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The Structure of *fac*-$Ce(OAsPh_3)_3Cl_3 \cdot CH_3CN$ and $Ce(OAsPh_3)_3(NO_3)_3$: Evidence for a Structural *trans* Influence

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Abstract

$Ce(OAsPh_3)_3Cl_3 \cdot CH_3CN$, $P\bar{1}$, with cell parameters $a = 11.614(1)$, $b = 12.009(2)$ and $c = 20.991(3)$ Å, $\alpha = 89.08(1)$, $\beta = 88.50(1)$, $\gamma = 64.40°(2)$, and $Z = 2$. Refinement of 320 parameters for 4710 reflections converged to $R = 0.052$ and $R_w = 0.067$. This is the first example of a Ln(III) chloride complex with octahedral coordination in which bulky triphenylarsenic oxide substituents are in a facial conformation. The Ce–O distance is shorter and the Ce–Cl distance is longer than expected and suggests that a structural *trans* influence dictates the conformation of the first coordination sphere.

$Ce(OAsPh_3)_3(NO_3)_3$, $P2_1/n$, with cell parameters $a = 15.14(2)$, $b = 21.31(3)$, $c = 17.81(1)$ Å, $\beta = 92.30°(4)$ and $Z = 4$. The crystals were of poor quality, but the structure is of sufficient accuracy to determine that the complex is facial based on octahedral coordination. Refinement of 313 parameters on 4070 reflections converged to $R = 0.115$ and $R_w = 0.138$.

Introduction

There have been many compounds reported of the type LnL_3X_3 where L is a monodentate neutral donor ligand and X is a halide or pseudo-halide [1–3]. In spite of the importance of these complexes in various processes, e.g., separations chemistry, little detailed structural work has been done and only a few of these complexes have been characterized by X-ray crystallography. For the chlorides, the X-ray structures of $Gd(DMP)_3Cl_3$ (DMP = 2,6-dimethyl-4-pyrone) [4] and $Pr(HMPA)_3Cl_3$, (HMPA = $OP[N(CH_3)_2]_3$) [5] have been reported in which both complexes have octahedral coordination. However only the second of these reports conformational characteristics. Reports of X-ray structures for complexes of this general type when X = NO_3 are equally rare. The only structures reported of which we are aware are those of $Yb(DMSO)_3(NO_3)_3$ [6, 7] (and the Eu(III) and Lu(III) analogues [8, 9]) and $Nd(AP)_3(NO_3)_3$ [10] (AP = antipyrine) which have been described as nine coordinate. Clearly, due to the small bite size of the nitrate ion, whether the structures of this type are described as nine or six coordinate is arbitrary. We choose the latter option for the purpose of discussion in this paper.

Excellent review articles have been published which cover lanthanide [3] and actinide [11] structural results for compounds of this type.

We report here the structures of two complexes, *i.e.* $Ce(OAsPh_3)_3Cl_3$ and $Ce(OAsPh_3)_3(NO_3)_3$, which have conformational properties which are different from those previously reported for similar lanthanide complexes.

Experimental

Preparations

Reagent grade acetonitrile was obtained from MCB Chemicals (EM Industries, Inc., Gibbstown, N.J.), dried overnight over potassium carbonate, and stored over 3 Å molecular sieves. Hydrated cerium(III) nitrate and hydrated cerium(III) chloride was obtained from Research Chemicals (Nucor Corporation, Phoenix, Ariz.) and was stored at 10 torr and *ca.* 60 °C. Lithium nitrate was obtained from Baker Chemical Co. (Phillipsburg, N.J.) and stored in a vacuum desiccator. $OAsPh_3$ was obtained from ICN K&K Labs (Plainview, N.Y.).

$Ce(NO_3)_3 \cdot 6H_2O$ (0.120 g, 0.28 mmol) and $OAsPh_3$ (0.193 g, 0.60 mmol) were dissolved in dry acetonitrile (5 ml). The acetonitrile was evaporated. The resulting solid/oil was dissolved in dichloromethane (2 ml) and the complex precipitated upon addition of n-pentane (2 ml). The brown solid was allowed to dry in air. Yield ~60%, based on metal content determined by gravimetric analysis performed by the ORNL Analytical Chemistry Division. Single crystal X-ray analysis (*vide infra*) revealed these to be $Ce(OAsPh_3)_3(NO_3)_3$.

