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

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Dedicated to Prof. Hans Hartl on the occasion of his 60$^{th}$ birthday


Thorium Complexes, Phosphine Oxides, Bis(diphenylphosphoryl)amide

The cationic thorium(IV) complexes [Th{Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$}$^2$(NO$_3$)$_3$]NO$_3$ and [Th{Ph$_2$P(O)NP(O)Ph$_2$}$^3$(dmso)$_2$]NO$_3$ have been synthesized by reactions of Th(NO$_3$)$_4$ · 5H$_2$O with bis(diphenylphosphino)ethane dioxide, Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$ (L$^1$), or ammonium bis(diphenylphosphoryl)amide, (NH$_4$)[Ph$_2$P(O)NP(O)Ph$_2$] (NH$_4$L$^2$), and subsequent recrystallization from dimethyl sulfoxide. The products have been studied spectroscopically and by X-ray crystallography.

The thorium atom is ten-co-ordinate in the [Th(L$^1$)$_2$(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 [Th(L$^2$)$_3$(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.