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The Crystal and Molecular Structure of Tetranitratobis(triphenylphosphine oxide)cerium(IV)

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The crystal and molecular structure of the new complex tetranitratobis(triphenylphosphine oxide)cerium(IV) $[Ce(NO_3)_4\{OP(C_6H_5)_3\}_2]$ has been determined by single-crystal X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/n$, with unit cell dimensions $a = 13.908\ (8)$, $b = 17.589\ (9)$, $c = 16.476\ (6)$ Å, and $\beta = 91.10\ (4)°$, and four molecules per unit cell. The data were collected on a diffractometer. The structure was solved by the heavy-atom technique. Positional and anisotropic thermal parameters have been refined by block-diagonal least-squares methods to a final R value, for 2868 observed reflections, of 0.047. Cerium is ten-coordinated to four bidentate nitrate groups and two oxygen atoms from triphenylphosphine oxide. The bond distances and angles are discussed. The isostructural thorium compound $Th(NO_3)_4\{OP(C_6H_5)_3\}_2$ is also described.

Introduction

The 4f and 5f transition elements, although almost entirely restricted to coordination with oxygen, nitrogen, and the halogens, form complexes having a large variety of coordination numbers and an even larger variety of coordination polyhedra.[1] The phosphoryl group, as a substituted phosphine oxide R_3PO or as an organic phosphate $(RO)_3PO$, is particularly notable for its ready formation of complexes with these metal ions.[2,3] This property has been much investigated in connection with solvent-extraction procedures[4] but the only structures established by X-ray analysis are apparently dinitratobis(triethyl phosphate)dioxouranium(VI) $[UO_2(NO_3)_2\{OP(OC_2H_5)_3\}_2]$[5] and trinitratoethanolbis(triphenylphosphine oxide)samarium(III) $[Sm(NO_3)_3C_2H_5OH(OP(C_6H_5)_3)_2]$,[6] having eight- and nine-coordination, respectively.

We have therefore prepared tetranitratobis(triphenylphosphine oxide)cerium(IV) and the analogous thorium compound and now report the crystal structure of the cerium complex. Comparison of X-ray powder patterns indicated that the thorium complex is isostructural.

The mode of coordination of the nitrate ion, and particularly the relation between this and its infrared spectrum, has been the subject of much discussion.[7] It is now evident that the bidentate (rather than monodentate) nitrate ion is normal in complexes with 4f and 5f transition metals and reasonably common in complexes with d transition metals; the presently reported structures provide examples of the ion remaining bidentate even in a sterically rather crowded situation.

Experimental Section

Tetranitratobis(triphenylphosphine oxide)cerium(IV).—Ammonium hexanitratocerate(IV) (0.500 g) in acetone (10 ml) was treated with triphenylphosphine oxide (0.507 g, 2 mol) in acetone (5 ml). The mixture was filtered from a white precipitate (NH_4NO_3) which immediately formed and the solvent was removed under reduced pressure. The sticky crystalline residue, which smelled of nitric acid, was recrystallized from acetonitrile giving 0.13 g of orange crystals, mp 237–239° dec. Crystals for X-ray analysis were obtained from benzene.

Reduction to the cerous state occurs in solution, recrystallization being attended with considerable loss, but the solid is stable in air. *Anal.* Calcd for $C_{36}H_{30}CeN_4O_{14}P_2$: C, 45.8; H, 3.2; N, 5.9. Found: C, 45.7; H, 3.2; N, 5.8. The compound is a nonelectrolyte at 3.3×10^{-4} M concentration in acetonitrile.

Tetranitratobis(triphenylphosphine oxide)thorium(IV).—Thorium nitrate hexahydrate (1.00 g) in acetone (10 ml) was treated with triphenylphosphine oxide (0.954 g, 2 mol) in acetone (10 ml) and the combined solutions were evaporated to dryness under reduced pressure. The sticky crystalline residue was extracted with three 15-ml portions of boiling benzene, and the combined extracts were filtered and concentrated to 20 ml by boiling. Well-formed crystals (1.06 g) were deposited and collected, mp 262–266°. *Anal.* Calcd for $C_{36}H_{30}N_4O_{14}P_2Th$: C, 41.7; H, 2.9; N, 5.4. Found: C, 42.0; H, 3.0; N, 5.45. The compound is a nonelectrolyte at 3.3×10^{-4} M concentration in acetonitrile.

A crystal of $Ce(NO_3)_4(OP(C_6H_5)_3)_2$ of approximate dimensions $0.27 \times 0.67 \times 0.75$ mm was used for collection of X-ray data. The crystal was bounded by $\{001\}$ faces perpendicular to the short dimension and by all forms of $\{101\}$, $\{\bar{1}01\}$, $\{1\bar{1}0\}$, $\{0\bar{1}0\}$. It was mounted on the b axis for data collection. Oscillation, Weissenberg, and precession X-ray photographs showed systematic absences $h + l \neq 2n$, for $h0l$ reflections; $k \neq 2n$, for $0k0$ reflections, uniquely defining space group $P2_1/n$. Cell dimensions were obtained by least-squares refinement of 18 values of 2θ determined on the diffractometer. (λ(Mo Kα) 0.7107 Å).

Crystal Data.—$Ce(NO_3)_4\{OP(C_6H_5)_3\}_2$, mol wt 944.51, is monoclinic with space group $P2_1/n$, $a = 13.908\ (8)$, $b = 17.589\ (9)$, $c = 16.476\ (6)$ Å, $\beta = 91.10\ (4)°$, $V = 4029.7$ Å^3, $d_m = 1.562\ (5)$ g cm^{-3} (by flotation in a mixture of carbon tetrachloride and chloroform), $d_c = 1.56$ g cm^{-3}, $Z = 4$, $\mu = 13.56$ cm^{-1} for Mo Kα radiation (λ 0.7107 Å), and $F(000) = 1896$.

The intensities of 3775 reflections were measured on a General Electric XRD-5 diffractometer using a θ–2θ scan technique, scanning across the peak for 60 sec and counting the background on each side of the peak for 30 sec. Zirconium-filtered molybdenum radiation (λ 0.7107 Å) was used. The scan rate was 2.0°/min, the takeoff angle being 4.0°. Some 2868 reflections were considered observed using the criteria $F_o \geqslant 2\sigma(F_o)$, where σ was determined from counter statistics. The intensity data were reduced to F_o's using a computer program of Ahmed and Saunder-

