

Melissa L. Matthews and Michael Webster*

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England

Correspondence e-mail:
m.webster@soton.ac.uk

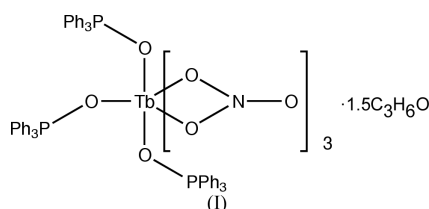
Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
Disorder in solvent or counterion
 R factor = 0.054
 wR factor = 0.135
Data-to-parameter ratio = 14.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tris(nitrato- $\kappa^2\text{O},\text{O}'$)tris(triphenylphosphine oxide- κO)terbium(III) acetone sesquisolvate

The title compound, $[\text{Tb}(\text{NO}_3)_3(\text{C}_{18}\text{H}_{15}\text{OP})_3] \cdot 1.5(\text{CH}_3)_2\text{CO}$, contains discrete molecules with nine-coordinate Tb atoms, all nitrate groups being bonded as symmetrical bidentate ligands; $\text{Tb}-\text{O}(\text{P}) = 2.307(4)$, $2.309(4)$ and $2.295(4)$ Å, and $\text{Tb}-\text{O}(\text{N}) = 2.467(4)$ - $2.539(4)$ Å.

Comment

As part of a continuing study into the solution equilibria found for lanthanide complexes of phosphine oxides, the complex $[\text{Tb}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_3] \cdot 1.5\text{Me}_2\text{CO}$, (I), was isolated (Cousins & Hart, 1967). The crystal structure reveals a nine-coordinate terbium bonded to three bidentate nitrate groups and three phosphine oxides, with 1.5 acetone molecules in the asymmetric unit, the latter arising from a partial occupancy for one solvent molecule. The three $(\text{P})\text{O}-\text{Tb}-\text{O}(\text{P})$ angles (Table 1) show that this complex may be described as *mer*-(pseudo)-octahedral, where the nitrate ligands have been replaced conceptually by monodentate ligands. The nitrate groups are symmetrically bonded, with the $\text{O}_c-\text{N}-\text{O}_c$ angle smaller (average 116°) than the ideal value in the free D_{3h} NO_3^- anion, where O_c is a coordinated O atom. As described previously (Valle *et al.*, 1986), the $\text{N}-\text{O}_c$ distances are *ca* 0.05 Å longer than $\text{N}-\text{O}_t$, where O_t is the terminal O atom. The $M-\text{O}-\text{P}$ angles are very variable among phosphine oxide complexes; in the present compound they are $154.7(3)$, $159.6(3)$ and $173.8(3)^\circ$.



Five other structurally characterized compounds with the same stoichiometry are known for Y (Deakin *et al.*, 2000), La (Huang *et al.*, 1987), Ce (Lin *et al.*, 1994), Sm (Sakamoto & Miyake, 1993) and Eu (Valle *et al.*, 1986), and all have a similar structure and are solvated ($2\text{Me}_2\text{CO}$ for Ce, Sm and Eu).

The $\text{Tb}-\text{O}(\text{P})$ and $\text{Tb}-\text{O}(\text{N})$ distances are a little longer than the corresponding values found in $[\text{Y}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_3] \cdot x\text{CH}_2\text{Cl}_2$ (Deakin *et al.*, 2000), where the Y compound is again '*mer*'; this reflects the relative ionic radii [M^{3+} (eight-coordinate): Y 1.159 Å and Tb 1.180 Å (Shannon, 1976)].

Experimental

Cooling a boiling acetone solution of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Ph_3PO (1:3) gave the title compound. Suitable crystals were isolated from the reaction product.

