

Synthesis of Cerium(III) and (IV) Complexes of Phenacyldiphenylphosphine Oxide. The Structure of $Ce(NO_3)_3[Ph_2P(O)CH_2C(O)Ph]_3$

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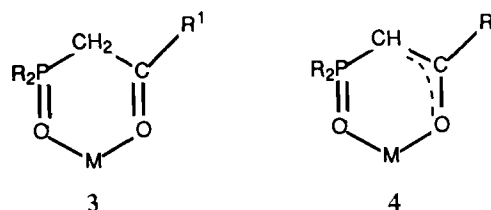
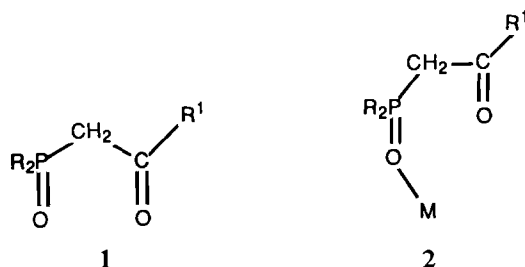
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Abstract

The complexes $Ce(NO_3)_3(HL)_3$ (**I**) and $Ce(NO_3)_3 \cdot L(HL)$ (**II**) have been prepared where $HL = Ph_2P(O)CH_2C(O)Ph$. The structure of **I** has been determined and shows that the cerium atom is ten coordinate. HL is bound as both bidentate and monodentate ligands with the third ligand showing intermediate bonding characteristics. The infrared spectra of the complex are discussed in terms of the observed modes of bonding. The thermally unstable Ce(IV) complex, **II**, contains the phosphine oxide bound as both neutral and anionic chelates, probably in a ten-coordinate complex.

Introduction

Although the coordination chemistry of phosphine oxides is extensive [1] relatively little work has been carried out on molecules which contain additional functional groups capable of coordinating to a metal. β -Ketophosphine oxides (**1**) can coordinate to metals in a variety of ways, for example **2** [2], **3** [3, 4] and **4** [5, 6], and this has led to interest in their application to hydrometallurgy [7]. We report the synthesis of Ce(III) and Ce(IV) complexes and the first structural characterisation of a β -ketophosphine oxide complex in which the ligand is coordinated as both a neutral chelating and monodentate ligand to the same metal.



Experimental

$Ph_2P(O)CH_2C(O)Ph$ (HL) was prepared as described previously [5].

Preparation of $Ce(NO_3)_3(HL)_3$ (**I**)

$Ce(NO_3)_3 \cdot 6H_2O$ (0.36 g 0.62 mmol) in 20 cm³ absolute ethanol was refluxed with HL (1.6 g 5.0 mmol) for 30 min. On cooling yellow crystals separated which were filtered and recrystallised from ethanol to give 0.9 g (84%), melting point (m.p.) 97 °C. *Anal.* Calc.: C, 55.95; H, 3.99; N, 3.26. Found: C, 55.83; H, 4.01; N, 3.25%.

Preparation of $Ce(NO_3)_3L(HL)$ (**II**)

$(NH_4)_2Ce(NO_3)_6$ (0.34 g 0.62 mmol) was refluxed with HL (0.4 g 1.25 mmol) in 20 cm³ ethanol for 30 min. On cooling a crude product was obtained which was recrystallised to give 0.39 g (70%), m.p. 149 °C(d). *Anal.* Calc.: C, 49.69; H, 3.54; N, 4.35. Found: C, 49.96; H, 3.56; N, 4.35%.

Crystal Data

$CeC_{60}H_{51}N_3O_{15}P_3$, $M = 1287.07$, triclinic, space group $P\bar{1}$, $a = 22.133(66)$, $b = 12.563(49)$, $c = 11.035(90)$ Å, $\alpha = 93.01(10)$, $\beta = 106.1(4)$, $\gamma = 96.21(20)^\circ$, $U = 2919.4$ Å³, $Z = 2$, $\mu = 8.45$ cm⁻¹, $\lambda(Mo K\alpha) = 0.7107$ Å, $F(000) = 1261.9$, $D_c = 1.464$ g cm⁻³.

The unit cell parameters were determined by least-squares refinement of omega measurements for different layers [8]. The intensities of 5882 unique

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reflections with $2\theta < 50^\circ$ and $(\pm h, \pm k, \pm l)$ were measured on a Stoe STADI-2 Weissenberg diffractometer, with graphite monochromated Mo K α radiation using an omega-scan technique. The data were corrected for Lorentz and polarisation effects to yield 4612 reflections with $I > 3\sigma(I)$.

All subsequent calculations were carried out using the computer program SHELX-76 [9]. An absorption correction was applied to the data with the maximum and minimum transmission factors 0.971 and 0.901 respectively. The cerium atom position was located and the structure was solved using standard Patterson and Fourier difference techniques.

