Syntheses and Structures of Thorium(IV) Complexes with Bis(diphenylphosphino)ethane Dioxide, $\text{Ph}_2\text{P(O)}\text{CH}_2\text{CH}_2\text{P(O)Ph}_2$, and Bis(diphenylphosphoryl)amide, $[\text{Ph}_2\text{P(O)NP(O)Ph}_2]^{-}$

Élida Bonfada$^a$, Ernesto Schulz-Lang$^a$, Renato André Zan$^a$, and Ulrich Abram$^b$

$^a$ Universidade Federal de Santa Maria, Departamento de Quimica, 97.111 Santa Maria-RS, Brazil
$^b$ Freie Universität Berlin, Institut für Chemie / Radiochemie, Fabeckstr. 34-36, D-14195 Berlin

Reprint requests to Prof. E. Schulz-Lang. Fax: (#55) 55 220 8031.
E-mail: eslang@quimica.ufsm.br

Dedicated to Prof. Hans Hartl on the occasion of his 60th birthday


Thorium Complexes, Phosphine Oxides, Bis(diphenylphosphoryl)amide

The cationic thorium(IV) complexes $[\text{Th}\{\text{Ph}_2\text{P(O)}\text{CH}_2\text{CH}_2\text{P(O)Ph}_2\}_2(\text{NO}_3)_3]\text{NO}_3$ and $[\text{Th}\{\text{Ph}_2\text{P(O)NP(O)Ph}_2\}_3(\text{dmsO})_2]\text{NO}_3$ have been synthesized by reactions of $\text{Th(NO}_3)_4\cdot 5\text{H}_2\text{O}$ with bis(diphenylphosphino)ethane dioxide, $\text{Ph}_2\text{P(O)}\text{CH}_2\text{CH}_2\text{P(O)Ph}_2$ ($L^1$), or ammonium bis(diphenylphosphoryl)amide, $(\text{NH}_4)[\text{Ph}_2\text{P(O)NP(O)Ph}_2]$ ($\text{NH}_4L^2$), and subsequent re-crystallization from dimethyl sulfoxide. The products have been studied spectroscopically and by X-ray crystallography.

The thorium atom is ten-co-ordinate in the $[\text{Th}(L^1)_2(\text{NO}_3)_3]^+$ cation with a coordination sphere which does not match one of the idealized polyhedra for ten-coordination. Th-O bonds have been found in the range between 2.342(3) (phosphine oxide) and 2.599(4) Å (nitrate).

An eight-coordinate thorium atom is found in the $[\text{Th}(L^2)_3(\text{dmsO})_2]^+$ cation. The almost ideal square-antiprismatic environment of the metal is occupied by oxygen atoms with Th-O bond lengths between 2.363(6) and 2.392(11) Å.

Introduction

Monofunctional organic ligands containing a phosphoryl group have not only been used to study the fundamental co-ordination chemistry of thorium but also to accomplish practical liquid-liquid extractions [1]. Structural studies, however, which report details of the coordination environment of the actinide element are rare [2 - 10]. The same holds true for thorium compounds with di- and tridentate ligands containing at least one phosphoryl group. Complexes containing thorium with the coordination numbers 10 and 12 have been described with diethyl(N,N’-diethylcarbamyl)-methylene phosphonate [11], 2,6-bis(diphenylphosphinomethyl)pyridine N,P,P’-trioxide [12] and N-isopropyl-bis(diphenylphosphinoyl)amine [13]. For the sterically more demanding ligand octamethylpyrophosphoramide-O,O’, however, a thorium complex of the composition $[\text{ThCl}_3L_2]$ has been described which contains an eight-coordinate actinide atom [14].

Here we present syntheses and structural characterizations of thorium(IV) complexes containing the potentially chelating neutral ligand bis(diphenylphosphino)ethane dioxide ($L^1$) and the anionic bis(diphenylphosphoryl)amide ($L^2$).^-`

Results and Discussion

The chelating phosphine oxide or phosphinoyl-amide ligands can easily be prepared by oxidation of bis(diphenylphosphino)ethane with $\text{H}_2\text{O}_2$ ($L^1$) and by oxidation of bis(diphenylphosphino)amine [15] in air ($L^2$). $L^2$ is readily deprotonated during
the reaction with liquid ammonia and yields the ammonium salt (NH₄)L².