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$CeCl_3 \cdot 6H_2O$ (0.11 g, 0.31 mmol) and $OAsPh_3$ (0.21 g, 0.65 mmol) were covered with dry acetonitrile (5 ml). If the temperature was kept significantly below 70 °C and air was bubbled through the solution, large milky white crystals were formed. If the solution was warmed to approximately 70 °C (to help dissolution of the $CeCl_3 \cdot 6H_2O$ which is only sparingly soluble in acetonitrile) and oxygen was bubbled through the solution for about 30 min, the originally colorless solution became intense yellow (almost orange). After centrifugation to remove any precipitate, the supernatant was allowed to cool slowly and over a period of hours small yellow crystals formed. These were washed with n-pentane (2 × 5 ml) and allowed to dry in air. Over a period of about a week these yellow crystals became white, presumably due to reduction from Ce(IV) back to Ce(III). Yield *ca.* 30%. Single crystal X-ray analysis (*vide infra*) revealed these to be $Ce(OAsPh_3)_3Cl_3$–acetonitrile.

IR spectra were taken and confirmed that the $OAsPh_3$ ligands were indeed coordinated to the metal through the oxygen of the ligand.

X-ray Diffraction Studies

$Ce(OAsPh_3)_3Cl_3$–CH_3CN

The lattice constants, obtained by refining 25 centered reflections ($11 \leqslant 2\theta \leqslant 20°$), are $a = 11.614(1)$, $b = 12.009(2)$, and $c = 20.991(3)$ Å, $\alpha = 89.08(1)$, $\beta = 88.50(1)$, $\gamma = 64.40(2)°$, $V = 2639.78$ Å^3, $M_r = 1254.26$ g/mol, $D_x = 1.574$ g/cm^3, space group $P\bar{1}$. Reflections in a hemisphere $h = \pm 12$, $k = 0–13$, and $l = \pm 21$, ($0 \leqslant 2\theta \leqslant 45°$) were collected by variable speed θ–2θ scans on a Enraf Nonius CAD-4 diffractometer equipped with a graphite monochromator and using Mo Kα radiation. Data were collected in a cold stream of N_2 (180 K) to arrest decomposition. The structure was solved using standard Patterson and difference Fourier methods and refined ($F(000) = 1246$) with full matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms [12]. Refinements included anisotropic thermal parameters for all atoms heavier than nitrogen and a correction for secondary extinction (1.03×10^{-7}) [13]. The Los Alamos Crystal Structure Codes [14] were used for all calculations. Data were corrected for absorption using the relative intensity of a low angle reflection measured as a function of Ψ (corrected to Φ) plus a superimposed spherical correction using a radius calculated from the average distance between the three most prominate directions of crystal development (*trans* 0.521 to 0.381). The function minimized was $R = \Sigma w^2[F_o - F_c]^2$ and weights were calculated as $w^2 = 4F^2/\sigma^2(I)$ where $\sigma(I) = \sigma_c(I) + (0.015 \times I)^2$; $\sigma_c(I)$ is the error based on counting statistics. The refinement of 320 parameters against 4710 observed reflections ($I \geqslant 2\sigma(I)$) converged to $R = 0.052$ and $R_w = 0.067$.