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TABLE I

ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ce(1)	0.0220 (1)	0.1554 (1)	0.1963 (1)	C(30)	0.4383 (9)	0.0337 (7)	0.3831 (8)
P(2)	0.2816 (3)	0.1853 (2)	0.2476 (2)	C(31)	0.4162 (11)	−0.0345 (7)	0.3480 (9)
P(3)	−0.2252 (3)	0.1038 (2)	0.2632 (2)	C(32)	0.3543 (11)	−0.0372 (6)	0.2834 (9)
O(4)	0.1788 (5)	0.1687 (4)	0.2179 (5)	C(33)	0.3136 (9)	0.0286 (7)	0.2528 (8)
O(5)	−0.1274 (5)	0.1260 (4)	0.2301 (4)	C(34)	0.2857 (8)	0.2569 (6)	0.3270 (7)
O(6)	0.0254 (7)	0.0150 (4)	0.2061 (5)	C(35)	0.2357 (10)	0.2401 (7)	0.3978 (7)
O(7)	0.0494 (8)	−0.0501 (5)	0.3167 (6)	C(36)	p.2332 (11)	0.2948 (8)	0.4574 (8)
O(8)	0.0564 (6)	0.0736 (4)	0.3168 (5)	C(37)	0.3846 (10)	0.3598 (8)	0.4497 (8)
N(9)	0.0425 (7)	0.0106 (5)	0.2806 (6)	C(38)	0.3328 (10)	0.3751 (7)	0.3843 (8)
O(10)	0.0540 (7)	0.2896 (4)	0.2378 (5)	C(39)	0.3333 (8)	0.3232 (6)	0.3203 (7)
O(11)	−0.0063 (8)	0.2172 (5)	0.3262 (5)	C(40)	−0.2904 (8)	0.0499 (6)	0.1845 (7)
O(12)	0.0232 (8)	0.3364 (5)	0.3556 (5)	C(41)	−0.2411 (10)	0.0037 (7)	0.1295 (8)
N(13)	0.0200 (8)	0.2829 (6)	0.3081 (6)	C(42)	−0.2903 (10)	−0.0391 (7)	0.0746 (8)
O(14)	0.1159 (5)	0.0965 (4)	0.0861 (5)	C(43)	−0.3861 (10)	−0.0358 (8)	0.0721 (8)
O(15)	−0.0392 (6)	0.1009 (4)	0.0695 (4)	C(44)	−0.4385 (10)	0.0055 (9)	0.1232 (9)
O(16)	0.0528 (7)	0.0637 (5)	−0.0293 (5)	C(45)	−0.3886 (9)	0.0491 (8)	0.1811 (9)
N(17)	0.0459 (7)	0.0863 (5)	0.0402 (5)	C(46)	−0.2881 (8)	0.1903 (6)	0.2883 (7)
O(18)	0.0566 (6)	0.2445 (4)	0.0829 (4)	C(47)	−0.3488 (9)	0.1948 (7)	0.3573 (7)
O(19)	−0.0914 (6)	0.2477 (4)	0.1280 (5)	C(48)	−0.3951 (10)	0.2631 (7)	0.3746 (8)
O(20)	−0.0492 (7)	0.3215 (4)	0.0325 (5)	C(49)	−0.3889 (9)	0.3217 (7)	0.3237 (8)
N(21)	−0.0283 (7)	0.2712 (5)	0.0805 (5)	C(50)	−0.3352 (10)	0.3176 (7)	0.2564 (8)
C(22)	0.3481 (8)	0.2160 (6)	0.1615 (7)	C(51)	−0.2824 (10)	0.2531 (7)	0.2367 (8)
C(23)	0.2995 (10)	0.2282 (9)	0.0878 (8)	C(52)	−0.2156 (8)	0.0444 (6)	0.3540 (7)
C(24)	0.3540 (10)	0.2459 (9)	0.0231 (9)	C(53)	−0.1475 (9)	0.0686 (7)	0.4115 (8)
C(25)	0.4482 (11)	0.2557 (8)	0.0284 (8)	C(54)	−0.1400 (11)	0.0255 (9)	0.4839 (8)
C(26)	0.4975 (11)	0.2466 (9)	0.0981 (9)	C(55)	−0.1983 (12)	−0.0344 (8)	0.4948 (9)
C(27)	0.4444 (9)	0.2248 (8)	0.1651 (8)	C(56)	−0.2632 (12)	−0.0579 (8)	0.4399 (9)
C(28)	0.3369 (8)	0.0990 (6)	0.2901 (7)	C(57)	−0.2725 (10)	−0.0184 (8)	0.3686 (8)
C(29)	0.4028 (9)	0.1025 (7)	0.3543 (7)				

Calculated Positional Parameters for Hydrogen Atoms

H(1)–C(23)	0.2251	0.2202	0.0811	H(16)–C(41)	−0.1646	0.0019	0.1314
H(2)–C(24)	0.3191	0.2534	−0.0337	H(17)–C(42)	−0.2517	−0.0728	0.0324
H(3)–C(25)	0.4865	0.2712	−0.0239	H(18)–C(43)	−0.4224	−0.0677	0.0291
H(4)–C(26)	0.5733	0.2548	0.1015	H(19)–C(44)	−0.5128	0.0069	0.1195
H(5)–C(27)	0.4814	0.2183	0.2199	H(20)–C(45)	−0.4275	0.0822	0.2220
H(6)–C(29)	0.4217	0.1538	0.3818	H(21)–C(47)	−0.3549	0.1486	0.3958
H(7)–C(30)	0.4860	0.0365	0.4325	H(22)–C(48)	−0.4366	0.2656	0.4253
H(8)–C(31)	0.4461	−0.0845	0.3695	H(23)–C(49)	−0.4272	0.3704	0.3374
H(9)–C(32)	0.3358	−0.0888	0.2564	H(24)–C(50)	−0.3299	0.3640	0.2186
H(10)–C(33)	0.2657	0.0250	0.2030	H(25)–C(51)	−0.2406	0.2505	0.1846
H(11)–C(35)	0.1996	0.1880	0.4053	H(26)–C(53)	−0.1055	0.1156	0.4030
H(12)–C(36)	0.1948	0.2831	0.5109	H(27)–C(54)	−0.0901	0.0420	0.5279
H(13)–C(37)	0.2828	0.3992	0.4967	H(28)–C(55)	−0.1907	−0.0647	0.5489
H(14) C(38)	0.3671	0.4270	0.3786	H(29)–C(56)	−0.3056	−0.1065	0.4502
H(15)–C(39)	0.3723	0.3342	0.2677	H(30)–C(57)	−0.3242	−0.0360	0.3250

son.[8] Absorption corrections were made using a program of Meulenaer and Tompa.[9] The transmission factors ranged from 0.678 to 0.835. The form factors were taken from the literature,[10] including the anomalous term $\Delta f'$ for the Ce atom.

Structure Analysis and Refinement.—The positions of the cerium atoms and two phosphorus atoms were evident from the Harker section and the three-dimensional Patterson map. A Fourier synthesis phased on these atomic positions showed chemically reasonable positions for an additional 25 atoms and the next three-dimensional Fourier map revealed all 57 nonhydrogen atoms.

Refinement proceeded normally using the block-diagonal least-squares approximation and converged initially at an R of 0.081, varying positional and individual isotropic temperature factors for all nonhydrogen atoms. Inclusion of anisotropic temperature factors reduced the R to 0.055. A difference map showed a number of peaks about 0.3 $e^-/\text{Å}^3$ above background, suggesting positions for all but two hydrogen atoms. The final refinement converged at $R = 0.047$ (weighted $R = 0.056$) and included each hydrogen atom in its calculated position with an assigned temperature factor 0.5 Å^2 greater than that of the carbon atom to which it is bonded. (The isotropic temperature factors used for the carbon atoms were those obtained just previous to the final refinement, when these were converted to anisotropic values.) All parameter shifts were less than one-tenth the standard deviation, indicating completion of refinement. A final difference map showed no electron density exceeding ± 0.5 $e^-/\text{Å}^3$, the maximum being near the cerium atoms. Throughout the refinement reflections were weighted in accordance to counting statistics using the scheme discussed by Stout and Jensen.[11] There appeared to be no systematic variation of mean $w|F_o - F_c|^2$ with $\lambda^{-1} \sin \theta$ or $|F_o|$, indicating relative correctness of the weighting scheme.

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(8) NRC-2, data reduction program, written by F. R. Ahmed and C. P. Saunderson. NRC-8, Fourier program, and NRC-10, structure factors least-squares block-diagonal program, were written by F. R. Ahmed, National Research Council, Ottawa, Ontario, Canada. These programs are adapted for the SDS Sigma-7 computer. The rest of these programs are written by C. N. Caughlan, G. D. Smith, and E. L. Enwall.

(9) J. D. Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(10) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A, p 202 and Table 3.3.1B, p 211.

(11) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457. The constant for instrumental instability was 0.02.

