Crystal and Molecular Structure of Bistriphenyl(ethyl)phosphonium Pentanitratocerium(III)

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Crystals of the title compound are monoclinic of space group $C2/c$ with $a = 19{\cdot}83(3)$, $b = 11{\cdot}05(2)$, $c = 21{\cdot}76(3)$ Å, $\beta = 108{\cdot}17°$, and $Z = 4$. The anion has crystallographic C_2 symmetry and the cerium atom is ten-co-ordinate, being chelated symmetrically by the five bidentate nitrate ligands. The mean Ce–O distance is 2·57(2) Å. The co-ordination geometry is not very readily described in terms of any idealised high co-ordination polyhedron, but if each nitrate ligand is considered as occupying one co-ordination site, then the arrangement closely approximates to a trigonal bipyramid. The structure was solved from X-ray photographic data by Patterson and Fourier methods and refined by least-squares techniques to R 9·8% for 1516 observed reflections.

COMPLEXES of the transition metals and lanthanides containing solely nitrate ion as ligands have been shown most often, to be high-co-ordination number species[1] and both eight- and twelve-co-ordinate geometries have been characterised in complexes[2–5] of general formulation $M(NO_3)_4{}^{n-}$ and $M(NO_3)_6{}^{n-}$.[6,7] In addition, the bidentate role of the nitrate ion leads to high co-ordination in $Ce(NO_3)_4,2Ph_3PO$,[8] and $Ln(NO_3)_3$,2bipyridyl (Ln = La,[9] Tb,[10]), all three species containing ten-co-ordinate metal atoms. Co-ordination number ten has also recently been charasterised in a variety of other complexes,[11,12] but in only one of these, $K_4[Th(C_2O_4)_4],4H_2O$,[13] does the co-ordination polyhedron apparently closely approximate to the most stable geometry predicted on the basis of ligand–ligand repulsions, namely the bicapped square antiprism of D_{4d} symmetry.[9] Since this complex contains effectively five bidentate ligands per thorium atom, it appeared of interest to examine one of the lanthanide nitrate complexes formulated as $Ln(NO_3)_3,2Ph_{4-x}R_xPNO_3$,[14] as it seemed that these might contain $Ln(NO_3)_5{}^{2-}$ ions with five equivalent bidentate ligands and so offer further information on ten-co-ordination stereochemistry. In addition, such a species would complete the series of complexes $M(NO_3)_x{}^{n-}$ where $x = 3$,[15] 4,[2–5] 5, and 6,[6,7] (and $n = 0$—3, dependent on M) and provide an opportunity to further examine the suggestion of Cotton and Bergman,[2] namely that if bidentate ligands of small 'bite' are viewed as occupying one co-ordination site in a polyhedron, then the resulting lower co-ordination number polyhedron closely approaches the accepted geometry observed for that co-ordination number, *e.g.* tetrahedral geometry for co-ordination number four. We elected to carry out an analysis on the $Ce(NO_3)_5{}^{2-}$ ion and find that this suggestion works well.

EXPERIMENTAL

The complex $[(C_6H_5)_3C_2H_5P]_2Ce(NO_3)_5$ was prepared from stoicheiometric quantities of triphenyl(ethyl)phosphonium bromide, silver nitrate, and cerium nitrate hexahydrate, following procedures similar to those used for preparing tetranitrato-metallate complexes of the first-row transition elements Mn—Zn.[3] Very pale yellow crystals suitable for X-ray analysis were obtained by recrystallisation from ethanolic solutions of the complex (Found: C, 46·50; H, 4·37; N, 6·59. Calc. for $C_{40}H_{40}CeN_5O_{15}P_2$: C, 46·51; H, 3·9; N, 6·78%. The i.r. spectrum (hexachlorobutadiene mull) gave peaks at 1290 and 1473 cm^{-1}, which suggested co-ordinated nitrate ions, and no peak at 1375 cm^{-1}, which would have indicated ionic nitrate.