$Ce(OAsPh_3)_3(NO_3)_3$

Data collection, structure solution and refinement as above except as follows. Lattice constants and intensity data were measured at room temperature. Cell information: $a = 15.14(2)$, $b = 21.31(3)$, $c = 17.81(1)$ Å, $\beta = 92.30°(4)$; $V = 5744.3$ Å^3; $D_x = 1.50$ g/cm^3; space group $= P2_1/n$. Transmission as a function of Ψ for a low angle reflection varied from 0.48 to 0.47. It should be noted that the quality of the data is significantly lower for this structure compared to that for the above compound as evidenced by broad reflections (scan width *ca.* 1.0–1.7°) which showed some structure when examined by the ω scan method. This is reflected both in the unusually large errors determined for the lattice constants and in the quality factors for the final structure. An attempt was made to partially correct for the crystal quality by collecting data over a complete hemisphere of data (h, k, l range: ±16, 0–19, ±22) and scanning over a large ω range (1.2°). Of the 7484 unique reflections (14715 measurements), 4465 were observed and used in the refinements. The value of $R_{int} = \Sigma(F - \langle F \rangle)/\Sigma\langle F \rangle$ over all equivalent data was 3.6%, about 2 times the value for a high quality data set. The final crystallographic R value, resulting from refinements including anisotropic thermal parameters for all atoms heavier than oxygen, was 0.115 ($R_w = 0.138$).

Results and Discussion

$Ce(OAsPh_3)_3Cl_3$–CH_3CN

The atomic coordinates and thermal parameters are listed in Table I. An ORTEP-II drawing is presented as Fig. 1. (Selected atomic distances and angles are also given, see Table III, below.)

The most interesting feature of this structure is the facial conformation of the $OAsPh_3$ ligands about the cerium atom. One would expect, due to the large size

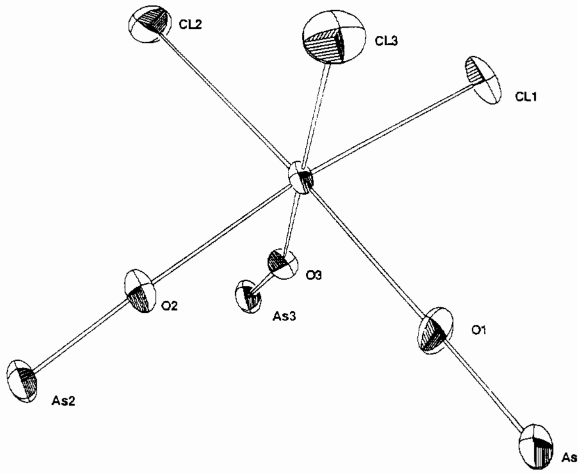

Fig. 1. Inner coordination sphere for $Ce(OAsPh_3)_3Cl_3$.

TABLE I. Fractional Coordinates and Thermal Parameters for $Ce(OAsPh_3)_3Cl_3$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce(1)	0.2831(1)	−0.0082(1)	0.2558(0)	1.60(4)	1.11(4)	2.09(4)	−1.40(6)	−0.10(6)	1.00(6)
Cl(1)	0.1989(3)	−0.1254(3)	0.3494(1)	4.0(2)	2.1(2)	3.0(2)	−4.0(3)	1.1(3)	0.8(3)
Cl(2)	0.0424(3)	0.1854(3)	0.2397(2)	2.0(2)	2.3(2)	6.0(2)	−1.1(3)	−1.6(3)	1.4(3)
Cl(3)	0.2352(3)	−0.1419(3)	0.1627(2)	3.6(2)	3.8(2)	3.8(2)	−3.0(4)	−0.0(3)	−1.9(3)
O(1)	0.492(1)	−0.169(1)	0.263(0)	1.9(5)	1.2(5)	3.9(5)	0.5(8)	0.1(8)	0.7(8)
As(1)	0.6364(1)	−0.2841(1)	0.2593(1)	2.0(1)	1.4(1)	2.8(1)	−1.1(1)	0.0(1)	1.0(1)
O(2)	0.372(1)	0.094(1)	0.189(0)	2.6(5)	2.5(5)	3.3(5)	−2.8(9)	−0.1(8)	2.9(8)
As(2)	0.4329(1)	0.1817(1)	0.1547(1)	2.2(1)	1.7(1)	2.4(1)	−2.0(1)	0.5(1)	1.3(1)
O(3)	0.305(1)	0.105(1)	0.340(0)	1.7(5)	2.0(5)	1.9(5)	−2.0(8)	−0.4(7)	1.1(7)
As(3)	0.2895(1)	0.2120(1)	0.3930(1)	2.0(1)	1.2(1)	2.2(1)	−1.4(1)	0.2(1)	0.6(1)

