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Th(IV) complexes with *cis*-ethylenebis(diphenylphosphine oxide): X-ray structures and NMR solution studies

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ABSTRACT

The complexation of $Th(NO_3)_4$ with the rigid diphosphoryl ligand *cis*-ethylenebis(diphenylphosphine oxide) has been investigated using X-ray crystallography, IR, NMR and CHN analysis. Three crystal polymorphs were grown out of methanolic solution where the 1:3 Th(IV)–ligand complex is ten-coordinate, and the metal is bound by three bidentate ligands and two nitrato groups. An additional metal–ligand complex with similar geometry was also grown from the non-coordinating solvent $CHCl_3$. Analysis of CD_3OD and $CDCl_3$ solutions of this complex using ^1H and ^{31}P NMR reveals that ligand exchange rates are fast on the NMR time scale in methanol-d_4, and slow on the NMR time scale in chloroform-*d*. Further, three additional crystal structures are reported describing the 1:1 and 1:2 Th(IV)–ligand complex, the 1:3 Th(IV)–ligand complex with an extra aqua ligand, and a serendipitous 1:3 Th(IV)–ligand structure where one ligand bears an epoxide.

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1. Introduction

The coordination chemistry of the actinide thorium continues to gain attention from researchers for uses in catalysis, energy production, and the production of new materials. Thorium is found in small quantities in nearly all rock, soil, and water samples in the form of ^{232}Th, its major isotope. Additional isotopes of Th have been identified (^{228}Th, ^{230}Th, ^{234}Th), but these are mainly decay products of other man-made radionuclides or from absorption in nuclear reactors. ^{232}Th has a half-life of 14 billion years and emits radiation through a long decay series beginning with an α-emission to give ^{228}Ra and ending with the stable isotope ^{208}Pb.

Due in part to its extremely high melting point (3300 °C), ThO_2 (aka "thoria") has found applications in light bulb elements, lantern mantles and heat-resistant ceramics [1,2]. It is a component of spent nuclear fuel from uranium-based nuclear reactors, and has itself been explored as an energy source [3]. There have also been a wide variety of reports directed toward the use of Th(IV) complexes as catalysts for chemical transformations [4]. A selection of reactions mediated by Th(IV) organometallic complexes include: C–H and C–O bond activation [5,6], hydrosilylation of alkenes and alkynes [7], hydroamination [7–10], aldehyde dimerization [11], and phosphonoester hydrolysis [12].

To this end, investigations into the synthesis and structure of high-denticity Th(IV) complexes will contribute to each of the diverse set of chemical areas described above. New organic ligands could find use as sequestering agents for Th(IV) out of nuclear waste streams, provide stereochemical control for catalytic transformations, or generate new thorium containing materials with unique properties. Interestingly, out of the over 750,000 structures in the Cambridge Structural Database [13] only 553 contain coordination complexes of thorium. Of these 553 reported structures, less than 100 are greater than nine-coordinate containing all oxygen donors. The need for additional structural information describing the coordination geometries available to this unique element is strong. We contribute to this area here with seven new crystal structures containing Th(IV) and a rigid, bidentate phosphine oxide ligand. The crystallographic work is accompanied by a complete set of high resolution spectra (IR, ^1H and ^{31}P NMR) used to characterize the isolated complex, as well as corresponding elemental analysis (CHN) data.

2. Experimental

2.1. Materials and measurements

All chemicals (including deuterated solvents) were purchased from Sigma–Aldrich, Fisher Scientific, Strem Chemicals, VWR or Acros Chemicals and used without further purification. ^1H, ^{13}C

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and ^{31}P NMR spectral data were recorded on a Varian Inova 400 FTNMR spectrophotometer. For ^{1}H and ^{13}C NMR, chemical shifts are expressed as parts per million (δ) relative to $SiMe_4$ (TMS, $\delta = 0$), and referenced internally with respect to the protio solvent impurity. For ^{31}P NMR, chemical shifts are expressed as parts per million (δ) relative to H_3PO_4 ($\delta = 0$). IR spectra were acquired neat on a Jasco 4100 FT-IR. Elemental (CHN) analysis of ligand **1** was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Elemental (CHN) analysis of the Th(IV) complex was performed by Atlantic Microlab Inc., Norcross, GA.

CAUTION!!! Natural thorium (primary isotope ^{232}Th) is a weak α-emitter (4.012 MeV) with a half-life of 1.41×10^{10} years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

