedral', with the phosphine

oxides being *cis*. The three planar NO_3 groups are approximately perpendicular to each other. The M—O—P angles are very variable among phosphine oxide complexes and in the present compound are 167.2 (2) and 164.4 (2)°. Three other compounds with the same stoichiometry were identified from the Cambridge Structural Database (Allen & Kennard, 1993) for Eu (Valle *et al.*, 1986), Nd (Huang *et al.*, 1985) and Sm (Sakamoto & Miyake, 1993) and it is likely that all are isomorphous. A related Ce^{III} complex with three triphenylphosphine oxides and three nitrate ligands has been reported (Lin *et al.*, 1994).

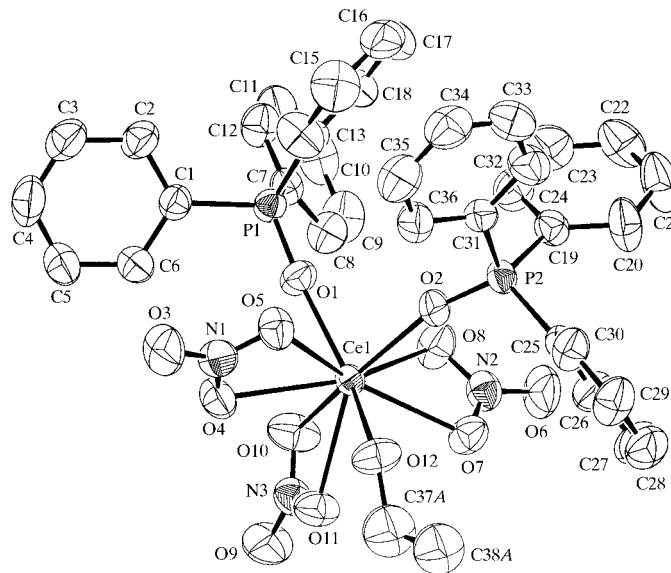


Figure 1

The molecular structure of (I) showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level, with H atoms omitted for clarity. The disordered ethyl group (C37A and C38A) is shown as one of the two contributors to the disorder.

Experimental

Cooling a boiling ethanol solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Ph_3PO (1:2) gave the title compound. Suitable crystals were isolated from the reaction product.

Crystal data

$[\text{Ce}(\text{NO}_3)_3(\text{C}_2\text{H}_6\text{O})(\text{C}_{18}\text{H}_{15}\text{OP})_2]$
 $M_r = 928.76$
 Monoclinic, $P2_1/n$
 $a = 17.202$ (2) Å
 $b = 10.9235$ (18) Å
 $c = 22.3209$ (16) Å
 $\beta = 105.667$ (7)°
 $V = 4038.4$ (9) Å³
 $Z = 4$

$D_x = 1.528$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.8\text{--}15.6^\circ$
 $\mu = 1.271$ mm⁻¹
 $T = 298$ (2) K
 Plate, colourless
 0.50 × 0.40 × 0.15 mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.587$, $T_{\text{max}} = 0.826$
 7353 measured reflections
 7102 independent reflections
 5317 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 20$
 $k = 0 \rightarrow 12$
 $l = -26 \rightarrow 25$
 3 standard reflections every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.091$
 $S = 1.031$
 7102 reflections
 504 parameters

Only H-atom U 's refined
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$

Table 1

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

Ce1—O1	2.369 (2)	P2—O2	1.501 (3)
Ce1—O2	2.385 (2)	O3—N1	1.224 (4)
Ce1—O4	2.580 (3)	O4—N1	1.265 (4)
Ce1—O5	2.596 (3)	O5—N1	1.259 (4)
Ce1—O7	2.549 (3)	O6—N2	1.213 (4)
Ce1—O8	2.575 (3)	O7—N2	1.268 (4)
Ce1—O10	2.563 (3)	O8—N2	1.270 (4)
Ce1—O11	2.572 (3)	O9—N3	1.217 (4)
Ce1—O12	2.515 (3)	O10—N3	1.265 (4)
P1—O1	1.502 (3)	O11—N3	1.258 (4)
O1—Ce1—O2	91.00 (9)	P1—O1—Ce1	167.25 (17)
O1—Ce1—O12	151.50 (10)	P2—O2—Ce1	164.39 (17)
O2—Ce1—O12	78.62 (10)	O3—N1—O5	121.2 (4)
O10—Ce1—O11	49.35 (10)	O3—N1—O4	121.4 (4)
O7—Ce1—O8	49.97 (9)	O5—N1—O4	117.4 (3)
O4—Ce1—O5	49.24 (9)		

The ethyl group originally had a very short C—C distance with elongated anisotropic displacement parameters and was later modelled as two disordered sites for both C atoms with restraints used on the O—C and C—C distances. H atoms were placed in calculated positions with a common refined isotropic displacement parameter, except for the H atom of the OH group, which was not included.

Data collection: *MSC/AFC-7S Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC-7S Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1104). Services for accessing these data are described at the back of the journal.

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