Atom	x	y	z	B	Atom	x	y	z	B
C(1)	0.768(1)	−0.228(1)	0.251(1)	1.9(2)	C(2)	0.829(1)	−0.236(1)	0.192(1)	2.5(3)
C(3)	0.924(1)	−0.191(1)	0.187(1)	3.0(3)	C(4)	0.949(1)	−0.141(1)	0.239(1)	2.9(3)
C(5)	0.889(1)	−0.132(1)	0.299(1)	3.2(3)	C(6)	0.794(1)	−0.176(1)	0.305(1)	2.7(3)
C(7)	0.667(1)	−0.381(1)	0.336(1)	1.6(2)	C(8)	0.790(1)	−0.462(1)	0.352(1)	2.4(3)
C(9)	0.807(1)	−0.539(1)	0.406(1)	2.9(3)	C(10)	0.701(1)	−0.530(1)	0.443(1)	3.0(3)
C(11)	0.578(1)	−0.450(1)	0.426(1)	3.1(3)	C(12)	0.559(1)	−0.370(1)	0.371(1)	2.6(3)
C(13)	0.653(1)	−0.390(1)	0.189(1)	1.5(2)	C(14)	0.763(1)	−0.504(1)	0.185(1)	2.7(3)
C(15)	0.775(1)	−0.583(1)	0.134(1)	3.0(3)	C(16)	0.681(1)	−0.546(1)	0.087(1)	3.6(3)
C(17)	0.575(1)	−0.435(1)	0.093(1)	3.9(3)	C(18)	0.558(1)	−0.354(1)	0.144(1)	2.9(3)
C(19)	0.546(1)	0.091(1)	0.087(1)	2.0(2)	C(20)	0.592(1)	0.154(1)	0.044(1)	3.8(3)
C(21)	0.678(2)	0.086(2)	−0.006(1)	4.7(4)	C(22)	0.711(2)	−0.038(2)	−0.010(1)	4.7(4)
C(23)	0.665(2)	−0.102(1)	0.032(1)	4.1(3)	C(24)	0.580(1)	−0.036(1)	0.082(1)	3.1(3)
C(25)	0.536(1)	0.228(1)	0.209(1)	1.8(2)	C(26)	0.486(1)	0.345(1)	0.236(1)	3.0(3)
C(27)	0.564(1)	0.378(1)	0.273(1)	3.5(3)	C(28)	0.691(1)	0.296(1)	0.280(1)	3.0(3)
C(29)	0.742(1)	0.176(1)	0.253(1)	2.6(3)	C(30)	0.661(1)	0.142(1)	0.218(1)	2.0(2)
C(31)	0.300(1)	0.329(1)	0.123(1)	2.1(2)	C(32)	0.180(1)	0.327(1)	0.114(1)	2.4(3)
C(33)	0.079(1)	0.433(1)	0.088(1)	3.6(3)	C(34)	0.100(1)	0.537(1)	0.072(1)	3.6(3)
C(35)	0.218(1)	0.539(1)	0.081(1)	3.6(3)	C(36)	0.319(1)	0.433(1)	0.105(1)	2.9(3)
C(37)	0.247(1)	0.369(1)	0.352(1)	1.5(2)	C(38)	0.168(1)	0.396(1)	0.299(1)	2.2(3)
C(39)	0.138(1)	0.513(1)	0.266(1)	3.0(3)	C(40)	0.188(1)	0.591(1)	0.290(1)	2.5(3)
C(41)	0.267(1)	0.561(1)	0.344(1)	2.7(3)	C(42)	0.294(1)	0.448(1)	0.375(1)	2.6(3)
C(43)	0.155(1)	0.231(1)	0.453(1)	1.5(2)	C(44)	0.093(1)	0.155(1)	0.445(1)	2.4(3)
C(45)	−0.005(1)	0.166(1)	0.491(1)	2.7(3)	C(46)	−0.035(1)	0.248(1)	0.542(1)	2.6(3)
C(47)	0.028(1)	0.325(1)	0.548(1)	2.7(3)	C(48)	0.125(1)	0.316(1)	0.502(1)	2.4(3)
C(49)	0.445(1)	0.172(1)	0.437(1)	1.5(2)	C(50)	0.453(1)	0.154(1)	0.503(1)	2.1(2)
C(51)	0.569(1)	0.124(1)	0.532(1)	2.4(3)	C(52)	0.674(1)	0.116(1)	0.496(1)	3.0(3)
C(53)	0.666(1)	0.137(1)	0.430(1)	3.8(3)	C(54)	0.550(1)	0.161(1)	0.400(1)	3.4(3)
N(1)	−0.051(1)	0.198(1)	0.004(1)	4.9(3)	C(55)	−0.059(1)	0.136(1)	0.046(1)	3.5(3)
C(56)	−0.065(1)	0.060(1)	0.100(1)	3.8(3)					