Treatment of Th(NO₃)₄·5H₂O with L¹ gives an almost colourless solid which can be recrystallized from CH₃CN/MeOH to yield yellow needles of [Th(L¹)₂(NO₃)₃](NO₃). The formation of the bischelate is irrespective of the metal-to-ligand ratio. The infrared spectrum of the complex shows an intense ν(PO) band at 1123 cm⁻¹ which is shifted to lower wave numbers by 37 cm⁻¹ from its value in L¹. This is indicative of coordination of the phosphoryl group to the metal. The proton NMR spectrum exhibits the expected signals for the methylene and phenyl protons of the ligand. The ³¹P resonance is observed at 34 ppm. Mass spectrometry gives evidence for the composition of the complex cation. The positive ion FAB spectrum shows the molecular ion [Th(L¹)₂(NO₃)₃]⁺ at m/z = 1278 with an intensity of 80% B. Only a few fragments are observed which can be assigned to loss of L¹ or two NO₃⁻ ligands.

Crystals of [Th(L¹)₂(NO₃)₃](NO₃)·H₂O suitable for an X-ray structure determination were obtained by slow evaporation of a saturated CH₃CN/MeOH solution. A representation [16] of the structure of the complex cation is given in Fig. 1. Selected bond lengths and angles are summarized in Table 1. The thorium atom is coordinated by two chelating phosphine oxide and three bidentate nitrato ligands giving a coordination number of ten. The coordination polyhedron of the metal cannot be fitted into any regular geometry of this coordination number and may best be described as a strongly distorted bicapped square antiprism with two nitrate oxygen atoms forming the caps (Fig. 2a). Main distortions are due to the distinct coordination abilities of nitrate and L¹ which result in O(nitrate)-Th-O(nitrate) angles between 49.1(1) and 49.9(1)° and O(L¹)-Th-O(L¹) angles of 72.5(1) and 74.4(1)°. The Th-O(L¹) bond lengths are found in the range between 2.342(3) and 2.417(3) Å. These values are significantly shorter than the Th-O(nitrate) bond.
A thorium complex with coordination number eight, \([\text{Th}(L^2)\text{dmso}_2](\text{NO}_3)\), is formed in the reaction of \(\text{Th(NO}_3)_4 \cdot 5\text{H}_2\text{O}\) with \((\text{NH}_4)L^2\) in methanol and subsequent recrystallization from dimethyl sulfoxide:

\[
\text{Th(NO}_3)_4 \cdot 5\text{H}_2\text{O} + 3 (\text{NH}_4)L^2 \rightarrow [\text{Th}(L^2)_3(\text{MeOH})_2](\text{NO}_3) + [\text{Th}(L^2)_3(\text{dmso})_2](\text{NO}_3)
\]  

The colourless solid which initially precipitated from the reaction mixture has been identified as \([\text{Th}(L^2)_3(\text{MeOH})_2](\text{NO}_3)\) by elemental analysis and its IR spectrum which gives no evidence for coordinated \(\text{NO}_3^-\) ligands. The solid is insoluble in most common solvents and can only be recrystallized from hot dmso which results in a secondary ligand exchange \(\text{MeOH} \leftrightarrow \text{dmso}\).

Owing to the low solubility of \([\text{Th}(L^2)_3(\text{dmso})_2](\text{NO}_3)\) no NMR and FAB mass spectra of sufficient quality could be obtained. A band at 1079 cm\(^{-1}\) in the infrared spectrum of the complex can be assigned to the \(\nu(\text{PO})\) vibration which is shifted to lower frequencies by 32 cm\(^{-1}\) with respect to the value for \((\text{NH}_4)L^2\). A band at 1384 cm\(^{-1}\) can be attributed to ionic nitrate.

