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Tetraaquatetrakis(trimethylphosphine oxide-κO)cerium(III) trichloride trihydrate

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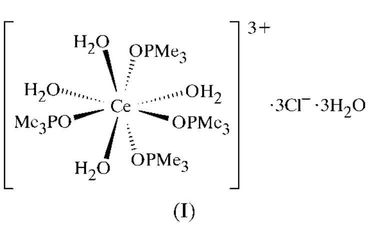
The title compound, $[Ce(C_3H_9OP)_4(H_2O)_4]Cl_3\cdot 3H_2O$, contains eight-coordinate Ce atoms in an approximate dodecahedral arrangement, with Ce—O(P) = 2.372 (2)–2.423 (2) Å and Ce—O(H_2) = 2.518 (2)–2.630 (2) Å.

Comment

During attempts to synthesize octahedral $[Ln(Me_3PO)_6]^{3+}$ cations (Ln is a lanthanide), the reaction of $CeCl_3\cdot 6H_2O$ with eight molar equivalents of Me_3PO in methanol was investigated. The product isolated was $[Ce(Me_3PO)_4Cl_3]\cdot 4H_2O$, as identified by analysis and IR spectroscopy, and, significantly, the complex was a non-electrolyte in freshly prepared nitromethane solution (Leung, 2001). Colourless crystals were isolated from a solution of this complex in nitromethane, which was allowed to evaporate in air over a period of three weeks. The crystals contained molecules of the title complex, $[Ce(Me_3PO)_4(H_2O)_4]Cl_3\cdot 3H_2O$, (I), showing that the initial complex had been converted into the mixed phosphine-oxide–aqua complex on standing in the polar solvent, the extra water coming from the atmosphere. Complexes of the type $[Ln(Me_3PO)_6][PF_6]_3$ have since been isolated from the reaction of $LnCl_3\cdot xH_2O$, Me_3PO and NH_4PF_6 in 1:8:3 molar ratios in methanol (Hill *et al.*, 2002). The structure of (I) is presented here.



(I)

The structure of (I) consists of a distorted eight-coordinate Ce^{III} cation composed of four *O*-donor phosphine oxide ligands and four water molecules. The Ce—O(P) distances are shorter [2.372 (2)–2.423 (2) Å] than the Ce—O(H_2) distances [2.518 (2)–2.630 (2) Å]. The oxygen geometry at the Ce atom is, to a good approximation, a triangulated dodecahedron (bisdisphenoid) with idealized D_{2d} symmetry. Of the two interpenetrating tetrahedra, the flattened tetrahedron is formed by the four Me_3PO groups and the elongated tetrahedron by the four H_2O ligands. The two trapezoidal planes often used to describe this geometry are similar, and are formed by atoms O1/O2/O6/O7 and O3/O4/O5/O8, respectively (Table 1 and Fig. 1).

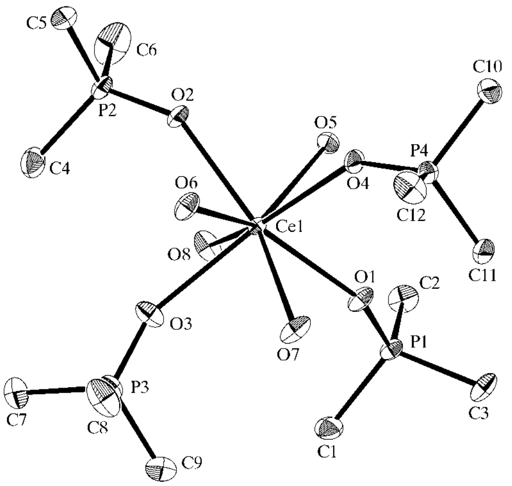


Figure 1
A view of the cation of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, and the Cl^- anions, hydrate molecules and H atoms have been omitted for clarity.

The *M*—O—P angles in phosphine oxide complexes are highly variable and, in the present case, are in the range 144.27 (12)–151.31 (13)°. All the O—P—C angles are larger than the idealized tetrahedral angles (by an average of 2°) and the C—P—C angles are correspondingly smaller.

Both H atoms of each water molecule are involved in hydrogen bonding, either to a Cl or an O atom. The shortest O—H···Cl distance involves atom O7 and the shortest O—H···O distance is between a coordinated water and a hydrate water molecule (Table 2).