[a] Anisotropic thermal motion is defined by $\exp[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + 2U'_{12}hk + 2U'_{13}hl + 2U'_{23}kl)]$, where $U'_{ij} = U_{ij}a^*_ia^*_j$ and U_{ij} $(i = j)$ is multiplied by 10^2 in the table and $(i \neq j)$ is multiplied by 2×10^2.

of these ligands, that they would be arranged in a meridial fashion to overcome steric repulsions and indeed the *mer* conformation was observed for the previously reported structure of $Pr(HMPA)_3Cl_3$ for which the average Pr–O and Pr–Cl distances are 2.353 and 2.72 Å respectively. The average Ce–O and Ce–Cl distances are 2.347 and 2.779 Å for the present structure. The trivalent ionic radii for Ce and Pr are 1.15 and 1.13 Å [15]. Clearly then the Ce–O bond is somewhat shorter and the Ce–Cl bond is longer than expected. Indeed, for the Pr complex, the Pr–Cl distance for the chloride *trans* to a HMPA ligand is significantly shorter than the distances to the two chlorides *trans* to one another. This observation suggests that a structural *trans* influence is operative in the present structure and may account for the difference in conformation in the two complexes.

Stronger bonding to the Ln elements for $OAsPh_3$ compared to $OPPh_3$ has been indicated by the vibrational studies of Cousins and Hart [16] and it is reasonable to suggest that structural *trans* influences should be more pronounced for the former ligand and

TABLE II. Fractional Coordinates and Thermal Parameters for $Ce(OAsPh_3)_3(NO_3)_3$[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce(1)	0.7366(1)	0.1803(1)	0.9538(1)	4.6(1)	4.0(1)	1.7(1)	−0.8(2)	3.5(1)	0.0(2)
As(1)	0.8115(2)	0.2327(2)	1.1602(2)	6.8(2)	5.4(2)	1.9(2)	1.7(4)	2.9(3)	−0.8(3)
As(2)	0.9656(2)	0.2249(1)	0,8856(1)	4.7(2)	4.5(2)	2.4(2)	−0.7(3)	3.6(3)	0.2(3)
As(3)	0.7535(2)	0.0433(2)	0.8077(2)	5.7(2)	5.0(2)	2.7(2)	−1.1(4)	3.7(3)	−1.5(3)