Phenyl rings were included as rigid groups with D_{6h} symmetry and C–C distances of 1.395 Å. Program restraints would not allow the inclusion of hydrogen atoms in conjunction with the anisotropic thermal refinement for the remaining atoms. The lowest final R factor was obtained by omitting the hydrogen atoms and refining all other atoms as anisotropic.

Final cycles of refinement employed a weighting parameter g (0.0011) $\{w = 1/[\sigma^2(F) + g(F)^2]\}$ and gave the final residual indices R $\{=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ 0.0661 and R_w $\{=[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{1/2}$ 0.0645. The final difference Fourier map was featureless and an analysis of the weighting scheme over $|F_o|$ and $\sin \theta/\lambda$ was satisfactory.

Results and Discussion

Two distinct C=O stretches are observed in the infrared spectrum of the cerium(III) complex, I, at 1675 and 1655 cm^{-1} (KBr) and at 1675 and 1630 cm^{-1} (CHCl_3) compared with 1680 cm^{-1} for the free ligand. This implies that the complex contains both monodentate and bidentate ligands and that the solid state structure persists in solution. The coordination shift is smaller than that generally observed for 1:1 complexes of TiCl_4 and SnCl_4 with $(\text{RO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{R}'$ [3], but similar to the shift for the coordinated acetone in $\text{UO}_2(\text{NCS})_2(\text{OPPh}_3)_2(\text{OCMe}_2)$ [10] and for the bidentate ligand in $\text{Sm}[(i\text{PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NET}_2]_2(\text{NO}_3)_3$ complex III [4]. However, similar shifts in $\nu(\text{CO})$ are also observed when the carbonyl oxygen is hydrogen bonded to coordinated water, for example in the erbium nitrate complexes of $(i\text{PrO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{NET}_2$ [4] and $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Ph}$ [11] and thus changes in the CO stretching frequency alone cannot be used as an unambiguous means of identification of bidentate β -ketophosphine oxides. The structure of I was thus determined to fully characterise the complex.

The complex contains discrete monomeric units and the structure is shown in Fig. 1. Figure 2 shows the coordination geometry about the cerium atom

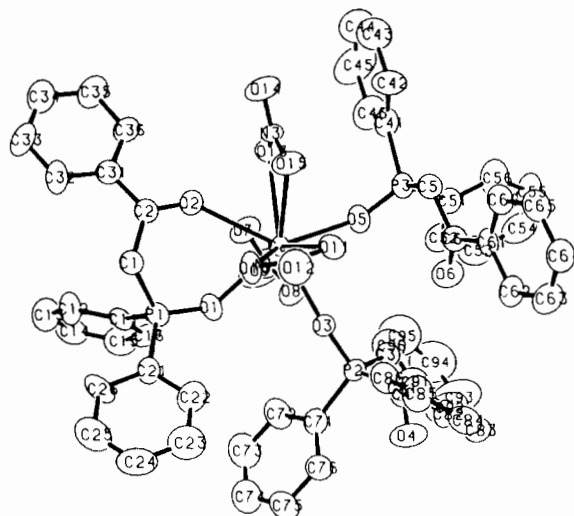


Fig. 1. The structure of $\text{Ce}(\text{NO}_3)_3[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Ph}]_3$.

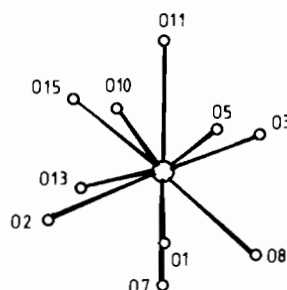


Fig. 2. The coordination geometry about the cerium atom.

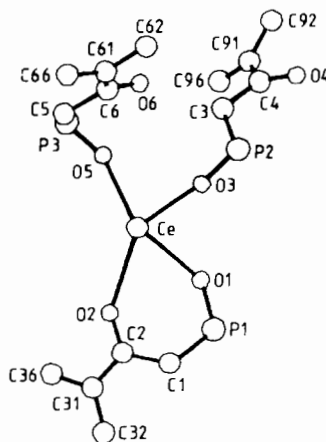


Fig. 3. Partial structure showing the geometry of the phosphine oxide molecules.

which can be considered as a distorted bicapped square antiprism similar to that observed for $\text{Ce}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2$ [12] and III [4].