TABLE II

ANISOTROPIC THERMAL PARAMETERS WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	β_{11}[a]	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Ce(1)	0.0047 (1)	0.0027 (1)	0.0025 (1)	−0.0001 (1)	−0.0009 (1)	0.0002 (1)
P(2)	0.0045 (3)	0.0038 (2)	0.0031 (2)	0.0002 (3)	−0.0013 (3)	−0.0007 (3)
P(3)	0.0047 (3)	0.0041 (2)	0.0031 (2)	0.0009 (4)	−0.0002 (4)	−0.0004 (4)
O(4)	0.0028 (6)	0.0042 (4)	0.0076 (5)	0.0025 (8)	0.0009 (9)	−0.0002 (8)
O(5)	0.0044 (6)	0.0044 (4)	0.0020 (3)	0.0002 (5)	−0.0008 (8)	0.0009 (7)
O(6)	0.0118 (8)	0.0038 (3)	0.0036 (4)	−0.0007 (7)	−0.0024 (10)	0.0016 (11)
O(7)	0.0210 (13)	0.0057 (5)	0.0069 (6)	0.0043 (9)	−0.0045 (15)	0.0050 (13)
O(8)	0.0089 (8)	0.0047 (4)	0.0047 (5)	0.0029 (7)	−0.0054 (10)	0.0001 (9)
N(9)	0.0076 (9)	0.0038 (5)	0.0069 (7)	0.0006 (9)	0.0004 (13)	0.0036 (11)
O(10)	0.0202 (12)	0.0016 (3)	0.0049 (5)	0.0001 (6)	−0.0014 (13)	−0.0006 (10)
O(11)	0.0205 (12)	0.0048 (4)	0.0036 (5)	−0.0037 (7)	0.0076 (13)	−0.0055 (13)
O(12)	0.0272 (15)	0.0046 (5)	0.0065 (6)	−0.0070 (9)	0.0022 (15)	0.0015 (15)
N(13)	0.0114 (12)	0.0050 (5)	0.0052 (6)	−0.0018 (10)	−0.0015 (15)	0.0036 (12)
O(14)	0.0051 (7)	0.0053 (4)	0.0051 (5)	−0.0027 (7)	0.0013 (9)	0.0005 (9)
O(15)	0.0077 (7)	0.0030 (3)	0.0033 (4)	−0.0016 (6)	−0.0031 (9)	−0.0010 (8)
O(16)	0.0145 (10)	0.0054 (5)	0.0038 (5)	−0.0019 (7)	0.0008 (11)	−0.0042 (11)
N(17)	0.0107 (11)	0.0033 (5)	0.0036 (5)	−0.0007 (8)	0.0003 (12)	−0.0022 (11)
O(18)	0.0070 (7)	0.0038 (4)	0.0039 (4)	0.0024 (6)	−0.0002 (9)	0.0027 (9)
O(19)	0.0069 (7)	0.0048 (4)	0.0053 (5)	0.0049 (7)	0.0010 (10)	0.0021 (9)
O(20)	0.0123 (9)	0.0048 (5)	0.0057 (5)	0.0035 (8)	−0.0036 (11)	0.0035 (10)
N(21)	0.0109 (10)	0.0022 (4)	0.0023 (5)	0.0013 (7)	−0.0052 (11)	0.0015 (10)
C(22)	0.0040 (10)	0.0047 (6)	0.0035 (7)	0.0020 (10)	0.0001 (13)	−0.0013 (12)
C(23)	0.0092 (14)	0.0118 (11)	0.0050 (8)	0.0086 (15)	−0.0027 (18)	−0.0089 (20)
C(24)	0.0089 (14)	0.0135 (12)	0.0060 (9)	0.0081 (17)	−0.0073 (19)	−0.0082 (22)
C(25)	0.0153 (18)	0.0099 (10)	0.0024 (7)	0.0032 (14)	0.0009 (18)	−0.0030 (22)
C(26)	0.0096 (15)	0.0138 (12)	0.0056 (10)	0.0064 (17)	0.0076 (19)	0.0049 (22)
C(27)	0.0057 (12)	0.0112 (10)	0.0046 (8)	0.0041 (14)	−0.0023 (16)	0.0053 (18)
C(28)	0.0049 (10)	0.0029 (6)	0.0052 (7)	0.0014 (10)	0.0024 (14)	0.0006 (12)
C(29)	0.0070 (11)	0.0044 (6)	0.0041 (7)	0.0004 (11)	−0.0061 (15)	0.0003 (14)
C(30)	0.0086 (13)	0.0058 (7)	0.0052 (8)	0.0025 (12)	−0.0050 (17)	0.0036 (16)
C(31)	0.0162 (18)	0.0045 (7)	0.0092 (11)	0.0010 (14)	−0.0086 (22)	0.0053 (19)
C(32)	0.0162 (17)	0.0011 (5)	0.0119 (11)	−0.0012 (12)	−0.0070 (23)	0.0035 (16)
C(33)	0.0086 (13)	0.0043 (6)	0.0055 (8)	−0.0002 (11)	−0.0036 (16)	−0.0024 (15)
C(34)	0.0046 (10)	0.0030 (5)	0.0040 (7)	−0.0014 (9)	−0.0017 (13)	0.0015 (12)
C(35)	0.0109 (14)	0.0049 (7)	0.0039 (7)	−0.0004 (11)	0.0002 (16)	−0.0016 (16)
C(36)	0.0123 (15)	0.0100 (9)	0.0031 (7)	−0.0038 (14)	−0.0002 (17)	−0.0029 (19)
C(37)	0.0123 (14)	0.0064 (8)	0.0054 (8)	−0.0052 (14)	−0.0015 (17)	−0.0018 (18)
C(38)	0.0125 (15)	0.0042 (7)	0.0066 (9)	−0.0055 (12)	−0.0034 (18)	−0.0008 (15)
C(39)	0.0069 (11)	0.0023 (6)	0.0054 (7)	0.0005 (10)	−0.0006 (14)	−0.0012 (12)
C(40)	0.0050 (10)	0.0029 (5)	0.0038 (7)	0.0000 (9)	−0.0020 (13)	−0.0025 (12)
C(41)	0.0086 (13)	0.0037 (6)	0.0059 (8)	0.0002 (11)	0.0007 (16)	0.0039 (14)
C(42)	0.0112 (14)	0.0056 (7)	0.0059 (9)	−0.0042 (13)	−0.0013 (18)	−0.0062 (17)
C(43)	0.0116 (14)	0.0071 (8)	0.0042 (8)	−0.0047 (13)	−0.0010 (17)	−0.0048 (18)
C(44)	0.0079 (14)	0.0100 (10)	0.0079 (10)	−0.0034 (16)	−0.0094 (19)	−0.0085 (19)
C(45)	0.0062 (12)	0.0079 (9)	0.0083 (10)	−0.0061 (15)	0.0034 (17)	0.0018 (17)
C(46)	0.0036 (9)	0.0037 (6)	0.0036 (6)	−0.0009 (9)	−0.0019 (12)	0.0001 (11)
C(47)	0.0071 (12)	0.0058 (7)	0.0046 (8)	0.0013 (11)	−0.0017 (15)	−0.0025 (14)
C(48)	0.0099 (13)	0.0043 (7)	0.0049 (8)	−0.0016 (11)	0.0033 (16)	0.0022 (15)
C(49)	0.0096 (13)	0.0040 (7)	0.0063 (8)	0.0000 (11)	0.0029 (17)	0.0040 (14)
C(50)	0.0131 (15)	0.0046 (7)	0.0067 (9)	0.0037 (12)	0.0050 (19)	0.0040 (16)
C(51)	0.0100 (13)	0.0043 (6)	0.0048 (8)	0.0031 (11)	0.0027 (16)	0.0019 (15)
C(52)	0.0054 (10)	0.0046 (6)	0.0032 (6)	0.0009 (10)	−0.0017 (13)	0.0024 (13)
C(53)	0.0056 (11)	0.0063 (8)	0.0062 (8)	0.0045 (13)	0.0011 (16)	−0.0024 (15)
C(54)	0.0132 (16)	0.0112 (10)	0.0034 (8)	0.0074 (14)	−0.0073 (18)	−0.0051 (21)
C(55)	0.0197 (20)	0.0064 (8)	0.0077 (10)	0.0097 (15)	−0.0026 (23)	−0.0112 (21)
C(56)	0.0204 (19)	0.0052 (8)	0.0072 (10)	0.0078 (14)	−0.0051 (23)	−0.0061 (20)
C(57)	0.0079 (13)	0.0058 (7)	0.0080 (10)	0.0021 (14)	−0.0016 (18)	−0.0038 (16)

[a] The form of anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)]$.