Atom	x	y	z	B	Atom	x	y	z	B
O(1)	0.774(1)	0.215(1)	1.074(1)	4.0(4)	C(1)	0.929(2)	0.226(1)	1.173(2)	3.6(6)
C(2)	0.986(2)	0.252(2)	1.230(2)	5.8(9)	C(3)	1.075(3)	0.245(2)	1.239(2)	6.7(9)
C(4)	1.121(2)	0.210(2)	1.183(2)	5.2(8)	C(5)	1.072(2)	0.185(2)	1.126(2)	5.0(7)
C(6)	0.979(2)	0.190(1)	1.116(2)	4.0(7)	C(7)	0.780(2)	0.315(1)	1.181(2)	4.0(6)
C(8)	0.761(2)	0.353(2)	1.121(2)	6.3(9)	C(9)	0.740(3)	0.421(2)	1.138(3)	8.8(12)
C(10)	0.734(3)	0.437(2)	1.215(3)	8.6(12)	C(11)	0.776(3)	0.403(3)	1.270(3)	10.7(14)
C(12)	0.779(3)	0.335(2)	1.256(2)	8.5(12)	C(13)	0.757(2)	0.175(1)	1.228(2)	3.8(6)
C(14)	0.682(2)	0.147(1)	1.203(2)	4.0(7)	C(15)	0.642(2)	0.102(2)	1.253(2)	6.8(10)
C(16)	0.690(3)	0.094(2)	1.326(2)	7.3(10)	C(17)	0.762(3)	0.123(2)	1.352(2)	7.2(10)
C(18)	0.803(2)	0.168(2)	1.301(2)	7.3(10)	O(2)	0.889(1)	0.183(1)	0.927(1)	3.4(4)
C(19)	0.958(2)	0.310(1)	0.904(2)	3.3(6)	C(20)	0.953(2)	0.353(2)	0.847(2)	4.4(7)
C(21)	0.955(3)	0.418(2)	0.863(3)	8.8(12)	C(22)	0.947(3)	0.435(2)	0.936(2)	7.8(11)
C(23)	0.951(3)	0.396(2)	0.998(2)	7.9(11)	C(24)	0.953(2)	0.331(2)	0.982(2)	5.0(8)
C(25)	1.077(2)	0.200(1)	0.923(1)	2.7(6)	C(26)	1.144(2)	0.242(2)	0.935(2)	5.0(8)
C(27)	1.230(3)	0.222(2)	0.962(2)	6.8(9)	C(28)	1.242(2)	0.158(2)	0.969(2)	5.3(8)
C(29)	1.177(2)	0.116(2)	0.956(2)	5.8(9)	C(30)	1.091(2)	0.136(1)	0.929(2)	4.2(7)
C(31)	0.960(2)	0.208(1)	0.778(1)	2.6(6)	C(32)	0.884(2)	0.195(2)	0.742(2)	4.9(8)
C(33)	0.879(2)	0.189(2)	0.659(2)	5.6(8)	C(34)	0.958(2)	0.200(1)	0.626(2)	4.9(8)
C(35)	1.033(2)	0.218(2)	0.660(2)	5.0(8)	C(36)	1.039(2)	0.225(2)	0.743(2)	5.6(8)
O(3)	0.734(1)	0.110(1)	0.851(1)	4.0(4)	C(37)	0.870(2)	0.022(1)	0.823(2)	3.9(7)
C(38)	0.904(2)	−0.006(2)	0.887(2)	4.9(8)	C(39)	0.990(2)	−0.026(2)	0.899(2)	6.1(9)
C(40)	1.051(3)	−0.016(2)	0.844(2)	7.9(11)	C(41)	1.016(3)	0.013(2)	0.773(2)	8.4(11)
C(42)	0.928(3)	0.028(2)	0.765(2)	7.7(11)	C(43)	0.680(2)	−0.023(1)	0.842(1)	3.1(6)
C(44)	0.697(2)	−0.083(1)	0.824(2)	4.0(7)	C(45)	0.638(3)	−0.130(2)	0.849(2)	6.8(10)
C(46)	0.568(2)	−0.117(2)	0.890(2)	6.1(9)	C(47)	0.551(3)	−0.053(2)	0.907(2)	6.9(10)
C(48)	0.608(2)	−0.005(2)	0.880(2)	5.6(8)	C(49)	0.724(2)	0.059(1)	0.703(2)	4.0(7)
C(50)	0.755(2)	0.017(2)	0.647(2)	6.5(10)	C(51)	0.727(3)	0.040(2)	0.568(3)	9.7(13)
C(52)	0.685(2)	0.092(2)	0.555(2)	6.9(10)	C(53)	0.653(3)	0.131(2)	0.610(3)	8.6(12)
C(54)	0.677(2)	0.118(2)	0.692(2)	6.6(10)	O(4)	0.582(1)	0.184(1)	0.894(1)	5.8(5)
N(1)	0.539(2)	0.211(1)	0.949(2)	6.3(7)	O(5)	0.463(2)	0.225(1)	0.935(1)	7.8(7)
O(6)	0.587(1)	0.222(1)	1.003(1)	5.7(5)	O(7)	0.729(1)	0.300(1)	0.946(1)	6.4(6)
N(2)	0.732(2)	0.308(1)	0.877(1)	4.2(6)	O(8)	0.748(1)	0.260(1)	0.843(1)	5.8(5)
O(9)	0.725(2)	0.358(1)	0.847(1)	7.0(6)	O(10)	0.655(1)	0.094(1)	1.027(1)	4.7(5)
N(3)	0.722(2)	0.064(1)	1.045(2)	5.4(7)	O(11)	0.795(2)	0.076(1)	1.023(1)	5.7(5)
O(12)	0.719(2)	0.015(1)	1.084(2)	9.0(8)					