Crystal Data.—$C_{40}H_{40}CeN_5O_{15}P_2$, $M = 1032{\cdot}4$, Monoclinic, $a = 19{\cdot}83(3)$, $b = 11{\cdot}05\ (2)$, $c = 21{\cdot}76(3)$ Å, $\beta = 108{\cdot}17°$, $U = 4529{\cdot}2$ Å^3, $D_m = 1{\cdot}45$ g.cc.$^{-1}$ (by flotation), $Z = 4$, $D_c = 1{\cdot}51$ g.cc^{-1}, $F(000) = 2092$. Systematic absences, hkl for $h + k \neq 2n$, $h0l$ for $l \neq 2n$, and $0kl$ for $k \neq 2n$ indicate space groups Cc (No. 9) or $C2/c$ (No. 15) shown to be the latter by subsequent successful analysis. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) = 10·5 cm^{-1}. Preliminary precession photographs.

A crystal of dimensions *ca.* 0·3 × 0·4 × 0·4 mm was selected for intensity measurement and was mounted with its c^* axis parallel to the spindle axis of a precession camera. Intensity data were recorded on multiple films (*i.e.* different exposures of the same zone) of reciprocal levels $h0$—$4l$, 0—$5kl$, and the diagonal levels $(h$—$h + 6)hl$ and the integrated values were measured photometrically by means of a Joyce–Loebl microdensitometer. Corrections were made for Lorentz and polarisation factors and all data placed on the same scale by intercomparison of reciprocal lattice rows common to several different photographs. Measurements were restricted to the region $0 \leqslant \sin \leqslant 0{\cdot}375$, there being very few reflections of measurable intensity outside this region. Approximately 2000 independent reflections in this region were accessible on the reciprocal levels collected, of which 1516 were classified observed and used in the final refinements.

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Structure Determination.—A three-dimensional Patterson map indicated that space group $C2/c$ was probably correct, and placed the cerium atom on the two-fold axis [position 4(e)]. The phosphorus atom was also located from the Patterson synthesis and three successive sequences of electron-density syntheses and least-squares treatments of the positional parameters found in the preceding syntheses, served to locate all non-hydrogen atoms in the asymmetric unit. R was then 16·8% and two further cycles of full-matrix refinement, including isotropic thermal parameters and a scale factor, with unit weights, reduced R to 12·6%. Introduction of variable weights, calculated according to $w^{\frac{1}{2}} = a/(b + cF_o)$, and allowing the cerium and phosphorus atoms to assume anisotropic thermal parameters, led to a residual of 9·8% after three further cycles of refinement. The weighted residual, R' $(=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}})$ was 11·1% and the function minimised in the refinement was $\Sigma w(|F_o| - |F_c|)^2$. The parameters b and c had the following values in the final cycle; (i) for $0 < F_o < 34{\cdot}0$, $b = 10{\cdot}4$, $c = -0{\cdot}044$; (ii) $34 < F_o < 194$, $b = 8{\cdot}4$, $c = 0{\cdot}015$; and (iii) $194 < F_o < 450$, $b = -6{\cdot}6$, $c = 0{\cdot}092$; $a = 1{\cdot}0$ for all three ranges.

TABLE 1

Atomic positional and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
Ce	0·0	0·2073(2)	0·25	*
N(1)	0·0	−0·0640(31)	0·25	4·71(78)
O(1)	0·0	−0·1701(27)	0·25	5·82(74)
O(2)	0·0550(9)	−0·0024(16)	0·2497(8)	4·70(38)
N(2)	0·1363(20)	0·3375(31)	0·2876(15)	8·32(78)
O(3)	0·1342(10)	0·2274(19)	0·2757(8)	5·15(41)
O(4)	0·0792(12)	0·3935(20)	0·2830(9)	6·39(48)
O(5)	0·1933(15)	0·3855(25)	0·3041(12)	9·09(67)
N(3)	0·0193(13)	0·2200(26)	0·3916(11)	5·95(51)
O(6)	0·0564(11)	0·1456(20)	0·3700(10)	6·64(49)
O(7)	−0·0229(11)	0·2851(22)	0·3535(9)	7·09(50)
O(8)	0·0287(12)	0·2272(22)	0·4489(11)	8·27(60)
P	0·2867(4)	0·2664(6)	0·1453(3)	*
C(1)	0·3130(14)	0·2795(29)	0·2320(12)	4·98(57)
C(2)	0·3471(21)	0·1715(39)	0·2755(18)	9·19(105)
C(11)	0·3687(14)	0·2445(22)	0·1203(12)	4·38(57)
C(12)	0·4016(13)	0·1338(24)	0·1399(11)	4·04(53)
C(13)	0·4654(16)	0·1207(28)	0·1246(14)	5·55(66)
C(14)	0·4855(15)	0·2044(34)	0·0899(13)	6·17(65)
C(15)	0·4531(16)	0·3167(30)	0·0696(14)	6·23(72)
C(16)	0·3886(16)	0·3283(27)	0·0853(14)	5·97(71)
C(21)	0·2425(14)	0·3975(23)	0·1091(12)	4·02(54)
C(22)	0·1714(16)	0·3966(28)	0·0642(13)	5·61(69)
C(23)	0·1397(18)	0·5014(32)	0·0308(15)	6·79(72)
C(24)	0·1692(17)	0·6068(28)	0·0504(14)	5·60(70)
C(25)	0·2399(20)	0·6135(35)	0·0963(17)	8·05(91)
C(26)	0·2728(15)	0·5118(28)	0·1292(13)	5·46(64)
C(31)	0·2287(14)	0·1407(24)	0·1203(12)	4·05(53)
C(32)	0·1812(15)	0·1144(27)	0·1523(13)	5·31(64)
C(33)	0·1296(14)	0·0181(26)	0·1269(12)	4·97(60)
C(34)	0·1336(16)	−0·0490(28)	0·0787(14)	5·77(67)
C(35)	0·1870(15)	−0·0257(27)	0·0455(13)	5·25(65)
C(36)	0·2333(13)	0·0736(23)	0·0678(11)	4·10(53)