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Crystal data

[Tb(NO₃)₃(C₁₈H₁₅OP)₃]-1.5C₃H₆O
M_r = 1266.88
 Monoclinic, *P*2₁/*n*
a = 11.0612 (10) Å
b = 19.180 (2) Å
c = 27.641 (4) Å
 β = 94.895 (7)°
V = 5842.7 (12) Å³
Z = 4

D_x = 1.440 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 41 633 reflections
 θ = 2.9–27.5°
 μ = 1.36 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.16 × 0.16 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
T_{min} = 0.847, *T_{max}* = 0.873
 40 261 measured reflections

10 247 independent reflections
 6620 reflections with *I* > 2σ(*I*)
R_{int} = 0.111
 θ_{\max} = 25.0°
h = -13 → 12
k = -22 → 22
l = -32 → 31

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.054
wR(*F*²) = 0.135
S = 1.03
 10 247 reflections
 711 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 9.57P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.83 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00179 (16)

Table 1

Selected geometric parameters (Å, °).

Tb1—O1	2.307 (4)	Tb1—O8	2.505 (4)
Tb1—O2	2.309 (4)	Tb1—O10	2.459 (4)
Tb1—O3	2.295 (4)	Tb1—O11	2.539 (4)
Tb1—O4	2.467 (4)	P1—O1	1.502 (4)
Tb1—O5	2.492 (5)	P2—O2	1.508 (5)
Tb1—O7	2.476 (4)	P3—O3	1.504 (5)
O1—Tb1—O2	85.51 (15)	P1—O1—Tb1	154.7 (3)
O1—Tb1—O3	84.27 (15)	P2—O2—Tb1	159.6 (3)
O3—Tb1—O2	150.09 (14)	P3—O3—Tb1	173.8 (3)
O4—Tb1—O5	51.43 (16)	O6—N1—O5	122.4 (6)
O7—Tb1—O8	51.26 (16)	O6—N1—O4	121.5 (6)
O10—Tb1—O11	51.23 (13)	O5—N1—O4	116.1 (5)

The large displacement parameter values of all the atoms of one of the acetone solvent molecules suggested partial occupancy, and the site-occupancy factor (sof) was set to 0.5 to bring the values close to those of the other acetone molecule. The atoms with sof of 0.5 were refined isotropically. H atoms were placed in calculated positions with a displacement parameter related to that of the bonded C atom; $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.2$ for phenyl H and 1.5 for methyl H atoms. The maximum electron-density peak is 1.5 Å from Tb1.

Data collection: COLLECT (Hooft, 1998) and DENZO (Otwinowski & Minor, 1997); cell refinement: COLLECT and DENZO; data reduction: COLLECT and DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

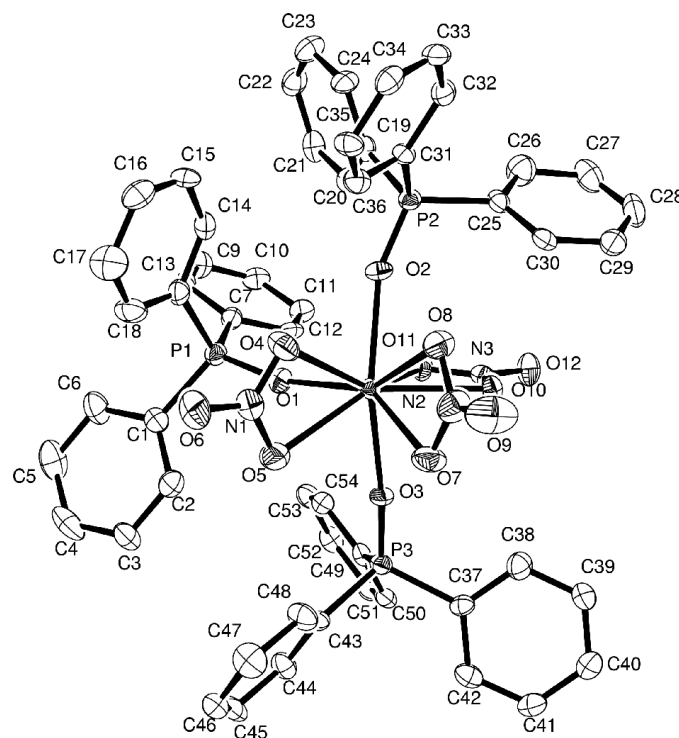


Figure 1

The molecular structure of [Tb(NO₃)₃(Ph₃PO)₃], showing the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level; H atoms and the Tb1 label have been omitted for clarity.

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