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Actinide Complexes with Schiff Bases: the First Crystal Structure of a Binuclear Thorium(IV) Complex with a Pentadentate Compartmental Ligand*

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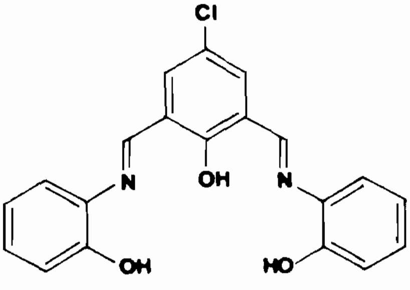
Binucleating Schiff bases have been extensively used for the preparation of homo- and hetero-dinuclear complexes [1]. These ligands are generally planar and especially designed to incorporate, in a planar fashion, two identical or different metal ions. The compartmental ligands represent a particular case of the above compounds and give rise to complexes with metal ions sharing at least one donor atom of the ligand. The 'end-off' ligands H_3L seem to be not suitable, in principle, for coordination of actinides owing to their coordination geometry and ionic radii [2], which are considerably different from those of the d-metal ions used for the synthesis of binuclear complexes.

Reaction of thorium(IV) salts with the potentially pentadentate compartmental Schiff base H_3L yields the complex $Mg[Th_2L_3]_2 \cdot 6H_2O$, the crystal structure of which, reported here, shows the compartmental behaviour of this ligand also with f-metal ions.



H_3L

Results and Discussion

Spectroscopic and mass spectrometry data reveal that for the ligand H_3L, obtained by condensation of 2,6-diformyl-4-chlorophenol and *o*-aminophenol in alcoholic solution, the equilibrium of Scheme 1 occurs [3].

By reaction of the preformed ligand H_3L, or of the precursors, with $Th(NO_3)_4 \cdot 4H_2O$ in the presence of the stoichiometric quantity of LiOH and $Mg(CH_3COO)_2 \cdot 4H_2O$, the orange complex $Mg[Th_2L_3]_2 \cdot 6H_2O$ was obtained. Infrared spectra of the powder and of the crystals (obtained by slow evaporation of the mother liquor or by recrystallization from dimethylformamide/diethyl ether of the crude product) show an identical shape along the whole range investigated, apart from the additional bands associated with dimethylformamide (dmf) for the crystals grown from such a solvent. In particular, for this compound there is an intense IR band at 1680 cm^{-1} due to $\nu(C=O)$. In both complexes the $\nu(C=N)$ of the coordinated Schiff bases lies at 1618 cm^{-1}. An exact comparison with the free ligand is difficult, since the ligand is predominantly in the oxazoline form. It should be noted, however, that the band at 3403 cm^{-1} due to $\nu(NH)$ disappears and the bands at 1642 and 1634 cm^{-1}, associable also with C=N, occur at a lower field on coordination.

Crystals of $Mg[Th_2L_3]_2 \cdot 6H_2O \cdot dmf$ are not stable in air; when dissolved in dimethylformamide and maintained in an atmosphere of aqueous vapour, they transform into $Mg[Th_2L_3]_2 \cdot 6H_2O$, which is identical (from a crystallographic point of view) to the complex obtained from the mother liquor.

Crystal Structure of $Mg[Th_2L_3]_2 \cdot 6H_2O$

Two formula units of the ionic complex $Mg[Th_2L_3]_2 \cdot 6H_2O$ are comprised in the monoclinic unit cell of the crystal; the complex anions $[Th_2L_3]^-$ and the H_2O molecules are in general positions, whereas the Mg^{2+} cations are in special positions on inversion centres at 0,0,0; 0,1/2,1/2. As shown in Fig. 1 each anion is a dinuclear unit, in which two Th atoms are bridged by three oxygen atoms from three different ligands. Each ligand, which is trianionic pentadentate, is coordinated with two atoms to the first Th atom, with two atoms to the second Th atom, and with the central oxygen atom to both Th atoms. Thus ligand 1, which comprises the five donor atoms O(1), N(1), O(2), N(2) and O(3), is coordinated to Th(1) through O(1) and N(2), to Th(2) through N(2) and O(3), and bridges both Th atoms through O(2). The two independent Th atoms are nona-coordinate in slightly distorted tricapped-trigonal prisms, the structural details of which are shown in Fig. 2.