Results and Discussion

The final atomic parameters and the anisotropic thermal parameters are given in Tables I and II. Tables III and IV give the interatomic distances and valence angles. The final observed and calculated structure factors are listed in Table V. Figure 1 shows the structure and Figure 2 the coordination of cerium.

The Coordination Polyhedron.—In these complexes, Ce(IV) and Th(IV) are ten-coordinated, two oxygen atoms from each nitrate group being bonded to cerium, together with two oxygen atoms from triphenylphosphine oxide molecules. Ce(IV) and Th(IV), which in their reported stereochemistry show a mutual resemblance, are typically eight-coordinated,[12] often in a

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[12] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

TABLE III

INTERATOMIC DISTANCES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atoms	Distance, Å	Atoms	Distance, Å
Ce(1)–O(4)	2.216 (7)	C(24)–C(25)	1.32 (2)
Ce(1)–O(5)	2.222 (7)	C(25)–C(26)	1.34 (2)
Ce(1)–O(6)	2.475 (7)	C(26)–C(27)	1.39 (2)
Ce(1)–O(8)	2.490 (8)	C(28)–C(29)	1.39 (2)
Ce(1)–O(10)	2.495 (7)	C(28)–C(33)	1.42 (2)
Ce(1)–O(11)	2.440 (8)	C(29)–C(30)	1.39 (2)
Ce(1)–O(14)	2.483 (8)	C(30)–C(31)	1.36 (2)
Ce(1)–O(15)	2.437 (7)	C(31)–C(32)	1.36 (2)
Ce(1)–O(18)	2.493 (8)	C(32)–C(33)	1.38 (2)
Ce(1)–O(19)	2.514 (8)	C(34)–C(35)	1.40 (2)
P(2)–O(4)	1.531 (8)	C(34)–C(39)	1.35 (2)
P(3)–O(5)	1.526 (8)	C(35)–C(36)	1.38 (2)
P(2)–C(22)	1.79 (1)	C(36)–C(37)	1.36 (2)
P(2)–C(28)	1.83 (1)	C(37)–C(38)	1.31 (2)
P(2)–C(34)	1.82 (1)	C(38)–C(39)	1.40 (2)
P(3)–C(40)	1.83 (1)	C(40)–C(41)	1.41 (2)
P(3)–C(46)	1.81 (1)	C(40)–C(45)	1.37 (2)
P(3)–C(52)	1.83 (1)	C(41)–C(42)	1.35 (2)
O(6)–N(9)	1.25 (1)	C(42)–C(43)	1.33 (2)
O(7)–N(9)	1.23 (1)	C(43)–C(44)	1.34 (2)
O(8)–N(9)	1.27 (1)	C(44)–C(45)	1.40 (2)
O(10)–N(13)	1.27 (1)	C(46)–C(47)	1.43 (2)
O(11)–N(13)	1.25 (1)	C(46)–C(51)	1.40 (2)
O(12)–N(13)	1.22 (1)	C(47)–C(48)	1.40 (2)
O(14)–N(17)	1.23 (1)	C(48)–C(49)	1.33 (2)
O(15)–N(17)	1.31 (1)	C(49)–C(50)	1.35 (2)
O(16)–N(17)	1.22 (1)	C(50)–C(51)	1.39 (2)
O(18)–N(21)	1.27 (1)	C(52)–C(53)	1.39 (2)
O(19)–N(21)	1.26 (1)	C(52)–C(57)	1.38 (2)
O(20)–N(21)	1.22 (1)	C(53)–C(54)	1.42 (2)
C(22)–C(23)	1.40 (2)	C(54)–C(55)	1.34 (2)
C(22)–C(27)	1.35 (2)	C(55)–C(56)	1.33 (2)
C(23)–C(24)	1.36 (2)	C(56)–C(57)	1.37 (2)

distorted square antiprism as in the tetraacetylacetonates $M(CH_3COCHCOCH_3)_4$ or in ceric and thorium fluorides. Dodecahedral coordination also occurs, as in the tetrakis(dibenzoylmethane) complexes, $M(C_6H_5COCHCOC_6H_5)_4$. Eight-coordination probably occurs also in the many compounds of the type ThX_4L_4 (X = halogen, L = monodentate ligand). Nine-coordination is rare but is exemplified by $NaTh_2F_9$ (tricapped trigonal prism).[13] Circumstantial evidence indicates possible ten-coordination in $Th(NO_3)_4$chdpm, where chdpm[4] is $\{(c\text{-}C_6H_{11})_2P(O)\}_2CH_2$. Eleven-coordination occurs in $Th(NO_3)_4 \cdot 5H_2O$ with bidentate nitrate ions[14] and icosahedral 12-coordination in $[Mg(H_2O)_6][Th(NO_3)_6] \cdot 2H_2O$[15] where the Th–O distances of 2.63 (5) Å are comparable with the 2.437 (8)–2.514 (8) Å Ce–O (nitrate) distances observed here after allowing for the decreased ionic radius of cerium (Ce^{4+}, 0.92 Å; Th^{4+}, 0.99 Å).

The coordination now observed in $Ce(NO_3)_4(OP(C_6H_5)_3)_2$ cannot fairly be rationalized in terms of any semiregular polyhedron because of the very different stereochemical requirements of the NO_3 and $OP(C_6H_5)_3$ groups. It may be described as a distorted trans-octahedral arrangement of two phosphoryl oxygen atoms and four nitate groups (each NO_3 group being considered to occupy a single coordination position[16]). The phosphoryl oxygen atoms, however, are not collinear with the Ce atom but subtend 155.0 (3)°, while the four nitrate ions have their planes inclined in the approximate shape of a four-bladed propeller. The Ce–O distances are 2.437 (8)–2.514 (8) Å for the nitrate group oxygens and significantly shorter, 2.216 (7) and 2.222 (7) Å, for the phosphoryl Ce–O contacts. This short bond is attained despite the fact that it leads to

