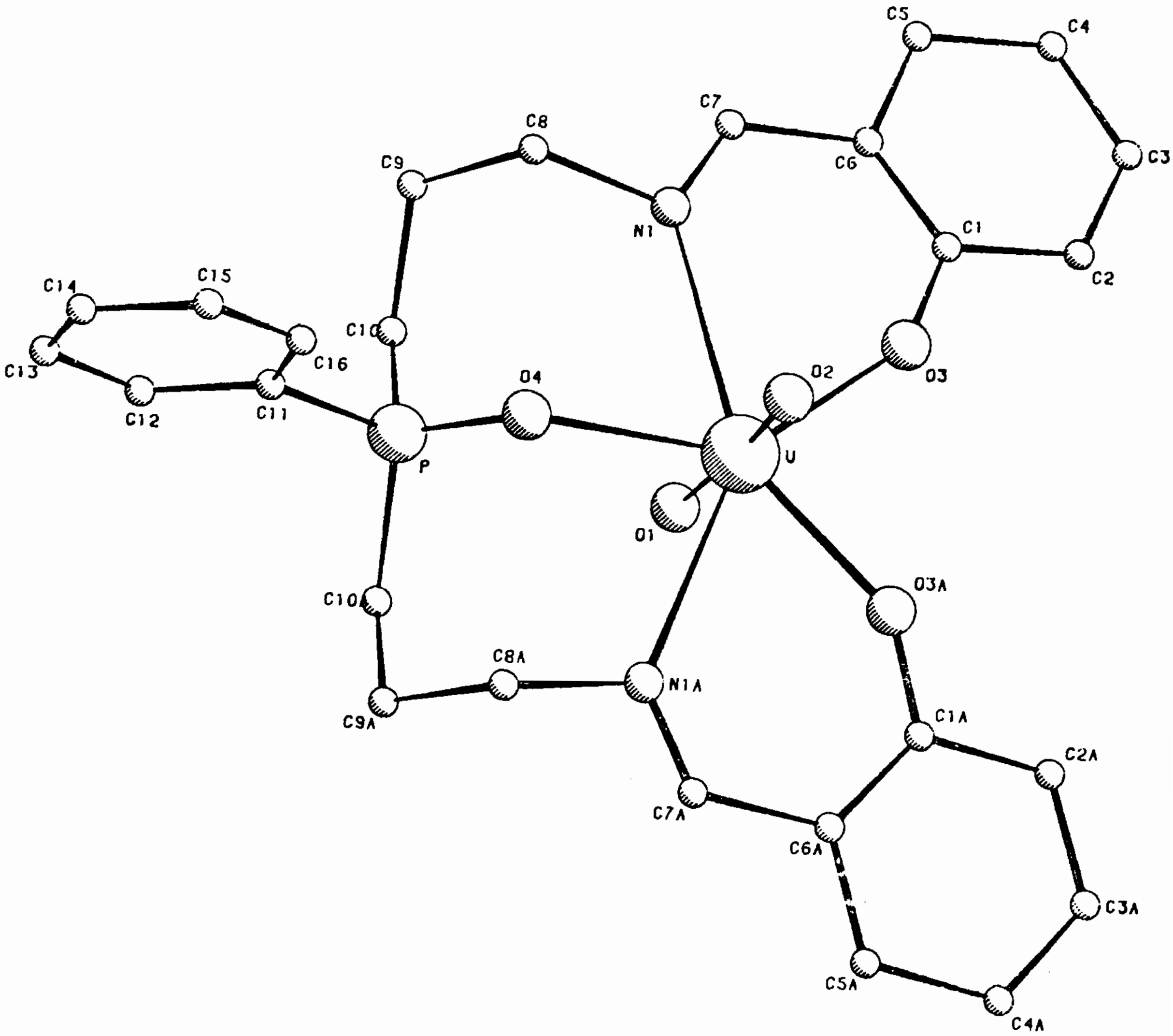

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Lanthanide and Actinide Complexes with Bidentate Ligands. Crystal Structure of Dimethylformamide-tetrakis(1-oxo-2-thiopyridinato)thorium(IV)

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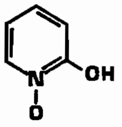
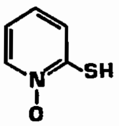
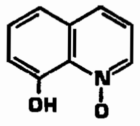
Actinide ions, owing to their large ionic radius, generally present high coordination numbers and thorium(IV), which has the maximum ionic radius among the tetravalent actinides, can easily reach a coordination number nine or ten with chelating ligands.



