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Oxydiacetato Complexes of Thorium(IV), the Crystal Structures of Tetraaquo Bis(oxydiacetato)thorium(IV) Hexahydrate and Di(sodium nitrate) Disodium Tris(oxydiacetato)thorium(IV)

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The crystal and molecular structures of $Th(oda)_2(H_2O)_4 \cdot 6H_2O$ *(1) and* $Na_2[Th(oda)_3] \cdot 2NaNO_3$ *(2) (oda = oxydiacetate) have been determined from three-dimensional X-ray diffraction data and refined by least squares to* $R = 0.049$ *and* $Rw = 0.049$ *for 2265 independent reflections for (1) and to* $R = 0.024$ *and* $Rw = 0.023$ *for 2196 independent reflections for (2).*

Crystal parameters are as follows: (1), tetragonal, space group $P4_12_12$, $a = 10.335(2)$, $c = 20.709(5)$ *Å and* $Z = 4$; *(2), monoclinic, space group* $C2/c$, $a = 17.096(5)$, $b = 9.451(2)$, $c = 16.245(4)$ *Å,* $\beta = 107.8(1)$ *and* $Z = 4$.

In both compounds the thorium atom lies on a crystallographic two-fold axis. The co-ordination number for thorium in (1) is 10 (bicapped square antiprism geometry), the compound is monomeric, the two oda ligands are tridentate to the metal, and four water molecules complete the coordination sphere; in thorium (2) the coordination number is 9 (tricapped trigonal prism geometry) with three oda ligands tridentate to the metal, the $[Th(oda)_3]^{2-}$ *and* NO_3^- *anions are held together through the sodium ions which are coordinated both to the oda carboxylic oxygens and to the nitrate oxygens.*

The Th–O coordination distances are: in (1) 2.411(8), 2.414(9) for the carboxylic oxygens, 2.479(10) and 2.486(8) for water molecules and 2.697(9) for the etheric oxygen and in (2) 2.384(3), 2.402(4) and 2.402(4) for the carboxylic oxygens, 2.559(5) and 2.562(4) Å for the etheric oxygens.

Introduction

The ability of the oxydiacetate ligand (oda) to give complexes with actinide ions was established both in the solid state [1–4] and in aqueous solution [5–7].

This ligand is characterized by the presence of five possible oxygen donor atoms and it behaves either as tridentate through the etheric and two carboxylic oxygen atoms [2] or as pentadentate giving rise to polymeric structures as in $[UO_2(oda)]_n$ [1] and $\{[Th(oda)(SO_4)(H_2O)] \cdot H_2O\}_n$ [4].

A recent thermodynamic study of thorium(IV) interactions with oxydiacetate in aqueous solution shows the formation of three successive mononuclear complexes. The free energy, enthalpy and entropy changes associated with their formation indicate that they are very stable chelate complexes and in addition the coordination of the third ligand seems to involve a drastic rearrangement in the metal ion coordination sphere [7].

In order to clarify the coordination modes in the solid state of thorium(IV)–oxydiacetate complexes having 1:2 and 1:3 metal to ligand ratios, we have determined the crystal and molecular structure of $Th(oda)_2(H_2O)_4 \cdot 6H_2O$ and $Na_2[Th(oda)_3] \cdot 2NaNO_3$.

Experimental

$Th(oda)_2(H_2O)_4 \cdot 6H_2O$ (*1*) was prepared by the addition of a solution of $H_2(oda)$ to a solution of thorium(IV) nitrate (2:1). The white crystals formed after several days were filtered and washed with

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TABLE I. Crystal Data.

Compound	(*1*)	(*2*)
Formula	$C_8H_{28}O_{20}Th$	$C_{12}H_{12}O_{21}Na_4N_2Th$
M	676.3	844.2
Space group	$P4_12_12$	$C2/c$
Crystal system	tetragonal	monoclinic
a/Å	10.335(2)	17.096(5)
b/Å	10.335(2)	9.451(2)
c/Å	20.709(5)	16.245(4)
β/°		107.8(1)
U/Å^3	2212	2499
Z	4	4
Dc/M gm^{-3}	2.03	2.24
F(000)	1304	1600
Radiation (λ/Å)	(MoKα(0.7107))	(MoKα(0.7107))
Reflections measured	3063	4851
Scan method	$\theta/2\theta$	$\theta/2\theta$
Scan speed/° min^{-1}	1.8	1.8
Scan width/°	1.2	1.2
Background counts per s of counting time	20	20
$2\theta_{max}$/°	50	50
σ limit $[I > n\sigma(I)]$	n = 3	n = 3
Unique observed reflections $(I \geqslant 3\sigma(I))$	2265	2196
Weighting scheme w	$6.5406[\sigma^2(Fo) + 0.000217(Fo)^2]^{-1}$	$1.4277[\sigma^2(Fo) + 0.000165(Fo)^2]^{-1}$
$R = (\Sigma[\lvert Fo\rvert - \lvert Fc\rvert]/\Sigma\lvert Fo\rvert)$	0.049	0.024
$R' = \left[\frac{\Sigma w[\lvert Fo\rvert - \lvert Fc\rvert]^2}{\Sigma w\lvert Fo\rvert^2}\right]^{1/2}$	0.049	0.023
μ(Mo-Kα)/cm^{-1}	65.1	58.4