TABLE IV

BOND ANGLES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atoms	Angle, deg	Atoms	Angle, deg
O(4)–Ce(1)–O(5)	155.0 (3)	Ce(1)–O(10)–N(13)	95.6 (6)
O(4)–Ce(1)–O(6)	94.4 (3)	Ce(1)–O(11)–N(13)	98.6 (7)
O(4)–Ce(1)–O(8)	76.1 (3)	O(10)–N(13)–O(11)	114.9 (10)
O(4)–Ce(1)–O(10)	71.7 (3)	O(10)–N(13)–O(12)	120.3 (10)
O(4)–Ce(1)–O(11)	89.2 (3)	O(11)–N(13)–O(12)	124.5 (10)
O(4)–Ce(1)–O(14)	68.4 (3)	Ce(1)–O(14)–N(17)	95.1 (6)
O(4)–Ce(1)–O(15)	120.4 (3)	Ce(1)–O(15)–N(17)	95.1 (6)
O(4)–Ce(1)–O(18)	81.4 (3)	O(14)–N(17)–O(15)	117.0 (9)
O(4)–Ce(1)–O(19)	127.6 (3)	O(14)–N(17)–O(16)	123.3 (9)
O(5)–Ce(1)–O(6)	76.6 (3)	O(15)–N(17)–O(16)	119.8 (9)
O(5)–Ce(1)–O(8)	80.4 (3)	Ce(1)–O(18)–N(21)	93.6 (6)
O(5)–Ce(1)–O(10)	108.3 (3)	Ce(1)–O(19)–N(21)	93.0 (6)
O(5)–Ce(1)–O(11)	73.6 (3)	O(18)–N(21)–O(19)	121.2 (9)
O(5)–Ce(1)–O(14)	126.4 (2)	O(18)–N(21)–O(20)	119.9 (9)
O(5)–Ce(1)–O(15)	79.0 (2)	O(19)–N(21)–O(20)	118.9 (9)
O(5)–Ce(1)–O(18)	121.9 (2)	P(2)–C(22)–C(23)	119.2 (9)
O(5)–Ce(1)–O(19)	71.4 (2)	P(2)–C(22)–C(27)	121.8 (9)
O(6)–Ce(1)–O(8)	50.9 (3)	C(23)–C(22)–C(27)	118.9 (12)
O(6)–Ce(1)–O(10)	157.4 (3)	C(22)–C(23)–C(24)	116.8 (13)
O(6)–Ce(1)–O(11)	113.1 (3)	C(23)–C(24)–C(25)	123.1 (14)
O(6)–Ce(1)–O(14)	67.8 (3)	C(24)–C(25)–C(26)	122.1 (14)
O(6)–Ce(1)–O(15)	70.7 (3)	C(25)–C(26)–C(27)	116.3 (14)
O(6)–Ce(1)–O(18)	132.3 (3)	C(26)–C(27)–C(22)	122.6 (13)
O(6)–Ce(1)–O(19)	133.2 (3)	P(2)–C(28)–C(29)	121.4 (9)
O(8)–Ce(1)–O(10)	107.3 (3)	P(2)–C(28)–C(33)	117.8 (9)
O(8)–Ce(1)–O(11)	65.8 (3)	C(29)–C(28)–C(33)	120.7 (11)
O(8)–Ce(1)–O(14)	104.3 (3)	C(28)–C(29)–C(30)	116.6 (11)
O(8)–Ce(1)–O(15)	121.0 (3)	C(29)–C(30)–C(31)	123.2 (12)
O(8)–Ce(1)–O(18)	157.4 (3)	C(30)–C(31)–C(32)	119.8 (13)
O(8)–Ce(1)–O(19)	147.0 (3)	C(31)–C(32)–C(33)	120.5 (13)
O(10)–Ce(1)–O(11)	50.9 (3)	C(32)–C(33)–C(28)	119.1 (11)
O(10)–Ce(1)–O(14)	120.1 (3)	P(2)–C(34)–C(35)	116.4 (9)
O(10)–Ce(1)–O(15)	131.6 (3)	P(2)–C(34)–C(39)	123.4 (9)
O(10)–C(1)–O(18)	64.8 (3)	C(35)–C(34)–C(39)	120.3 (11)
O(10)–Ce(1)–O(19)	67.6 (3)	C(34)–C(35)–C(36)	117.8 (12)
O(11)–Ce(1)–O(14)	157.4 (3)	C(35)–C(36)–C(37)	120.2 (13)
O(11)–Ce(1)–O(15)	150.2 (3)	C(36)–C(37)–C(38)	122.0 (13)
O(11)–Ce(1)–O(18)	114.4 (3)	C(37)–C(38)–C(39)	119.9 (12)
O(11)–Ce(1)–O(19)	89.7 (3)	C(38)–C(39)–C(34)	119.7 (11)
O(14)–Ce(1)–O(15)	52.4 (2)	P(3)–C(40)–C(41)	121.0 (9)
O(14)–Ce(1)–O(18)	66.6 (3)	P(3)–C(40)–C(45)	121.0 (9)
O(14)–Ce(1)–O(19)	106.1 (3)	C(41)–C(40)–C(45)	117.9 (11)
O(15)–Ce(1)–O(18)	80.0 (2)	C(40)–C(41)–C(42)	120.4 (12)
O(15)–Ce(1)–O(19)	70.4 (2)	C(41)–C(42)–C(43)	119.3 (13)
O(18)–Ce(1)–O(19)	52.2 (2)	C(42)–C(43)–C(44)	124.1 (13)
O(4)–P(2)–C(22)	107.3 (5)	C(43)–C(44)–C(45)	117.2 (13)
O(4)–P(2)–C(28)	110.2 (5)	C(44)–C(45)–C(40)	121.1 (13)
O(4)–P(2)–C(34)	112.3 (5)	P(3)–C(46)–C(47)	121.6 (8)
C(22)–P(2)–C(28)	109.4 (5)	P(3)–C(46)–C(51)	119.5 (9)
C(22)–P(2)–C(34)	110.6 (5)	C(47)–C(46)–C(51)	118.8 (10)
C(28)–P(2)–C(34)	106.9 (5)	C(46)–C(47)–C(48)	119.4 (11)
O(5)–P(3)–C(40)	108.1 (5)	C(47)–C(48)–C(49)	120.2 (12)
O(5)–P(3)–C(46)	107.8 (5)	C(48)–C(49)–C(50)	121.2 (12)
O(5)–P(3)–C(52)	112.8 (5)	C(49)–C(50)–C(51)	122.6 (12)
C(40)–P(3)–C(46)	111.2 (5)	C(50)–C(51)–C(46)	117.7 (11)
C(40)–P(3)–C(52)	108.1 (5)	P(3)–C(52)–C(53)	114.9 (9)
C(46)–P(3)–C(52)	108.8 (5)	P(3)–C(52)–C(57)	124.5 (9)
Ce(1)–O(4)–P(2)	169.2 (5)	C(53)–C(52)–C(57)	120.6 (11)
Ce(1)–O(5)–P(3)	173.2 (4)	C(52)–C(53)–C(54)	116.6 (11)
Ce(1)–O(6)–N(9)	97.4 (6)	C(53)–C(54)–C(55)	119.8 (13)
Ce(1)–O(8)–N(9)	95.9 (6)	C(54)–C(55)–C(56)	123.9 (15)
O(6)–N(9)–O(7)	122.9 (10)	C(55)–C(56)–C(57)	118.4 (14)
O(6)–N(9)–O(8)	115.7 (9)	C(56)–C(57)–C(52)	120.7 (13)
O(7)–N(9)–O(8)	121.4 (10)		

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(13) W. H. Zachariasen, *Acta Crystallogr.*, **2**, 390 (1949).

(14) T. Ueki, A. Zalkin, and D. H. Templeton, *ibid.*, **20**, 836 (1966).

(15) S. Scavnicar and B. Prodic, *ibid.*, **18**, 698 (1965).

(16) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1165 (1963).

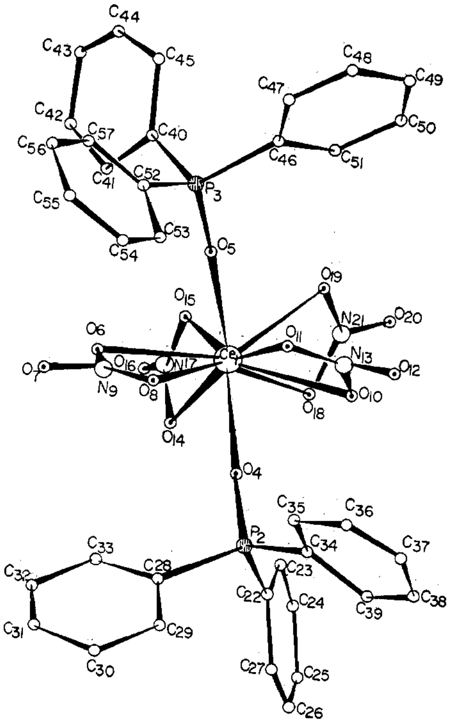

Figure 1.—The structure of tetranitratobis(triphenylphosphine oxide)cerium(IV).