There are no reports to date of structurally characterized lanthanide–phosphine oxide complexes with the same stoichiometry as (I), but the structures of two Ce^{III} complexes of triphenylphosphine oxide, namely the nine-coordinate $[Ce(Ph_3PO)_3(NO_3)_3]$ (Lin *et al.*, 1994) and $[Ce(Ph_3PO)_2(EtOH)(NO_3)_3]$ (Levason *et al.*, 2000), have been reported. The structure of the six-coordinate arsine oxide complex $[Ce(Ph_3AsO)_3Cl_3]\cdot MeCN$ has also been described (Ryan *et al.*, 1987).

Experimental

Colourless crystals of (I) were isolated from a solution of $[Ce(Me_3PO)_4Cl_3]\cdot 4H_2O$ in nitromethane, which was allowed to evaporate in air over a period of three weeks.

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Table 1
Selected geometric parameters (Å, °).

Ce1—O1	2.3926 (19)	Ce1—O5	2.5827 (18)
Ce1—O2	2.372 (2)	Ce1—O6	2.6300 (19)
Ce1—O3	2.4230 (19)	Ce1—O7	2.528 (2)
Ce1—O4	2.3896 (19)	Ce1—O8	2.518 (2)
O2—Ce1—O1	145.66 (7)	O2—Ce1—O6	73.50 (7)
O4—Ce1—O3	149.91 (7)	O7—Ce1—O6	69.45 (6)
O3—Ce1—O8	67.02 (6)	P1—O1—Ce1	149.58 (12)
O1—Ce1—O7	70.96 (6)	P2—O2—Ce1	144.83 (12)
O4—Ce1—O5	75.84 (7)	P3—O3—Ce1	151.31 (13)
O8—Ce1—O5	67.32 (6)	P4—O4—Ce1	144.27 (12)

Crystal data

$[Ce(C_3H_9OP)_4(H_2O)_4]Cl_3\cdot 3H_2O$
$M_r = 740.87$
Triclinic, $P\overline{1}$
$a = 10.2753$ (10) Å
$b = 11.1003$ (10) Å
$c = 15.6822$ (15) Å
$\alpha = 70.406$ (10)°
$\beta = 82.483$ (10)°
$\gamma = 74.161$ (10)°
$V = 1619.6$ (3) Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 600 reflections
$\theta = 2.9$–27.5°
$\mu = 1.89$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.26 × 0.20 × 0.16 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.656$, $T_{\max} = 0.739$
18 262 measured reflections
5444 independent reflections
4908 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.073$
$\theta_{\max} = 25°$
$h = -12 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.064$
$S = 1.03$
5444 reflections
281 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0184P)^2 + 0.6782P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.88$ e Å^{-3}

Methyl-group H atoms were positioned geometrically, with C—H distances of 0.98 Å, and the water H atoms were located in a difference electron-density map. The latter were not refined and all H atoms were given a fixed isotropic displacement parameter.

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5X···Cl1$^{\rm i}$	0.95	2.24	3.161 (2)	164
O5—H5Y···O9$^{\rm ii}$	0.85	2.25	2.933 (3)	137
O6—H6X···Cl2$^{\rm iii}$	0.80	2.45	3.242 (2)	173
O6—H6Y···Cl3$^{\rm iii}$	0.89	2.40	3.295 (2)	176
O7—H7X···Cl2$^{\rm iii}$	0.92	2.18	3.067 (2)	163
O7—H7Y···Cl2$^{\rm i}$	0.97	2.14	3.068 (2)	160
O8—H8X···O10	0.92	1.87	2.755 (3)	159
O8—H8Y···O9	0.92	1.94	2.818 (3)	160
O9—H9X···Cl3	0.94	2.32	3.250 (2)	168
O9—H9Y···Cl1$^{\rm iv}$	0.93	2.48	3.260 (2)	141
O10—H10X···Cl3	0.90	2.37	3.265 (2)	172
O10—H10Y···O11$^{\rm v}$	0.92	1.92	2.840 (3)	173
O11—H11X···Cl1$^{\rm vi}$	0.87	2.33	3.193 (2)	179
O11—H11Y···Cl1	0.95	2.43	3.271 (2)	147

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $x-1, y, z$; (iv) $x, y, z-1$; (v) $1-x, -y, 1-z$; (vi) $1-x, -y, 2-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1541). Services for accessing these data are described at the back of the journal.

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