\([\text{Th}(L^2)_3(\text{dmso})_2](\text{NO}_3)\) crystallizes in the monoclinic space group C2/c with the thorium atom and N(2) situated on a two-fold axis. The resulting coordination environment of thorium is a square antiprism (Fig. 2b). A representation of the molecular structure [16] is given in Fig. 3. Table 2 contains selected bond lengths and angles. The chelate rings only slightly deviate from planarity with maximum deviations of 0.45 Å (O1, P1, N1, P2, O2, Th) and 0.01 Å (O3, P3, N2, P3', O3', Th) from a mean least-squares plane. This reflects extended delocaliz-
Table 2. Selected bond lengths [Å] and angles [°] in the complex cation of [Th(L²)₃(dmso)₂](NO₃).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th-O(1)</td>
<td>2.363(6)</td>
<td>1.519(6)</td>
</tr>
<tr>
<td>Th-O(2)</td>
<td>2.376(8)</td>
<td>1.515(7)</td>
</tr>
<tr>
<td>Th-O(3)</td>
<td>2.379(8)</td>
<td>1.509(8)</td>
</tr>
<tr>
<td>Th-O(61)</td>
<td>2.392(11)</td>
<td></td>
</tr>
<tr>
<td>O(1)-Th-O(2)</td>
<td>0.79(2)</td>
<td>0.78(3)</td>
</tr>
<tr>
<td>O(1)-Th-O(3)</td>
<td>1.14(1)(4)</td>
<td>1.45(5)(3)</td>
</tr>
<tr>
<td>O(1)-Th-O(61)</td>
<td>0.72(4)</td>
<td>1.40(5)(3)</td>
</tr>
<tr>
<td>O(1)-Th-O(1)'</td>
<td>0.81(3)</td>
<td>1.14(1)(3)</td>
</tr>
<tr>
<td>O(1)-Th-O(2)'</td>
<td>0.74(2)</td>
<td>0.75(3)(4)</td>
</tr>
<tr>
<td>O(1)-Th-O(3)'</td>
<td>1.15(1)(3)</td>
<td>0.72(7)(6)</td>
</tr>
<tr>
<td>O(1)-Th-O(61)'</td>
<td>0.14(5)(2)</td>
<td>0.72(5)(3)</td>
</tr>
</tbody>
</table>

Symmetry operator: (') 1 - x, y, 0.5 - z

The Th-O(L²) bonds are in the range between 2.363(6) and 2.379(8) Å which is shorter than in a thorium(IV) complex with the comparable ligand N-isopropyl-bis(diphenylphosphinoylammine (L³), [Th(L³)₃(NO₃)₂]²⁺ [13]. This may be attributed to the higher coordination number in the latter compound which results in unfavourably small bite angles for L³ (mean value: 65.5°, non-bonding O-O 'bite distance': mean value: 2.631 Å). The corresponding mean values for L² in [Th(L²)₃(dmso)₂]⁺ are 78.1° and 2.866 Å. Similar values have been found for [Th(NO₃)₄{(EtO)₂P(O)CH₂C(O)NEt₂}] [11] and [ThCl₄{(Me₂N)₂P(O)OP(O)(NMMe₂)₂}] [14].

It should be noted that the reactions of thorium nitrate with L² and L³ under comparable conditions yield different products, the mono-cationic...
[Th(L\(^2\))(dms)\(_2\)]\(^{2+}\) (coordination number 8) and the di-cationic [Th(L\(^3\))(dms)\(_2\)]\(^{2+}\) (coordination number 10) [13]. This may be explained by the ability of the deprotonated ligand L\(^2\) to compensate partially the high charge of the metal centre and, thus, to avoid high coordination numbers which cause considerable repulsion between the sterically demanding ligands.

Further studies on the coordination chemistry of actinides with chelating ligands containing phosphoryl and thiophosphoryl donor sites are in progress in our laboratories.

**Experimental**

Th(NO\(_3\))\(_4\) · 5H\(_2\)O was prepared by dissolving ThO\(_2\) in HNO\(_3\) and concentrating the resulting solution. L\(^1\) was prepared by the oxidation of bis(diphenylphosphino)ethane with H\(_2\)O\(_2\) in ethanol. (NH\(_4\))L\(^2\) was obtained by treating HL\(^2\) [17] with liquid ammonia and subsequent recrystallization from methanol.

IR spectra were recorded on a Bruker IFS28 instrument in KBr. NMR spectra were measured in CDCl\(_3\) on DPX-200 and DPX-400 (BRUKER) spectrometers with TMS and H\(_2\)PO\(_4\) as internal standards. FAB\(^+\) mass spectra were obtained using a TSQ 70 (Finnigan MAT) instrument with nitrobenzyl alcohol as matrix.