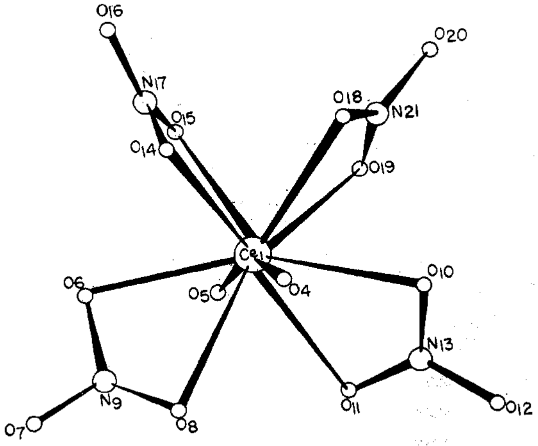

Figure 2.—Coordination of cerium.

considerable ligand–ligand repulsion in the coordination sphere; thus O_4–O_{14} = 2.65 (2) Å and O_5–O_{11} = 2.80 (2) Å, and some nitrate–nitrate contacts are also rather unfavorable, *e.g.*, O_8–O_{11} = 2.68 (2) Å. This latter close approach may be caused by the nonlinearity of the O_5–Ce–O_4 system, the two nitrate groups to which O_8 and O_{11} belong being twisted into closer mutual contact by the relatively close approach of the phosphoryl oxygen atoms (O_5–O_{11} = 2.80 (2) Å; O_4–O_{10} = 2.77 (2) Å). The cause of this nonlinearity is of interest. It may be of electrostatic origin, the 25° distortion leading to a lower ligand–ligand repulsive potential energy term over the complex as a whole. It is also possible that the distortion affords better π bonding between the filled P–O π system and the empty 5d orbitals of Ce(IV), as in a linear situation good overlap would be limited to d_{xz} and d_{yz}; the infrared evidence discussed below supports the possibility of such π bonding. The P–O–Ce systems are nearly linear (P_3–O_5–Ce = 173.2 (4)°; P_2–O_4–Ce = 169.2 (5)°); distortion of a similar system has been observed before.[17] It seems doubtful whether intermolecular packing forces would be sufficiently great to cause these distortions.

Nitrate Groups.—In each nitrate group the N–O distances differ only slightly from each other and average to 1.25 (3) Å. This may be compared with 1.218 (4) Å found in sodium nitrate,[18] 1.268 (21) Å in lead nitrate,[19] 1.21 (1) Å in triethylenediaminenickel(II) nitrate,[20] and an average distance of 1.24 (1) and 1.25 (1) Å found in rubidium uranyl nitrate[21] and uranyl nitrate hexahydrate,[22] respectively. The bond angles in the nitrate groups vary slightly from the ideal value of 120°, apparently the result of coordination with cerium. For the four nitrate groups the angles have the ranges 115.7 (9)–122.9 (9), 114.9 (9)–124.5 (9), 117.0 (9)–123.3 (9), and 118.9 (9)–121.2 (9)°. Two nitrates show the largest deviations but all are greater than four or five standard deviations. Similar variations are observed in the nitrate groups in rubidium uranyl nitrate[21] (117.5 (9)–121.2 (9)°) and uranyl nitrate hexahydrate[22] (115.6 (5)–122.2 (2) and 114.6 (5)–122.7 (2)°). All the nitrate groups are nearly planar. Table VI shows least-squares planes and dihedral angles between the nitrate planes.

Triphenylphosphine Oxide Groups.—The P–O distances of 1.531 (8) and 1.526 (8) Å are longer than normal phosphoryl bonds but somewhat shorter than esterified P–O bonds. Other bond lengths and angles do not differ significantly from expected values.

There are 15 intermolecular distances below 3.5 Å varying from 2.86 (2) to 3.45 (2) Å. The closest contacts are between O(15) and O(16), 2.98 (2) Å, O(16) and O(16), 2.86 (2) Å, and O(16) and N(17), 2.98 (2) Å, all of which are between atoms in one nitrate group and those in another related by a center of symmetry. All these distances are greater than the required van der Waals clearances. Cerium and phosphorus do not have any contacts less than 4.0 Å.

Infrared Spectra.—The vibrational frequencies of the PO and NO_3 groups in these compounds are as follows (cm^{-1}). $Ce(NO_3)_4(OP(C_6H_5)_3)_2$: NO_3, 1262 (s, b) (ν_1), 1023 (m) (ν_2), 1538 (s, b) (ν_4), 803 (s) (ν_6); PO, 1048 (s). $Th(NO_3)_4(OP(C_6H_5)_3)_2$: NO_3, 1265 (s, b) (ν_1), 1017 (m) (ν_2), 1540 (s, b) (ν_4), 806 (s) (ν_6); PO 1059 (s) (Nujol mulls and Perkin-Elmer 337). In addition there is absorption, perhaps partly due to the PO group, at 1134 cm^{-1} (Th compound) and 1120 cm^{-1} (Ce), but these assignments are uncertain as free $OP(C_6H_5)_3$ itself absorbs at 1119 cm^{-1}, this peak being enhanced in the complexes.

These values may be compared with those obtained[23]

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[21] G. A. Barclay, T. M. Sabine, and J. C. Taylor, *ibid.*, **19**, 205 (1965).

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TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS

h	$\lvert F_o\rvert$	$\lvert F_c\rvert$
L=	0 K=	0
2	187	184
4	274	276
6	64	66
12	46	45
L=	0 K=	1
1	218	204
3	137	136
4	131	137
5	94	96
6	60	64
7	68	64
8	107	110
10	45	45
11	20	23
12	79	82
L=	0 K=	2
0	164	154
2	90	100
3	142	135
4	102	100
5	115	119
6	77	73
7	122	121
9	58	65
11	70	68
13	62	62
L=	0 K=	3
1	173	171
4	108	102
5	69	77
7	87	90
8	40	41
9	33	31
11	28	30
12	29	29
13	19	23
L=	0 K=	4
0	128	128
1	63	60
2	60	62
3	25	19
5	36	40
6	98	98
7	56	62
8	55	54
9	64	63
11	65	64
13	29	25
L=	0 K=	5
1	119	111
2	47	49
3	42	39
4	38	35
5	26	22
6	86	86
7	80	77
8	107	107
9	22	27
10	71	67
11	55	53
12	76	68
L=	0 K=	6
0	62	57
1	77	73
2	83	84
4	117	116
6	123	124
7	26	28
8	29	32
9	23	26
10	21	21
11	25	28
L=	0 K=	7
1	145	143
2	87	84
3	62	66
4	22	24
5	119	117
6	42	44
7	64	66
8	65	63
9	28	33
10	38	40
12	34	35
L=	0 K=	8
1	42	34
2	25	31
5	120	115
7	95	101
9	73	70
11	71	67
L=	0 K=	9
1	101	99
2	20	16
3	82	85
4	24	30
5	50	51
6	55	58
7	64	66
8	37	42
9	26	29
10	46	42
11	25	30
L=	0 K=	10
0	109	110
1	38	39
2	119	112
3	28	25
4	70	66
5	38	36
6	55	57
9	27	20
10	21	24
L=	0 K=	11
2	54	54
3	17	17
4	31	33
5	16	18
6	82	80
8	50	49
10	65	55
L=	0 K=	12
0	90	86
2	78	77
3	19	23
4	69	67
5	50	56
6	20	27
7	44	45
9	57	55
L=	0 K=	13
1	116	114
3	71	66
5	66	67
8	28	24
L=	0 K=	14
0	25	26
1	32	34
2	82	82
3	49	50
4	31	34
5	37	37
6	36	33
7	58	55
L=	0 K=	15
1	29	26
2	29	29
3	27	20
4	42	46
5	29	32
6	60	58
L=	0 K=	16
0	71	64
2	87	83
4	50	47
L=	1 K=	0
1	114	104
-1	197	189
3	85	80
-3	283	285
5	163	158
-5	130	125
7	236	226
-7	225	217
9	104	92
-9	86	81
11	69	57
-11	63	60
13	78	76
-13	53	46
L=	1 K=	1
0	85	81
1	225	222
-1	204	207
2	83	75
-2	91	84
3	387	400
-3	206	206
-4	151	157
5	45	52
-5	96	97
6	70	68
-6	89	88
-7	46	42
8	69	71
-8	90	98
9	39	46
10	23	23
-10	34	38
11	23	26
12	65	65
-12	46	47
-13	24	25
L=	1 K=	2
0	337	360
1	70	67
-1	136	136
2	138	137
-2	22	14
3	79	76
-3	146	147
4	240	247
-4	57	56
5	98	94
-5	44	37
-6	32	33
7	43	39
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TABLE V (*Continued*)