[a] Anisotropic thermal motion is defined by $\exp[-2\pi^2(U'_{11}h^2 + U'_{22}k^2 + U'_{33}l^2 + 2U'_{12}hk + 2U'_{13}hl + 2U'_{23}kl)]$, where $U'_{ij} = U_{ij}a^*_i a^*_j$ and U_{ij} $(i = j)$ is multiplied by 10^2 in the table and $(i \neq j)$ is multiplied by 2×10^2.

for the early lanthanides. Of course, if a structural *trans* influence is indeed operative in this complex, covalent bonding is strongly implied. The generality of this result should be established by further structural studies.

$Ce(OAsPh_3)_3(NO_3)_3$

The atomic coordinates and thermal parameters are listed in Table II. An ORTEP-II drawing is presented as Fig. 2. A list of selected atomic distances and angles is given in Table III.

The crystal structure of this complex, while not of the highest quality, clearly establishes the general conformational characteristic of the complex. On the basis of a pseudo-octahedral coordination geometry, from which the complex is (Table III) grossly distorted, the conformation can be described as meridial. Previous structures (see 'Introduction') of this type are facial. An explanation of this interesting difference would require a much larger data base and a detailed molecular mechanics analysis of the problem. Within the accuracy of the determination, all metrical parameters are unexceptional.

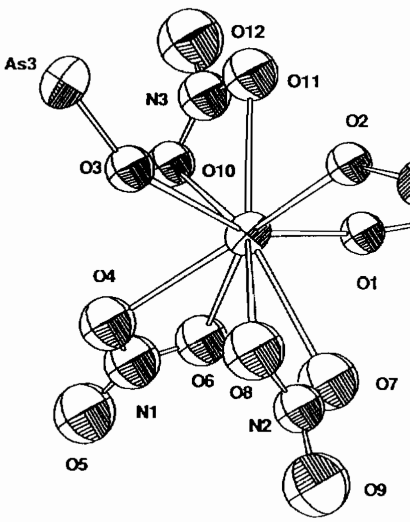

Fig. 2. Inner coordination sphere for Ce(OAsPh$_3$)$_3$(NO$_3$)$_3$.

TABLE III. Selected Distances and Angles[a]

Distances		Angles	
Ce(OAsPh$_3$)$_3$Cl$_3$			
Ce–Cl(1)	2.792(3)	Cl(1)–Ce–Cl(2)	94.0(1)
Ce–Cl(2)	2.782(3)	Cl(1)–Ce–Cl(3)	90.0(1)
Ce–Cl(3)	2.763(3)	Cl(2)–Ce–Cl(3)	90.4(1)
Ce–O(1)	2.367(7)	O(1)–Ce–O(2)	86.8(2)
Ce–O(2)	2.341(7)	O(1)–Ce–O(3)	94.7(2)
Ce–O(3)	2.334(7)	O(2)–Ce–O(3)	87.4(2)
As(1)–O(1)	1.650(7)	O(1)–Ce–Cl(1)	89.6(2)
As(2)–O(2)	1.654(7)	O(1)–Ce–Cl(2)	176.2(2)
As(3)–O(3)	1.659(7)	O(1)–Ce–Cl(3)	88.5(2)
		O(2)–Ce–Cl(1)	171.5(2)
		O(2)–Ce–Cl(2)	89.6(2)
		O(2)–Ce–Cl(3)	97.5(2)
		O(3)–Ce–Cl(1)	85.1(1)
		O(3)–Ce–Cl(2)	86.6(1)
		O(3)–Ce–Cl(3)	174.1(2)
Ce(OAsPh$_3$)$_3$(NO$_3$)$_3$			
Ce–N(1)	3.05(3)	N(1)–Ce–N(2)	77.8(6)
Ce–N(2)	3.04(2)	N(1)–Ce–N(3)	96.0(8)
Ce–N(3)	2.97(3)	N(2)–Ce–N(3)	171.5(7)
Ce–O(1)	2.32(1)	O(1)–Ce–O(2)	88.7(6)
Ce–O(2)	2.37(1)	O(1)–Ce–O(3)	156.1(6)
Ce–O(3)	2.37(1)	O(2)–Ce–O(3)	87.4(2)
Ce–O(4)	2.53(2)	O(1)–Ce–N(2)	97.6(6)
Ce–O(6)	2.62(2)	O(1)–Ce–N(3)	77.4(6)
Ce–O(7)	2.56(2)	O(1)–Ce–N(1)	99.2(7)
Ce–O(8)	2.61(2)	O(2)–Ce–N(1)	160.6(6)
Ce–O(10)	2.59(2)	O(2)–Ce–N(2)	83.6(6)
Ce–O(11)	2.67(2)	O(2)–Ce–N(3)	102.9(7)
		O(3)–Ce–N(1)	97.2(7)
		O(3)–Ce–N(2)	102.5(6)
		O(3)–Ce–N(3)	83.7(6)