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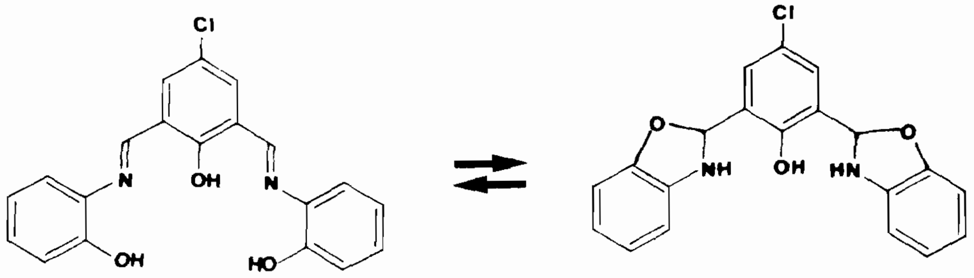


Scheme 1.

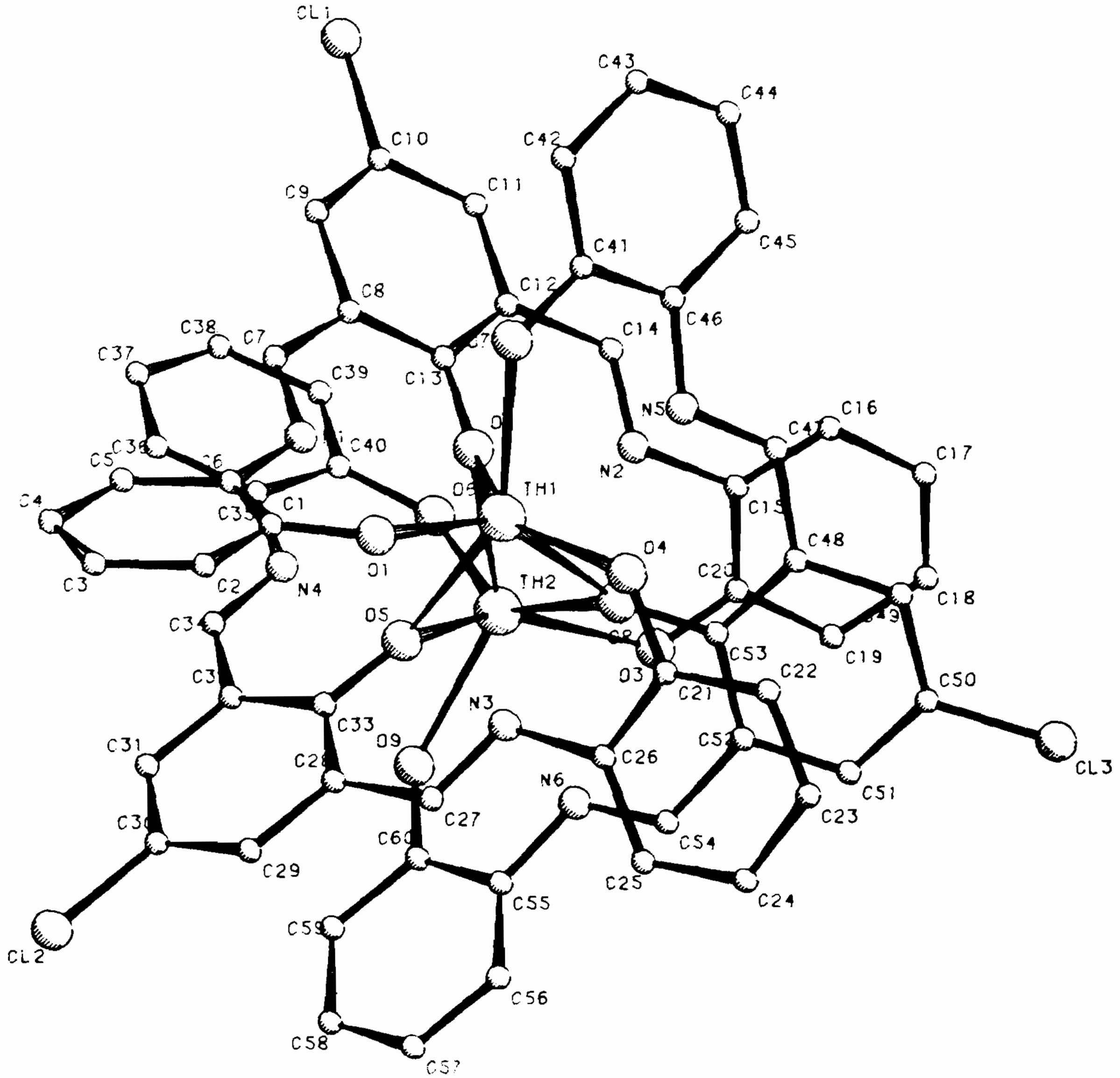
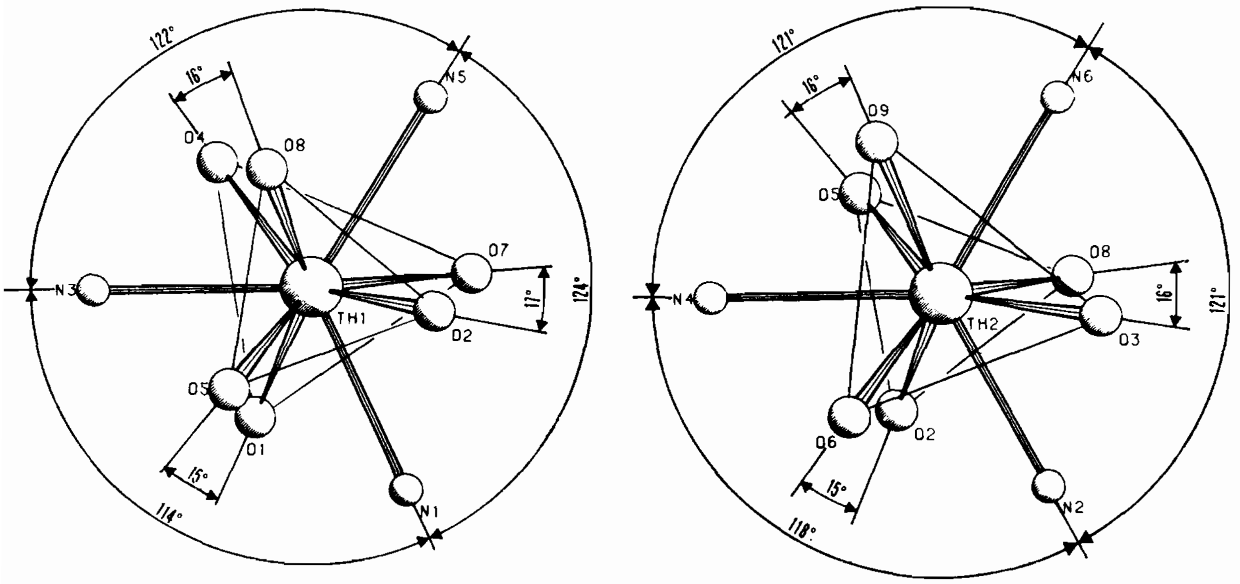


Fig. 1. The structure of the $[Th_2L_3]^-$ anion.

Th–O bonds are of two types: bonds with non-bridging oxygen atoms are in the range 2.25–2.36 Å, with a mean of 2.32 Å for Th(1)–O and 2.31 Å for Th(2)–O; bonds with bridging oxygen atoms are, as expected, significantly longer, in the range 2.41–2.50 Å, with a mean of 2.45 Å for Th(1)–O and 2.49 Å



(A) (B)

Fig. 2. Coordination polyhedron (A) around Th(1), and (B) around Th(2).

for Th(2)–O. Th–N bonds are mostly longer than the corresponding Th–O bonds, being between 2.69 and 2.78 Å, with a mean of 2.73 Å for Th(1)–N and 2.75 Å for Th(2)–N. Structural details in the ligand are normal. C=N double bonds are localized at N(1)=C(7) and N(2)=C(14) for ligand 1, at N(3)=C(27) and N(4)=C(34) for ligand 2 and at N(5)=C(47) and N(6)=C(54) for ligand 3, as expected. The Mg^{2+} cations are octahedrally surrounded by six water molecules. The distances of the O(4) and O(7) ligand oxygens from the two water molecules are compatible with $O\cdots H_2O$ hydrogen bonding.

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