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-6	36	38
7	67	76
-7	28	26
-8	36	33
9	48	52
-9	56	55
L=	9 K=	5
1	58	59
-1	83	84
2	20	26
3	77	77
-3	73	72
4	24	26
-4	32	35
5	55	52
-5	106	107
6	39	40
-6	22	26
-7	54	54
8	20	22
-8	18	18
9	46	46
-9	36	37
L=	9 K=	6
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2	43	42
-2	31	29
3	61	66
-3	48	50
4	41	40
-4	24	27
5	71	75
-6	72	73
7	74	79
-7	85	87
8	29	33
9	93	101
-9	60	56
-10	20	17
L=	9 K=	7
0	26	25
1	27	23
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2	14	15
3	21	19
-3	19	18
4	37	40
-4	36	41
5	86	90
-5	40	38
6	50	41
-6	31	26
-7	17	24
8	70	75
-8	70	68
9	23	19
-9	24	24
L=	9 K=	8
0	94	99
1	40	39
-1	42	43
2	105	103
-2	97	99
3	32	34
-3	26	25
4	86	88
-4	112	112
-5	41	43
6	51	52
-6	49	49
-7	40	41
8	35	31
-8	45	43
L=	9 K=	9
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1	79	82
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2	22	21
-2	33	32
3	64	68
-3	68	68
4	54	56
5	51	57
-5	33	32
6	65	62
-6	68	62
-7	27	26
8	43	41
-8	52	53
L=	9 K=	10
0	36	33
1	23	28
2	39	37
-2	48	53
3	58	58
-3	29	27
4	16	17
5	62	62
-5	56	64
6	28	34
-6	17	23
7	54	55
-7	57	56
L=	9 K=	11
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2	16	20
3	50	52
-3	70	69
4	35	34
-4	20	25
5	59	60
-5	38	40
L=	9 K=	12
0	84	79
-1	24	31
2	30	32
-2	22	19
3	23	28
-3	18	19
4	52	50
-4	49	48
5	33	32
-5	35	34
L=	9 K=	13
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L=	10 K=	0
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2	187	187
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4	74	74
-4	43	46
6	85	84
-6	103	102
8	25	31
-8	37	32
10	30	32
L=	10 K=	1
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1	78	75
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2	33	34
-2	50	51
3	85	86
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-4	60	59
5	24	28
-5	38	43
6	81	84
-6	81	81
7	40	41
-7	28	26
8	20	22
-8	30	30
9	19	18
10	81	77
-10	59	58
L=	10 K=	2
0	22	21
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2	61	64
-2	17	17
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8	19	19
9	52	59
-9	79	76
L=	10 K=	3
0	50	49
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-1	108	107
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-2	19	13
3	109	110
-3	63	61
4	19	24
-4	19	20
5	74	71
-5	76	80
6	22	28
7	42	42
-7	23	19
9	48	49
-10	34	33
L=	10 K=	4
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2	48	49
-2	69	68
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-4	20	20
5	31	27
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-6	60	62
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-7	53	51
8	48	51
9	52	55
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7	24	30
-7	19	18
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-6	58	57
7	38	44
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2	79	86
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2	19	19
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-3	22	25
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L=	10 K=	13
1	85	87
-1	43	38
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-6	63	62
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-8	48	47
-9	23	18
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8	34	36
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L=	11 K=	5
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5	97	100
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-4	20	23
L=	11 K=	12
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1	30	30
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L=	12 K=	0
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8	78	89
-8	48	53
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3	84	85
4	55	60
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5	32	30
-5	27	29
6	28	30
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7	40	44
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6	31	33
7	29	30
-7	57	53
8	25	25
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1	54	53
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5	93	95
7	63	68
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4	68	70
5	23	28
-5	17	22
6	68	70
-6	19	17
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-8	43	40
L=	12 K=	5
0	78	74
1	34	30
2	72	72
-2	82	83
4	47	49
-4	94	92
5	46	43
-6	65	63
-8	45	38
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2	86	90
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3	28	27
4	80	86
-4	25	31
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6	74	75
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L=	12 K=	7
0	36	39
1	64	65
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2	26	20
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3	62	64
-3	18	14
4	30	33
-4	31	29
5	72	75
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L=	12 K=	8
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3	27	31
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-4	25	31
-5	59	61
L=	12 K=	9
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1	27	28
-1	32	26
2	43	43
-2	44	43
3	20	20
-3	24	25
-4	49	51
L=	12 K=	10
0	47	43
2	46	46
-2	19	19
-3	22	20
L=	12 K=	11
0	47	43
L=	13 K=	0
1	99	101
-1	49	54
3	32	33
-3	74	77
5	76	83
-5	70	75
-7	40	39
L=	13 K=	1
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2	18	15
-2	43	41
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4	56	63
-4	48	53
5	62	65
-6	42	40
7	42	47
-7	42	40
L=	13 K=	2
1	45	45
2	76	80
-2	20	14
4	67	67
-4	48	50
6	78	78
-6	19	16
L=	13 K=	3
0	75	71
2	64	63
-2	84	83
3	60	59
4	81	80
-4	54	58
-6	61	62
7	27	25
L=	13 K=	4
1	33	31
-1	81	97
2	33	32
3	70	69
-3	65	62
-4	24	23
5	40	42
-5	71	72
6	47	50
-7	20	18
L=	13 K=	5
1	39	37
-2	58	59
3	59	63
5	59	55
-5	23	22
-6	21	18
L=	13 K=	6
1	97	92
-1	78	82
3	40	43
-3	113	113
4	26	23
5	25	33
-5	56	59
L=	13 K=	7
0	51	50
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-1	28	29
2	47	49
-2	55	57
4	26	32
-4	57	60
5	47	44
L=	13 K=	8
0	38	30
2	48	49
-3	20	20
4	57	60
L=	13 K=	9
0	42	37
1	38	40
2	40	41
-2	48	51
L=	14 K=	0
0	24	29
2	28	36
-4	65	68
6	61	64
-6	30	30
L=	14 K=	1
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2	47	46
-2	57	58
3	23	26
-3	23	27
4	80	83
-4	41	42
5	32	35
-5	18	14
-6	39	42
L=	14 K=	2
0	34	30
1	89	88
-1	78	81
2	29	28
3	78	81
-3	64	62
-4	17	15
5	80	86
-5	49	51
L=	14 K=	3
0	61	58
-1	17	20
2	33	37
-3	33	34
4	35	43
-4	25	29
5	40	33
-5	39	38
L=	14 K=	4
1	86	81
-1	33	46
3	33	29
-3	64	64
4	26	21
-4	30	27
5	39	43
-5	37	38
L=	14 K=	5
0	75	76
2	80	77
-2	87	91
4	70	75
-4	48	50
L=	14 K=	6
2	35	36
-2	21	22
3	39	37
-4	20	18
L=	14 K=	7
0	42	44
1	37	33
2	31	36
-2	54	55
L=	15 K=	0
1	96	100
-1	60	60
3	52	58
-3	59	64
L=	15 K=	1
0	47	47
2	46	51
-2	25	23
-3	33	39
4	50	60
-4	32	34
L=	15 K=	2
0	18	19
1	46	43
-1	28	31
-2	33	36
-3	29	34
-4	65	63
L=	15 K=	3
0	62	61
2	71	68
-2	69	72
-3	32	35
L=	15 K=	4
1	36	36
-1	33	28
-2	38	38
-3	21	22
L=	15 K=	5
-1	33	31
-2	48	49