water and methanol and vacuum dried. They were identified by X-ray data as $Th(oda)_2(H_2O)_4 \cdot 6H_2O$. It is interesting to point out that if the crystals are not dried, they show a tendency to became opaque and deteriorate easily under X-ray but if vacuum dried they are stable. $Na_2[Th(oda)_3] \cdot 2NaNO_3$ (*2*) was prepared by published methods [3].

Single-crystal Data Collection

The crystal and refinement data are summarized in Table I. The X-ray intensity data were collected on a Philips PW 1100 four circle automated diffractometer with graphite-monochromated MoKα radiation. The unit cells were determined on the basis of 25 strong reflections found by mounting the crystals at random and varying the orientation angles ϕ and χ over a range of 120° each with the detector position varying between $\theta = 6$ and $\theta = 10°$. For the determination of precise lattice parameters 18 strong reflections with $8° \leqslant \theta \leqslant 13°$ were considered.

The intensities of the reflections 3 2 1 and 8 4 1 for (*1*) and 2 2 2 and $\bar{5}$ 1 $\bar{4}$ for (*2*) monitored at 100 reflection intervals did not show significant variations. The intensity data were corrected for Lorentz-polarization effects and for absorption following the method of North *et al.* [8]. The structures were solved by standard methods and refined by full-matrix least-squares.

The structure of complex (*1*) was refined with anisotropic thermal parameters assigned to the non hydrogen atoms. Hydrogen atom contributions (for the oda ligand only) were used as fixed atoms in calculated positions (d_{C-H} = 0.95 Å and U_{iso} = 0.07 Å^2). The refinement of the structure in the alternative space group $P4_32_12$ gave convergency to R values significantly higher with respect to the space group $P4_12_12$, confirming that the original choice was correct.

The structure of complex (*2*) was refined as for (*1*), the hydrogens were introduced as fixed atoms in calculated positions (d_{C-H} = 0.95 Å, and U_{iso} = 0.07 Å^2).

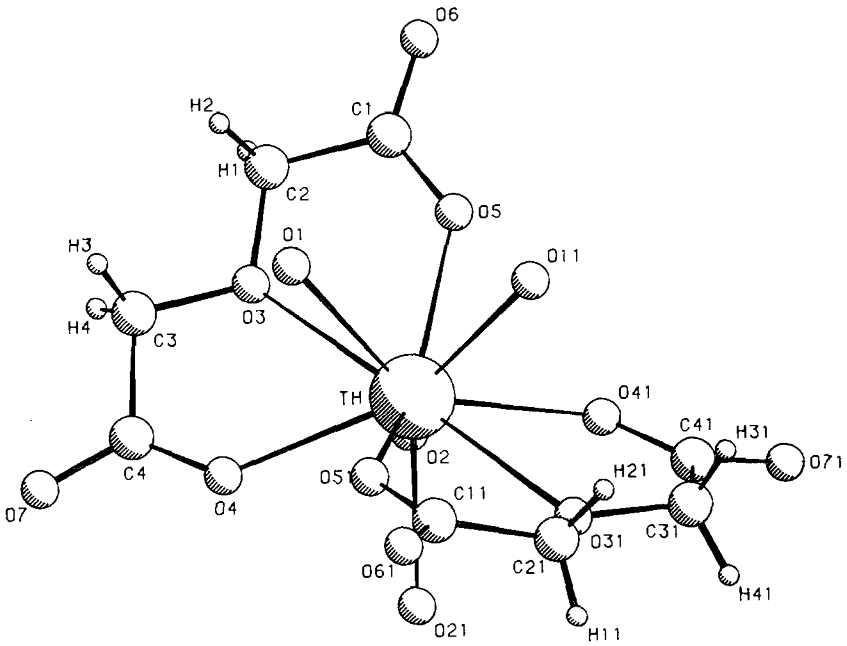


Fig. 1. View of the Th(oda)$_2$(H$_2$O)$_4$ molecule down *a*.