**Syntheses**

[Th(L\(^1\))(dms)\(_2\)]\(^{2+}\) (coordination number 8): Th(NO\(_3\))\(_4\) · 5H\(_2\)O (57 mg, 0.1 mmol) was dissolved in 1 ml of MeOH and L\(^1\) (164 mg, 0.4 mmol) dissolved in about 30 ml of CH\(_3\)CN was added. The mixture was heated to reflux for 3 h to give a clear yellow solution. An almost colourless solid precipitated upon cooling and evaporation of the solvent. Recrystallization from CH\(_3\)CN/MeOH gave yellow needles. Yield: 103 mg (76%). C\(_{52}\)H\(_{60}\)N\(_4\)O\(_7\)P\(_4\)Th: Calcd C 45.9, H 3.7, N 4.1. Found: C 43.9, H 3.5, N 4.3%.

IR (cm\(^{-1}\)): 1123s (PO), 1520m, 1289m, 1026m (NO\(_3\)\(^-\)). FAB\(^+\) MS: m/z = 1278 (80% B) M\(^+\), 1155 (5% B) [Th(L\(^1\))(dms)\(_2\)]\(^{2+}\)\(^{+}\), 848 (55% B) [Th(L\(^1\))(dms)\(_2\)]\(^{2+}\)\(^{+}\). \(^1\)H NMR (CDCl\(_3\)): 2.52 ppm m 4H (CH\(_2\)) 7.45 - 7.72 ppm m 20H (phenyl). \(^{31}\)P (CDCl\(_3\)): 34.06 ppm.

[Th(L\(^2\))(dms)\(_2\)]\(^{4+}\) (coordination number 8): Th(NO\(_3\))\(_4\) · 5H\(_2\)O (57 mg, 0.1 mmol) was dissolved in 1 ml of MeOH and (NH\(_4\))L\(^2\) (173 mg, 0.4 mmol) dissolved in about 10 ml of MeOH was added. The mixture was heated to reflux for 3 h to give a clear colourless solution. After reducing its volume to about 5 ml it was kept in a refrigerator. Tiny colourless needles, which have been analyzed as [Th(L\(^2\))(MeOH)\(_2\)\(_2\)]\(^{4+}\) (NO\(_3\))\(_2\), deposited over a period of one week. Recrystallization from hot dms gave colourless needles of [Th(L\(^2\))(dms)\(_2\)]\(^{4+}\) (NO\(_3\))\(_2\). Yield: 135 mg (80%). C\(_{76}\)H\(_{72}\)N\(_4\)O\(_{17}\)P\(_6\)S\(_2\)Th: C 53.7, H 4.2, N 3.3. Found: C 52.9, H 4.0, N 3.5%. IR (cm\(^{-1}\)): 1079s (PO), 1384s (NO\(_3\)\(^-\)).
X-ray crystal structure determination

The X-ray intensities were collected on an automated single crystal diffractometer CAD4 (Enraf-Nonius, Delft). HELENA [18] was used for data reduction. The structures were solved by direct methods using SHELXS97 [19]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL97 [20]. An empirical absorption correction (Psi scans) [18] was applied. Hydrogen atoms were included in calculated positions. The SMe\textsubscript{2} part of the dmso ligands and the phenyl ring C(21)-C(26) in [Th(L\textsuperscript{3})\textsubscript{3}(dmso)\textsubscript{2}]\textsuperscript{+} are disordered and have been refined with 50 per cent occupancy for two distinct positions.

Crystal data and more details of the data collections and refinements are contained in Table 3. Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre ([Th(L\textsuperscript{1})\textsubscript{2}(NO\textsubscript{3})\textsubscript{3}(NO\textsubscript{3}) \cdot H\textsubscript{2}O: CCDC 137756 and [Th(L\textsuperscript{3})(dmso)\textsubscript{2}(NO\textsubscript{3})]: CCDC 137757

Acknowledgement

We gratefully acknowledge financial support from CNPq, FAPERGS and the DAAD and thank Prof. Dr. Joachim Strähle, Tübingen, for the opportunity to collect the X-ray data sets.

[16] E. Keller, SCHAKAL, a program for the presentation of crystal structures, University of Freiburg (1997).
[18] A. Spek, HELENA, PLATON, programs for data reduction and handling of crystal structure data, University of Utrecht (1997).