A partial structure showing only the phosphine oxide coordination geometries is shown in Fig. 3. The cerium atom is bound to one bidentate and two

TABLE 1. Selected bond lengths (Å) and angles (°) within the coordinated ligands^a

	Ph ₂ P(O)CH ₂ C(O)Ph				
	Bidentate	'Oriented'	Monodentate		
Bond lengths					
Ce–O	2.447(9)	2.400(8)	2.411(8)		
O=P	1.493(8)	1.496(10)	1.477(8)		
P–C	1.805(12)	1.823(19)	1.828(12)		
C–C	1.522(20)	1.529(19)	1.471(19)		
C–O	1.241(15)	1.207(19)	1.197(20)		
C–Ph	1.462(14)	1.485(16)	1.501(17)		
Ce–O(C)	2.609(8)	4.55 ^b	6.48 ^b		
Bond angles					
Ce–O–P	140.9(5)	147.3(5)	156.8(5)		
O–P–C	112.9(6)	112.7(6)	107.9(5)		
P–C–C	111.1(8)	111.2(9)	118.4(11)		
C–C–O	119.4(10)	120.1(12)	123.4(13)		
C–O–Ce	143.3(9)				
O–Ce–O	68.1(3)				
Nitrate ions					
Bond lengths					
Ce–O(7)	2.623(9)	Ce–O(8)	2.630(9)		
N(1)–O(7)	1.234(15)	N(1)–O(8)	1.244(16)	N(1)–O(9)	1.213(17)
Ce–O(10)	2.579(8)	Ce–O(11)	2.750(9)		
N(2)–O(10)	1.261(14)	N(2)–O(11)	1.250(14)	N(2)–O(12)	1.234(14)
Ce–O(13)	2.672(10)	Ce–O(15)	2.526(10)		
N(3)–O(13)	1.246(14)	N(3)–O(14)	1.191(16)	N(3)–O(15)	1.257(15)
Bond angles					
O(8)–N(1)–O(7)	116.4(12)	O(9)–N(1)–O(7)	122.2(12)		
O(9)–N(1)–O(8)	121.4(12)	O(11)–N(2)–O(10)	118.3(10)		
O(12)–N(2)–O(10)	121.2(11)	O(12)–N(2)–O(11)	120.5(11)		
O(14)–N(3)–O(13)	121.6(11)	O(15)–N(3)–O(13)	115.9(11)		
O(15)–N(3)–O(14)	122.5(11)				

^aSee 'Supplementary Material'. ^bNon-bonded distances.

monodentate ligands. The monodentate ligands are not equivalent. The carbonyl oxygen atom of one is oriented towards the metal in a similar manner to that observed in UO₂(NO₃)₂(Ph₂P(O)CH₂C(O)Ph)₂ [5], whilst the third ligand has its C=O group directed away from the metal. The orientation of C=O towards the metal increases its steric requirements and is presumably compensated for by a weak attraction between the carbonyl oxygen and cerium atom. Thus the coordinated HL ligands can be thought of as undergoing a transition from chelating through an 'oriented' stage to a monodentate ligand.

This transition from bidentate to monodentate coordination is reflected by some of the bond lengths and angles within the coordinated ligands which are shown in Table 1. It is interesting to note that although the carbonyl oxygen of the 'oriented' ligand lies well beyond the normal Ce–O bonding

distance the weak interaction with the metal atom does produce a pronounced affect on its structure. In some respects it appears to have intermediate properties between its bidentate and monodentate counterparts. For instance during the change from bidentate to monodentate coordination the C–Ph distance increases. The dihedral angle between the CCO plane and that of the phenyl ring (see Fig. 3) changes from almost coplanar for the bidentate and oriented ligands, i.e. the angles between planes C(1)C(2)O(2) and C(32)C(31)C(36) and between C(5)C(6)O(6) and C(66)C(61)C(62) respectively, to 30° for the corresponding angle in the monodentate ligand. These changes are consistent with the expected increase in conjugation between the carbonyl group and the phenyl ring on coordination. On chelation the Ce–O and C–O bond lengths both increase.

Two of the nitrate groups are unsymmetrically bound to the metal whilst the third is symmetric. This asymmetry is not reflected in the N—O distances where the cerium—oxygen bond length has no significant effect on the corresponding N—O distance.

The corresponding Ce(IV) complex, **II**, is of interest as it contains the ligand as both neutral and anionic chelates. The production of **II** by reaction of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ with HL proceeds with spontaneous deprotonation of one of the HL molecules and loss of nitrate ion. The infrared spectrum shows a single band at 1630 cm^{-1} assigned as $\nu(\text{CO})$ for the neutral chelating ligand. The CO stretch for the anionic ligand is not observed due to an intense broad absorption at 1450 cm^{-1} from the coordinated nitrate which occurs in the same region of the spectrum as the CO stretch.

The complex decomposes violently on melting at $149\text{ }^\circ\text{C}$ and a dry bulk sample spontaneously ignited on gentle warming. The unstable nature of this compound has precluded further characterisation, and attempts to grow crystals suitable for structure determination have proved unsuccessful. Spectroscopic evidence suggests that the complex contains bidentate nitrate ions and is thus probably ten coordinate, although further deductions concerning its geometry cannot be made.

Supplementary Material

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical

Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

Acknowledgements

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