TABLE VI

EQUATIONS OF THE LEAST-SQUARES PLANE REFERRED TO ORTHOGONAL AXES[a]

Plane	Atoms	a	b	c	D, Å	S, Å^2
1	O(6), O(7), O(8), N(9)	0.9733	−0.0436	−0.2252	−0.3698	0.2289×10^{-3}
2	O(10), O(11), O(12), N(13)	0.9224	−0.2520	0.2926	0.6174	0.1637×10^{-2}
3	O(14), O(15), O(16), N(17)	0.0745	0.9437	−0.3223	0.1267	0.3688×10^{-6}
4	O(18), O(19), O(20), N(21)	0.2619	0.6970	0.6675	0.4120	0.5445×10^{-4}

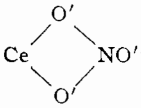
Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg	Planes	Angle, deg
1 and 2	33	1 and 4	86	2 and 4	75
1 and 3	84	2 and 3	75	3 and 4	63

[a] $\bar{X} = x + z \cos \beta$; $\bar{Y} = y$; $\bar{Z} = z \sin \beta$. $a\bar{X} + b\bar{Y} + c\bar{Z} = D$. S is the sum of squares of deviation of atoms from the plane; D is the origin to plane distance in ångströms. All atoms given equal weight.

for $Ce(NO_3)_3(OP(C_6H_5)_3)_3$: NO_3, 1304, 1295 (ν_1), 1029 (ν_2), 1493, 1460 (ν_4), 818 (ν_6); PO, 1147. In free $OP(C_6H_5)_3$, the PO stretch is at 1195 cm^{-1}.

In these Ce(IV) and Th(IV) complexes, the splitting (into ν_1 and ν_4) of the E′ vibration of D_{3h} NO_3^- is considerably greater than observed[23–25] for a variety of lanthanide(III) complexes. This is expected, but it is worth notice that there is rather little geometrical distortion of the coordinated nitrate groups in the structure of $Ce(NO_3)_4(OP(C_6H_5)_3)_2$, the splitting presumably arising mainly from coupling with Ce–O′ vibrations rather than from a difference between the O′–N and N–O″ bond orders (I). The ν_6 mode again shows a greater shift from the free-nitrate position (831 cm^{-1}) than observed[23–25] in a variety of lanthanide(III) com-



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plexes. The frequencies of the ν_1, ν_4, and ν_6 absorptions might well be used to assign the oxidation state of a complexed lanthanide or actinide in the unlikely event of its being in doubt. The infrared spectrum of $CsPa(NO_3)_6$[26] supports this possibility. In this context, the uranyl ion behaves both in some chemical properties and as regards the infrared spectra of its nitrato complexes[27] as if it were $^-O–U^{4+}–O^-$.

The effect of coordination on the P–O frequency of phosphine oxides has been discussed previously.[28] The shift to low frequency is here much greater than observed[3,23] for lanthanide(III) complexes and similar to that observed[2] for U(IV), and we attribute the additional shift to delocalization of the P–O π-electron density into the metal 5d (Ce) or 6d (Th) orbitals. However, the mean P–O distance of 1.53 Å indicates that this link still possesses considerable double-bond character. It is relevant that the lanthanide contraction increases the P–O frequency along the series La(III)–Lu(III),[23] suggesting that metal–oxygen π bonding is here unimportant, compared with coupling with the metal–oxygen bond and the inductive effect on the P–O σ bond. Indeed, the generally accepted view that there is little covalent character in lanthanide compounds but moderate covalent character in actinide compounds probably reflects not so much the difference in principal quantum number as the difference in commonly occurring oxidation states.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND
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A Structural Study of Two Products of the Reaction of Phosphorus Pentachloride with Titanium Tetrachloride. The Crystal and Molecular Structures of Bis(tetrachlorophosphonium) Di-μ-chloro-octachlorodititanate(IV), $[PCl_4]_2[Ti_2Cl_{10}]$, and Tetrachlorophosphonium Tri-μ-chloro-hexachlorodititanate(IV), $[PCl_4][Ti_2Cl_9]$[1a]

BY T. J. KISTENMACHER[1b] AND G. D. STUCKY*

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Reaction of PCl_5 with $TiCl_4$ in $POCl_3$ has led to a crystalline product of empirical formula $PTiCl_9$. The crystal system is triclinic, space group C_i^1-$P\bar{1}$. The cell constants for the reduced cell are a = 8.919 (1) Å, b = 9.474 (1) Å, c = 6.913 (1) Å, α = 95.90 (1)°, β = 95.90 (1)°, and γ = 100.98 (1)°. The calculated density of 2.34 g/cm^3 for 2 $PTiCl_9$ formula units per cell is to be compared to the observed density of 2.32 ± 0.02 g/cm^3. Of 3387 independent reflections collected by counter methods, 2571 were considered to be observed and were used to refine the structure by full-matrix least squares to a conventional R factor of 6.9%. The structure consists of PCl_4^+ and edge-bridged bioctahedral $Ti_2Cl_{10}^{2-}$ ions, the latter located on crystallographic centers of inversion. Reaction of a solution of PCl_3 in $SOCl_2$ with $TiCl_4$ in $SOCl_2$ led to a crystalline product of empirical formula PTi_2Cl_{13}. The crystal system is orthorhombic with possible space groups D_{2h}^{16}-$Pnma$ or C_{2v}^{9}-$Pn2_1a$. The cell constants are a = 29.126 (12) Å, b = 10.521 (2) Å, and c = 11.514 (3) Å. The calculated density for eight PTi_2Cl_{13} formula units per cell is 2.22 g/cm^3 and the observed density is 2.28 ± 0.04 g/cm^3. A total of 1950 counter-collected observed and unobserved reflections were used to refine the structure by full-matrix least squares to a conventional R factor of 7.6%, assuming space group $Pnma$. Some indication of disorder or lower space group symmetry was found. The structure consists of PCl_4^+ and $Ti_2Cl_9^-$ ions. The anions are an unusual example of face-shared bioctahedra containing first-row transition metal ions in the formal oxidation state +4.

Introduction

Adducts of the type $(PCl_5)_n \cdot mTiCl_4$, where n and m are integers, were first reported by Weber.[2] Treatment of a PCl_3–$TiCl_4$ solution with Cl_2 gas led to the complex $PCl_5 \cdot TiCl_4$. In a series of experiments[3–5] Groeneveld studied the reaction of PCl_5 and $TiCl_4$ in $POCl_3$ and $SOCl_2$. Addition of PCl_5 to a solution of $TiCl_4$ in $POCl_3$ produced the complex $PCl_5 \cdot TiCl_4$. Addition of PCl_3 to a solution of $TiCl_4$ in $SOCl_2$ was also reported to give the 1:1 adduct. Conductometric titration of a solution of $TiCl_4$ in $POCl_3$ with PCl_5 in $POCl_3$ indicated complexes of stoichiometry $PCl_5 \cdot TiCl_4$ and $2PCl_5 \cdot TiCl_4$. Only the 1:1 adduct was reported to be isolable. Payne[6] found that the conductometric titration of $TiCl_4$ in CH_3CN with PCl_5 in CH_3CN

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