TABLE II. Atomic Fractional Coordinates (X10^4) with e.s.d.s in Parentheses for (*1*).

Atoms	*x*	*y*	*z*
Th	1997	1997	0
O(1)	3485(10)	3306(10)	−674(5)
O(2)	1590(9)	−374(8)	−18(6)
O(3)	3283(9)	630(10)	−905(4)
O(4)	1113(9)	1761(9)	−1071(4)
O(5)	4095(9)	1093(9)	244(4)
O(6)	6056(9)	307(11)	56(5)
O(7)	975(11)	1223(13)	−2107(4)
O(8)	8114(11)	152(10)	−778(5)
O(9)	2647(12)	3473(14)	6557(6)
O(10)	9134(17)	8234(15)	8392(7)
C(1)	4969(13)	598(13)	−120(7)
C(2)	4621(13)	375(16)	−810(6)
C(3)	2964(15)	763(15)	−1567(6)
C(4)	1552(13)	1264(15)	−1585(7)

Neutral atom scattering factors [9] were used in the structure solution as thorium anomalous dispersion terms [10] were included in the Fc calculation. All calculations were carried out using the SHELX 76 program system [11].

Fractional coordinates for non hydrogen atoms, bond lengths and angles and contact distances are shown in Tables I–VII.

TABLE III. Atomic Fractional Coordinates (X10^4) with e.s.d.s in Parentheses for (*2*).

Atoms	*x*	*y*	*z*
Th	5000(0)	5453(0)	2500(0)
Na(1)	2480(2)	3420(3)	3033(2)
Na(2)	2517(1)	505(2)	10(1)
N(1)	2139(3)	5447(6)	1598(3)
O(1)	4011(2)	4269(4)	1347(2)
O(2)	3339(2)	2452(4)	594(2)
O(3)	5000(0)	2745(5)	2500(0)
O(4)	5967(2)	4717(4)	1780(2)
O(5)	6632(2)	4770(5)	801(3)
O(6)	5022(2)	6782(4)	1133(2)
O(7)	4039(2)	7353(4)	1997(2)
O(8)	3396(2)	9071(4)	1120(3)
O(9)	2103(3)	4129(5)	1491(4)
O(10)	2175(3)	5959(5)	2311(3)
O(11)	2170(3)	6225(5)	992(3)
C(1)	4418(4)	1939(6)	1855(4)
C(2)	3875(3)	2942(6)	1215(3)
C(3)	6119(3)	5234(6)	1112(4)
C(4)	5620(3)	6514(6)	701(4)
C(5)	4466(4)	7887(6)	768(4)
C(6)	3915(3)	8134(5)	1323(4)

Results and Discussion

Th(oda)$_2$(H$_2$O)$_4$·6H$_2$O

Figure 1 represents a view down *a* of the Th(oda)$_2$(H$_2$O)$_4$ molecule with the atom numbering scheme.

TABLE IV. Distances (Å) and Principal Angles (°) with e.s.d.s in Parentheses for $[Th(ODA)_2(H_2O)_4]\cdot 6H_2O$ (*1*).

Distances

a) Thorium coordination polyhedron

$Th-O(3)_{eth.}$	2.697(9)	$Th-O(1)_{wat.}$	2.479(10)
Th–O(4)	2.411(8)	$Th-O(2)_{wat.}$·	2.486(8)
Th–O(5)	2.414(9)		

b) oda ligand

C(1)–O(5)	1.28(2)	C(4)–O(4)	1.27(2)
C(1)–O(6)	1.22(2)	C(4)–O(7)	1.24(2)
C(3)–O(3)	1.42(2)	C(1)–C(2)	1.49(2)
C(2)–O(3)	1.42(2)	C(3)–C(4)	1.55(2)

Angles

a) Thorium environment[a]