[a] The mean carbon–carbon distances for the rings range from 1.39(1) to 1.40(1) Å and the average C–C–C angle is 119(1)°.

Supplementary Material

Observed and calculated structure factors and their sigma values can be obtained upon request from the Los Alamos National Laboratory authors.

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References

1 C. M. Mikulski, S. Cocco and N. DeFranco, *Inorg. Chim. Acta, 67,* 61 (1982).

2 P. N. Kapoor and R. Saraswati, *Inorg. Chim. Acta, 110,* 63 (1985).

3 D. K. Koppikar, P. V. Sivapullaiah, L. Ramakrishnan and S. Soundararajan, *Struct. Bonding (Berlin), 34,* 135 (1978).

4 V. Tazzoli, A. Della Giusta, M. Cola, A. Coda and C. Castellani Bisi, *Acta Crystallogr., Sect. A., 28,* S88 (1972).

5 L. J. Radonovich and M. D. Glick, *J. Inorg. Nucl. Chem., 35,* 2745 (1973).

6 K. K. Bhandary, H. Manohar and K. Venkatesan, *Cryst. Struct. Commun., 2,* 99 (1973).

7 K. K. Bhandary, H. Manohar and K. Venkatesan, *J. Chem. Soc., Dalton Trans.,* 288 (1975).

8 L. A. Aslanov, L. I. Soleva, S. S. Goukhberg and M. A. Porai-Koshits, *Zh. Strukt. Khim., 12,* 1113 (1971).

9 L. A. Aslanov, L. I. Soleva and M. A. Porai-Koshits, *J. Struct. Chem., 14,* 998 (1975).

10 K. K. Bhandary, H. Manohar and K. Venkatesan, *Acta Crystallogr., Sect. B, 32,* 861 (1976).

11 J. H. Burns, 'Structural Chemistry of Compounds of the Actinide Elements', *ORNL Report #TM-8221,* Oak Ridge National Laboratory, Tenn., 1982.

12 (a) D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography, Kynoch Press, Birmingham, U.K., 1974, Table 2.2A; (b) D. T. Cromer, Table 2.3.1.

13 (a) W. H. Zachariasen, *Acta Crystallogr., 23,* 558 (1967); (b) A. C. Larson, *Acta Crystallogr., 23,* 664 (1967); (c) A. C. Larson, in F. R. Ahmed (ed.), 'Crystallographic Computing', Munksgaard, Copenhagen, 1970, p. 291.

14 A. C. Larson, *Am. Crystallogr. Assoc. Program Abstr., Ser. 2, 5*(2), 67 (1977).

15 R. D. Shannon, *Acta Crystallogr., Sect. A, 32,* 751 (1976).

16 D. R. Cousins and F. A. Hart, *J. Inorg. Nucl. Chem., 29,* 2965 (1967).