* Anisotropic thermal parameters (Å^2): for Ce: B_{11} 3·38(11), B_{22} 2·42(12), B_{33} 3·36(10), and B_{13} 1·10(6); for P: B_{11} 4·26(34), B_{22} 4·14(38), B_{33} 3·80(33), B_{12} 0·04(31), B_{13} 1·65(26), and B_{23} −0·23(27). The form of the ellipsoid is: $\exp(\sum_i\sum_j h_ih_jr_i^*r_i^* B_{ij}/4)$ and r_i^* is the i^{th} reciprocal axis.

Final positional and thermal parameters are listed in Table 1, while observed and calculated structure factors are listed in Supplementary Publication No. SUP 20757 (9 pp., 1 microfiche).* The majority of calculations were carried out by use of the '*X*-ray '63' program system as adapted for use on the Atlas computer at Harwell.[16] The neutral atom scattering factors used in the analysis were taken from ref. 17, and for the cerium atom from ref. 18. Anomalous dispersion corrections were applied for the cerium atom.[19]

RESULTS AND DISCUSSION

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Co-ordination Polyhedron

Ce–O(2)	2·562(16)	Ce–O(6)	2·591(20)
Ce–O(3)	2·553(18)	Ce–O(7)	2·582(20)
Ce–O(4)	2·555(19)		

O(2)–Ce–O(2′)	50·4(5)	N(3)–Ce–N(3′)	173·4(6)
O(3)–Ce–O(4)(θ_C)	50·1(6)	N(3)–Ce–N(1)	92·7(5)
O(6)–Ce–O(7)($2\theta_A$)	49·3(7)	N(3)–Ce–N(2)	83·2(5)
O(3)–Ce–O(3′)	169·8(6)	N(3)–Ce–N(2′)	94·2(5)
O(4)–Ce–O(2′)($2\theta_B$)	162·8(7)	N(1)–Ce–N(2)	119·1(5)
O(4)–Ce–O(4′)	72·8(7)	N(2)–Ce–N(2′)	121·7(6)
O(2)–Ce–O(3)(θ_C)	70·3(6)		

(*b*) Nitrate Ions

N(1)–O(1)	1·172(45)	O(1)–N(1)–O(2)	122·0(11)
N(1)–O(2)	1·288(25)	O(2)–N(1)–O(2′)	116·0(20)
N(2)–O(3)	1·241(39)	O(3)–N(2)–O(4)	118·5(26)
N(2)–O(4)	1·270(40)	O(3)–N(2)–O(5)	118·6(28)
N(2)–O(5)	1·183(43)	O(4)–N(2)–O(5)	121·9(32)
N(3)–O(6)	1·284(34)	O(6)–N(3)–O(7)	118·8(24)
N(3)–O(7)	1·212(35)	O(6)–N(3)–O(8)	120·0(23)
N(3)–O(8)	1·206(32)	O(7)–N(3)–O(8)	121·2(24)

