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Preparation and Structure of Tetrachlorobis[tris(dimethylamido)phosphine] oxidecerium(IV)

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In the course of our studies of the coordination chemistry of the 5f transition metals, comparisons with 4f transition element analogues were occasionally made where possible, in order to compare 5f and 4f element character [1–3]. Tris(dimethylamido)phosphine oxide (tdpo) proved to be an important neutral donor ligand in the study of actinoid halide coordination chemistry especially in that of the six coordinated species [4, 5]. In the light of the above and since the $UCl_4(tdpo)_2$ complex has been particularly well studied regarding its chemical behaviour and properties [4], including molecular structure [6, 7] it was of interest to establish whether $CeCl_4(tdpo)_2$ can be isolated, and if so to compare its properties and structure with that of its uranium analogue. Such an investigation would facilitate close comparison between a quadrivalent actinoid chloro complex of this type and a 4f analogue in a six coordinated environment which is uncommon for inner transition elements [8].

As a result of the strong oxidative strength of Ce(IV) species in acid medium and the corresponding ease with which these are reduced to the tervalent state by halide ions (except fluoride), the preparation of $CeCl_4$ or even coordination compounds of the type $CeCl_4L_2$ (L = neutral donor ligand) have not been reported in the literature. The solid dipyridinium complex $(C_5H_6N)_2CeCl_6$ is, however, quite stable (it can be dried at 120 °C *in vacuo*). Tris(dimethylamido)phosphine oxide is a neutral, moderately strong P=O donor ligand which is comparable to the chloride in its coordination properties, *e.g.* donor strength [9], ligand field strength [10] and the coordination number forced upon metal ions [11]. The solid actinoid $MCl_4(tdpo)_2$ complexes all proved to be relatively stable and non-solvoscopic as indicated by their low solubility in polar non-aqueous solvents [4]. The ligand can therefore be regarded as particularly suitable for the stabilization of $CeCl_4$, especially since it stabilises similar complexes where the free tetrachloride has not yet been isolated, *e.g.* $PuCl_4(tdpo)_2$ [5].

Pure $CeCl_4(tdpo)_2$ was prepared [11] by dissolving ammoniumhexanitratocerate(IV) in acetone followed by the addition of the corresponding amount of tdpo. After filtration of the precipitated ammonium nitrate a slight excess of concentrated hydrochloric acid was added followed by dimethoxypropane. Red crystals formed slowly from the orange solution. *Anal.* $CeCl_4(tdpo)_2$, Calcd.: Cl 22.15, C 22.51, N 13.12, H, 5.67. Found: Cl 21.98, C 22.3, N 13.2, H 5.6%. The product is stable at room temperature, and decomposition only starts at 150 °C; it can be kept indefinitely in a relatively dry atmosphere.

The infrared spectrum resembles that of $UCl_4(tdpo)_2$ except for the expected shift of the asymmetric metal chloride vibrations from 250 cm^{-1} (U) to 272 cm^{-1} (Ce) due to the mass difference between the U and the Ce atoms. The P=O stretching frequency in $CeCl_4(tdpo)_2$ is shifted to 1035 cm^{-1} (from 1200 cm^{-1} for the free ligand) as compared to 1046 cm^{-1} for $UCl_4(tdpo)_2$ which represents a ca 7% difference in the P=O stretch frequency shift between the U and Ce analogues. This is in accord with the expected higher Lewis acidity of Ce(IV).

The title compound crystallises in the monoclinic system, space group $P2_1/n$, a = 14.239(5), b = 10.542(5), c = 9.120(5) Å, β = 93.35(5)°, V = 1366.6 Å^3. The density D_m = 1.60 g cm^{-3} (D_c = 1.555 g cm^{-3} for Z = 2); the linear absorption coefficient, μ = 20.51 cm^{-1}. The intensities of 1365 independent reflections were measured with a Philips PW 1100 automatic four-circle diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). In order to render absorption errors negligible a spherical crystal, ground and mounted in a Lindeman glass capillary in the dry box, was used (radius 0.15 ± 0.015 mm, μR = 0.3 ± 0.03). 866 reflections having $|F_{rel}| \geq 1.65\,|F_{rel}|$ were labelled as "observed" and used for the structural solution and refinement. Since the Ce atoms must be situated at symmetry centres (*e.g.* at 0, 0, 0; ½, ½, ½), trial positions for the lighter atoms followed from difference electron density syntheses. These were refined by a full-matrix least-squares procedure (program system SHELX [12]), the non-hydrogen atoms vibrating anisotropically, while a common isotropic temperature factor was assigned to all hydrogen atoms. The latter were placed at calculated positions, 1.08 Å from their parent C atoms before each cycle, first as $-CH_3$ rigid bodies and finally in a riding model. The final value of R was 0.055. One of the carbon atoms, C(22) (Fig. 1), persistently showed anomalous behaviour with regard to its x-co-ordinate; this resulted in