HpyOO



HpyOS



HQuin

For the uranyl(VI) complexes prepared, the general formulation of the type $[UO_2L_2S]S$, where the coordinate solvent molecule (S) can be replaced by more basic monodentate ligands as Ph_3PO, dmso, dma or dmf, is supported by the elemental analysis as well as by the lowering of the νN–O stretching frequency and by the corresponding lowering of the P–O, S–O and C–O stretching frequencies upon coordination. For these complexes a coordination number seven, in an approximately pentagonal bipyramidal coordination geometry, can be reasonably attributed to the uranium atom.

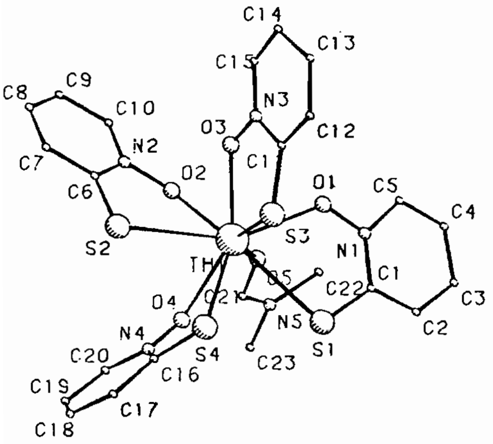
Thorium(IV) complexes of the type $[ThL_4S] \cdot xS$ were obtained with the potentially five-membered chelate ligands HpyOO and HpyOS, whereas complexes of the type $[Th(Quin)_4] \cdot xS$ were obtained with the six-membered chelate ligand HQuin. The coordinated solvent molecule in the first two complexes can be replaced by Ph_3PO, dmso, dma, dmf, as supported by the elemental analysis and by the i.r. spectra.

It must be noted that $[Th(Quin)_4] \cdot xS$ is, for instance, insoluble in dmso and remains uncharged. This behaviour seems to be ascribed to the observed tendency of thorium(IV) towards higher coordination number in complexes with five-membered chelate ligands, while it preferably maintains a coordination number eight, when forming complexes with six-membered chelate ligands.

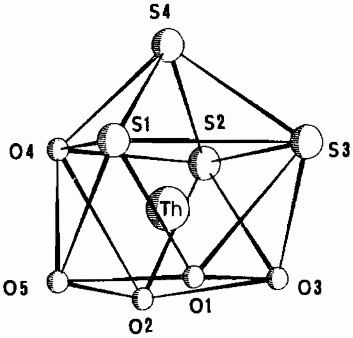
On the contrary $Th(pyOO)_4 \cdot 2H_2O$ or $Th(PhOO)_2 \cdot MeOH$, well as $Th(pyOS)_4 \cdot H_2O$ rapidly dissolve in dmso, giving rise to complexes formulable as $ThL_4 \cdot 2dmso$. These complexes can be formulated, from infrared evidences, as $[ThL_4(dmso)]$ dmso with the central metal ion nine-coordinated: a band at about 1000 cm^{-1} was assigned to the νS–O stretching frequency of the coordinated molecule, whereas a second band at about 1025 cm^{-1} can be probably ascribed to the uncoordinated dmso.

For a correct knowledge of the coordination geometry of the prepared complexes, crystals of $Th(pyOS)_4(dmf)$, suitable for an X-ray structural analysis, were grown from a dimethylformamide/diethylether solution.

$Th(pyOS)_4dmf$ is a nine-coordinate chelate with eight donor atoms contributed by the four monoanionic bidentate ligands and the ninth by the solvent molecule.



The coordination polyhedron is a distorted monocapped square antiprism with S(4) as cap. The thorium atom lies 1.38 Å above the base of the polyhedron O(1), O(2), O(3), O(5) and 1.08 Å below the base of the pyramidal cap S(1), S(2), S(3), O(4). The mean planes for the atoms comprising the two 'square' bases are approximately parallel with 2.4° between their normals.



The lanthanum(III) complexes are of the type LnL_3xH_2O or $Li[LnL_4]xH_2O$, the coordination number seems to be most likely eight, even if the stoicheiometry of $Ln(pyOO)_3H_2O$ and $Ln(Quin)_3$ supports coordination number seven and six respectively.

In these complexes however a partial oligomerization cannot be ruled out.

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The Electrochemistry of Mononuclear and Dinuclear Complexes of Transition and Inner Transition Metal Ions with Compartmental Ligands

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Electrochemical studies on binuclear complexes can serve to get light on the function of metalloenzymes incorporating two metal ions in close proximity at the active site. In this connection, compart-