(*c*) $[PPh_3C_2H_5]^+$

P–C(1)	1·884(26)	P–C(11)	1·800(26)
P–C(21)	1·747(26)	P–C(31)	1·778(27)
C(1)–C(2)	1·543(51)		
C(1)–P–C(11)	108·6(12)	C(11)–P–C(21)	109·5(11)
C(1)–P–C(21)	110·2(12)	C(11)–P–C(31)	110·2(12)
C(1)–P–C(31)	109·4(13)	C(21)–P–C(31)	108·9(12)
C(2)–C(1)–P	120·4(23)		

Phenyl rings: distances C(*ij*)–C(*ik*)

Ring	Mean	Max.	Min.
(1)	1·385	1·433(41)	1·330(44)
(2)	1·402	1·449(43)	1·314(46)
(3)	1·403	1·479(42)	1·315(39)

Angles C(*ij*)–C(*ik*)–C(*il*)

(1)	119·9	127·2(32)	111·0(29)
(2)	119·6	122·0(28)	116·6(24)
(3)	119·9	122·6(24)	117·1(23)

Structure of the Anion.—The final structural information is presented in Table 2 and in Figures 1 and 2. The ten-co-ordinate pentanitratocerium(III) ion has crystallographically imposed C_2 symmetry, but no higher pseudosymmetry. The five nitrate ions are arranged around the cerium atom in what might be termed trigonal bipyramidal fashion with nitrate ions (1), (2), and (2′) constituting the equatorial plane and ions (3) and (3′) occupying the two axial sites (Figures 1 and 2). Comparison of the N(i)–Ce–N(j) angles [N(i) being taken as equivalent to the midpoints of the edges spanned

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

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by the ligands] listed in Table 2 with those of 180, 120, and 90° expected for a trigonal bipyramid give the measure of the deviation from this description of the

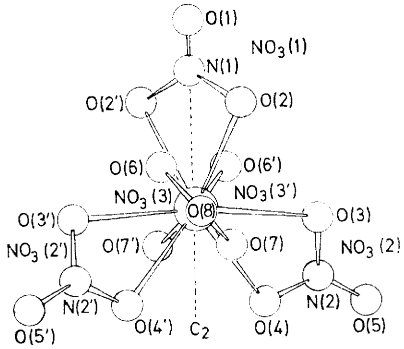

FIGURE 1 A view of the $[Ce(NO_3)_5]^{2-}$ ion projected on a plane normal to the c axis

polyhedron. In contrast to the tetra-[2,3] and hexanitrato-species[6,7] which approximate fairly closely the higher point-group symmetries D_{2d} and T_h respectively, being each in turn subgroups of T_d and O_h, the $Ce(NO_3)_5{}^{2+}$ ion perhaps better illustrates and supports the principle originated by Bergman and Cotton;[2] for the highest point-symmetry achievable with this species is C_2 (which is also crystallographically observed) and yet the adherence to the trigonal bipyramid is readily seen.

The severe constraints imposed by the short bite of the nitrate ion ligand make difficult a description of the ten-co-ordinate polyhedron in terms of one of the idealised geometries for this co-ordination number.[9] The best 'fit' would appear to be the bicapped dodecahedron of D_2 point-symmetry, with oxygen atoms O(6), O(7), O(4), and O(2') (and the two-fold related set) defining the trapezoidal planes (positions A and B in the polyhedron in Figure 2) and O(3) and O(3') defining the positions of type C on the two-fold axis of the polyhedron.[9] The idealised angles calculated for minimum ligand repulsive energy in this geometry are θ_A 32·8, θ_B 77·0, and θ_C 60·0°, which can be compared with the values of 24·7, 81·4, and 60·2 (mean of two) respectively, observed in the present structure. Figure 1 indicates that the atoms constituting the trapezoidal planes are far from coplanarity and that the 'axial' nitrates (3) and (3') are almost normal to one another, rather than at 60° as required for the D_2 geometry.