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TABLE I. Structural Details for $MCl_4(tdpo)_2$ Complexes (M = U, Ce). Unless indicated otherwise, mean values and estimated standard deviations (in parentheses) are given

	$UCl_4(tdpo)_2$ [7]	$CeCl_4(tdpo)_2$
Bond lengths (Å)		
M–Cl	2.615(5)	2.600(5)
M–O[a]	2.23(1)	2.22(1)
P–O[a]	1.50(1)	1.51(1)
P–N	1.61(1)	1.63(1)
N–C[b]	1.47(2)	1.45(2)
N(2)–C(22)	1.36(4)	1.34(3)
Bond Angles (°)		
M–O–P[a]	163.1(6)	163.4(7)
Cl–M–Cl[a]	89.7(2)	90.2(2)
Cl–M–O	90.6(3)	89.8(3)
O–P–N[c]	107.4(7)	107.3(7)
O–P–N(3)[a]	116.1(6)	116.2(8)
N–P–N[b]	106.5(5)	106(1)
N(1)–P–N(2)	114.0(6)	114.5(8)
C–N–C[b]	110(2)	113(2)

[a]Only one crystallography independent estimate. [b]Excluding bonds/angles involving atom C(22). [c]Excluding the next table entry.

a value for the N(2)–C(22) bond length (1.34 Å), significantly shorter than the other similar bonds, and which is chemically unacceptable*. Attempts to refine the structure with the problem atom fixed at its expected position (*i.e.* giving a bond length and angles which correspond to the mean of the other values, as reported in Table I) gave no improvement in R; it increased to 0.062 while the thermal parameter U_{11} refined to an unrealistic value (0.5640 Å^2).

The structure of the molecule (drawn with the desk-plotter program PLOT-2D [14]) is shown in Fig. 1, the numbered atoms being those in the asymmetric unit; the bond lengths and angles of greatest interest are shown. Mean values for the various bond lengths and angles are compared in Table I with the corresponding values for $UCl_4(tdpo)_2$.

Not only is the cerium(IV) complex isomorphous with its uranium(IV) analogue but, remarkably, the two structures are practically identical within experimental error; whereas the Ce–Cl bond length is 2–3 combined standard deviations shorter than that of U–Cl, e.s.d.'s of the order of 0.005 Å in such structures are, in our opinion, underestimated [15] and the significance of this bond length difference is therefore questionable. Furthermore, if the Ce–Cl bond were the shorter of the two, one might have expected a smaller unit cell since the packing is highly similar; actually, the unit cell of the cerium complex is *larger* by about 17 Å^3. (Cell dimensions for $UCl_4(tdpo)_2$ [17] : $a = 14.141(5)$, $b = 10.530(5)$, $c = 9.076(5)$ Å; $\beta = 93.33(5)°$, V = 1349.2 Å^3).

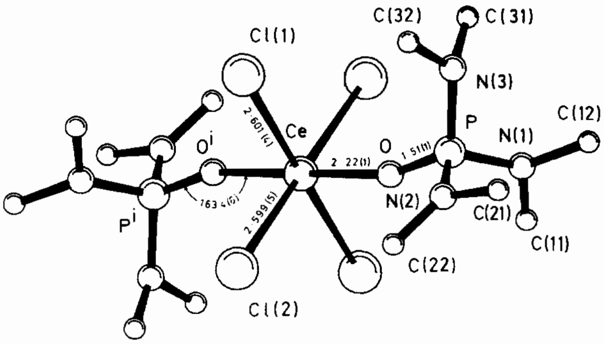

Figure 1. The molecular configuration of $CeCl_4(tdpo)_2$ (hydrogen atoms omitted).

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*Surprisingly, the corresponding atom in the isostructural $UCl_4(tdpo)_2$ [6, 7] displays exactly the same anomalous behaviour; this is discussed in more detail elsewhere [13].