2.2. Synthesis of ligand **1**

For the preparation of ligand **1**, a slightly modified procedure of that described by Daigle and co-workers [14] was followed, and the ^{31}P NMR data from Gallagher et al. was used to confirm the stereochemistry of the alkene in the final product [15]. *cis*-ethylenebis(diphenylphosphine) (0.250 g, 0.631 mmol) was dissolved in tetrahydrofuran (2.50 mL) at 290 K. To this solution, 30% H_2O_2 (0.25 mL) was added drop wise with stirring over 5 min while keeping the solution chilled in an ice bath under an inert atmosphere of nitrogen gas. The ice bath was removed 20 min after completion of the addition, and the reaction was allowed to stir for an additional 2 h. The resultant white slurry was placed in a crystallization dish for 24 h to facilitate solvent evaporation. The crude product was recrystallized from boiling benzene (125 mL) and dried under reduced pressure for 24 h to yield *cis*-ethylenebis(diphenylphosphine oxide) (*cis*-dppeO_2) **1** as a white solid (0.178 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.64 (m, 8H), 7.49–7.42 (m, 4H), 7.40–7.18 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3 (dd, $J_{CP} = 3.0$, 95 Hz, C_{ipso}), 132.7 (dd, $J_{CP} = 4.0$, 110 Hz, C=C *alkene*), 132.0 (s, C_{para}), 131.6 (dd, $J_{CP} = 5.0$, 6.0 Hz, C_{meta}); ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.6 (s); ^{1}H NMR (400 MHz, CD_3OD): δ 7.71–7.63 (m, 8H), 7.62–7.49 (m, 5H), 7.52–7.32 (m, 9H); ^{31}P NMR (162 MHz, CD_3OD): δ 23.2 (s); mp = 228–230 °C, IR (neat) $\nu = 1490$, 1434 (C=C), 1173 (P=O) cm^{-1}; *Anal.* Calc. for $C_{26}H_{22}O_2P_2$ (found): C, 72.89 (72.58); H, 5.18 (4.89); N, 0.00 (0.03).

2.3. Synthesis of 1:3 Th–ligand **1** complex

cis-dppeO_2 **1** (0.100 g, 0.252 mmol) was dissolved in MeOH (15.0 mL) at 290 K. To this solution, thorium(IV) nitrate hydrate (0.037 g, 0.078 mmol) was added. The mixture was stirred for 24 h until it became a homogenous solution. The volatiles were removed via rotary evaporation and dried via Schlenk line for 24 h to yield the resultant complex, Th$(NO_3)_2$-**1**$_3$·$(NO_3)_2$, as a white solid (0.130 g, 95% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 7.92–7.72 (m, 2H), 7.71–7.35 (m, 14H), 7.27–7.15 (m, 6H); ^{31}P NMR (162 MHz, CD_3OD): δ 31.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.9 (s), 31.5 (s), 21.5 (s); IR (neat) $\nu = 1496$, 1438 (C=C), 1141 (P=O) cm^{-1}; *Anal.* Calc. for $C_{78}H_{66}N_4O_{18}P_6Th \cdot 4.5H_2O$ (found): C, 50.74 (50.63); H, 4.09 (4.09); N, 3.03 (3.21).

2.4. Crystal structure determination and refinement

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. The total number of images was based on results from the program COSMO [16] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software [17] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software [18], which corrects for Lp. Scaling and absorption corrections were applied using SADABS [19] multi-scan technique, supplied by George Sheldrick. The structures were solved either by the direct method or the Patterson Expansion method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97 [20], which are incorporated in OLEX2 [21,22]. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystals used for the diffraction study showed no decomposition during data collection. Further crystallographic data and experimental details for structural analysis of all the complexes are summarized in Tables 2, 4 and 7, and selected bond lengths and angles with their estimated standard deviations are given in Tables 3, 5, 6, 8 and 9. Complete tables for each structure reported here, along with diagrams

Table 2
Crystal and structure refinement data for **2–3**.

Data	Structure **2**	Structure **3**
Empirical formula	$C_{78}H_{66}N_3O_{15}P_6Th$	$C_{79}H_{66}Cl_4N_4O_{18}P_6Th$
Formula weight	1703.19	1919.02
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
CCDC number	1052114	1052127
a (Å)	13.0917(14)	11.956(3)
b (Å)	17.0276(18)	51.299(15)
c (Å)	19.920(2)	16.463(5)
α (°)	87.449(1)	90.00
β (°)	79.494(1)	95.647(4)
γ (°)	81.881(1)	90.00
V (Å^3)	4321.5(8)	10048(5)
Z	2	4
D_{calc} (g cm^{-3})	1.309	1.268
μ (mm^{-1})	1.895	1.743
Crystal size (mm)	0.31 × 0.262 × 0.141	0.306 × 0.169 × 0.122
Minimum/maximum transmission	0.8757	0.7878
hkl ranges	$-15 \leqslant h \leqslant 15$, $-20 \leqslant k \leqslant 20$, $-23 \leqslant l \leqslant 24$	$-14 \leqslant h \leqslant 14$, $-61 \leqslant k \leqslant 58$, $-19 \leqslant l \leqslant 19$
Total reflections	15815	78368
Unique reflections	13184	18058
R_{int}	0.0789	0.0793
Parameters	910	770
R_1[a] (all data)	0.0505	0.1158
R_1[a] ($I > 2\sigma(I)$)	0.0393	0.0890
wR_2[b] (all data)	0.1034	0.2025
wR_2[b] ($I > 2\sigma(I)$)	0.0981	0.1937
Max/min residual (e Å^{-3})	1.335/−0.759	2.63/−2.01
Goodness-of-fit (GOF) on F^2	1.044	1.093

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2]^2]^{1/2}$.

Table 1
Infrared absorption bands (cm^{-1}) of *cis*-dppEO (**1**) and the Th$(NO_3)_2$-**1**$_3$·$(NO_3)_2$ complex.

Compound	ν(P=O)	ν(C=C)	ν(C=C)	ν(N=O)	$\nu_a(NO_2)$	$\nu_s(NO_2)$	ν(NO)	Ionic nitrate
1	1173	1490	1434	–	–	–	–	-
Th$(NO_3)_2$-**1**$_3$·$(NO_3)_2$	1141	1496	1438	1437	1296	1027	809	1396