The mean cerium–oxygen bond distance is 2·569(15) compared to 2·64 Å in $Ce(NO_3)_6{}^{3-}$ and the lengthening of the Ce–O distance in the latter is probably attributable to the expansion of the co-ordination sphere by the addition of one more nitrate-ion ligand. In contrast,

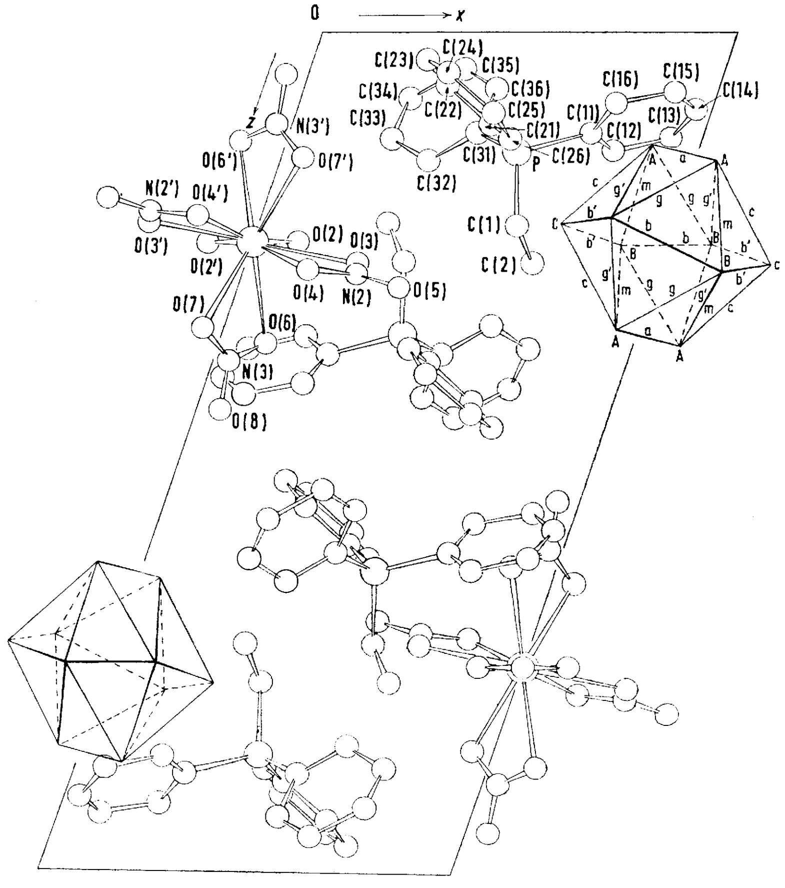

FIGURE 2 The contents of one half unit cell of the structure projected on the (010) plane. Framework diagrams of the co-ordination polyhedron in the pentanitrato-ion are illustrated and the edges and vertices are labelled according to the numbering system for the D_2 polyhedron given in ref. 9

the ten-co-ordinate cerium(IV) complex, $Ce(NO_3)_4,$-$2Ph_3PO$ has mean Ce–O (nitrate) distances 2·48(2) Å, while the Ce–O distance in $Ce(NO_3)_6^{2-}$ is 2·51(1) Å. The difference in Ce–O distances is in accord with expectation and compatible with the difference between the ionic radii of Ce^{3+} and Ce^{4+} of *ca.* 0·12 Å. The observed general trend in N–O distances in the NO_3 ligands is similar to that found in other species containing bidentate nitrate ligands, namely that the terminal bonds [*viz.* N(1)–O(1), N(2)–O(5), and N(3)–O(8)] are shorter than the bonds involving the co-ordinated oxygen atoms.[1] However, the standard deviations involved are too large for us to conclude that the differences are statistically significant.

Structure of the Cation.—Pertinent structural information on the triphenyl(ethyl)phosphonium ion is included in Table 2(*c*) and the relative orientations of the cations in the unit cell, and of the rings in one ion, are illustrated in Figure 2. The mode of packing in this structure and the orientations of the cations bear a marked resemblance to those observed for the tetraphenylarsonium salts of $Co(NO_3)_4^{2-}$ and $Mn(NO_3)_4^{2-}$ and there is, in fact, quite a close resemblance between the unit-cell dimensions and the pattern of intensity distribution for the two systems. The three crystallographically independent phenyl rings are planar to within the relatively large standard deviations of this determination, the maximum deviations being 0·042 Å. The phosphorus atom however is situated 0·08, 0·073, and 0·095 Å out of the planes of rings (1), (2), and (3). The mean carbon–carbon distance is 1·396(48) and the mean C–C–C angle 119·8(32)°, the standard deviations being calculated from the distribution of individual values about the mean.

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