O(5)–Th–O(3)	60.0(3)	O(4)–Th–O(2)	79.8(4)
O(3)–Th–O(4)	59.6(3)	O(1)–Th–O(3)	65.7(3)
O(4)–Th–O(41)	140.3(3)	O(1)–Th–O(2)	129.4(4)
O(4)–Th–O(51)	75.6(3)	O(1)–Th–O(11)	68.9(3)
O(4)–Th–O(31)	119.4(3)	O(1)–Th–O(31)	116.6(3)
O(4)–Th–O(11)	142.0(3)	O(3)–Th–O(31)	177.5(3)
O(2)–Th–O(3)	63.7(3)		

b) oda ligand

Th–O(5)–C(1)	131.6(8)	O(4)–C(4)–C(3)	117(1)
Th–O(4)–C(4)	132.7(9)	C(1)–C(2)–O(3)	110(1)
O(5)–C(1)–O(6)	125(1)	C(4)–C(3)–O(3)	106(1)
O(4)–C(4)–O(7)	125(1)	C(3)–O(3)–Th	120.5(8)
O(6)–C(1)–C(2)	118(1)	C(2)–O(3)–Th	118.7(7)
O(7)–C(4)–C(3)	118(1)	C(2)–O(3)–C(3)	112(1)
O(5)–C(1)–C(2)	117(1)		

[a] Atoms with the second figure 1 are those of symmetry y, x, –z.

TABLE V. Distances (Å) and Principal Angles (°) with e.s.d.s in Parentheses for $Na_2[Th(oda)_3]\cdot 2NaNO_3$ (*2*).

Distances

a) Thorium coordination polyhedron

Th–O(1)	2.384(3)	Th–O(4)	2.402(4)	Th–O(7)	2.402(4)
Th–O(3)	2.559(5)	Th–O(6)	2.562(4)		

b) (oda) and $NaNO_3$ ligands

O(1)–C(2)	1.282(7)	O(4)–C(3)	1.287(8)	O(7)–C(6)	1.283(7)
C(2)–O(2)	1.228(5)	C(3)–O(5)	1.220(8)	C(6)–O(8)	1.225(7)
C(1)–C(2)	1.500(7)	C(3)–C(4)	1.513(9)	C(5)–C(6)	1.508(10)
C(1)–O(3)	1.425(6)	C(4)–O(6)	1.428(8)	O(6)–C(5)	1.415(7)
N(1)–O(9)	1.257(7)	N(1)–O(10)	1.239(7)	N(1)–O(11)	1.243(7)

c) Sodium coordination polyhedron[a]

Na(1)–O(9)	2.480(7)	Na(2)–O(2)	2.334(4)

(*continued on facing page*)

TABLE V. *(continued)*

Na(1)–O(10)	2.651(6)	Na(2)–O(8)^{III}	2.385(4)
Na(1)–O(4)^{1}	2.855(5)*	Na(2)–O(5)^{IV}	2.369(5)
Na(1)–O(5)^{1}	2.401(5)	Na(2)–O(1)^{V}	2.865(3)*
Na(1)–O(7)^{II}	2.772(5)*	Na(2)–O(2)^{V}	2.440(4)
Na(1)–O(8)^{II}	2.403(6)	Na(2)–O(9)^{V}	2.730(7)
Na(1)–O(10)^{II}	2.504(6)	Na(2)–O(11)^{V}	2.478(6)
Na(1)–O(11)^{II}	2.567(6)		

*non bonded distances

Angles

a) Thorium environment[a]

O(1)–Th–O(3)	62.0(1)	O(1)–Th–O(4)	84.8(1)	O(4)–Th–O(7)	123.5(1)
O(4)–Th–O(6)	61.6(1)	O(1)–Th–O(6)	75.2(1)	O(4)–Th–O(41)	146.3(1)
O(6)–Th–O(7)	61.9(1)	O(1)–Th–O(7)	80.6(1)	O(4)–Th–O(61)	139.4(1)
O(1)–Th–O(11)	124.0(1)	O(3)–Th–O(4)	73.2(1)	O(4)–Th–O(71)	83.2(1)
O(1)–Th–O(41)	79.5(1)	O(3)–Th–O(6)	119.4(1)	O(6)–Th–O(61)	121.3(1)
O(1)–Th–O(61)	135.8(1)	O(3)–Th–O(7)	138.4(1)	O(6)–Th–O(71)	74.8(1)
O(1)–Th–O(71)	149.9(1)	O(4)–Th–O(6)	61.6(1)	O(7)–Th–O(71)	83.2(1)

b) (oda) ligands

Th–O(3)–C(1)	122.3(3)	Th–O(6)–C(4)	122.8(3)	Th–O(6)–C(5)	122.6(4)
O(3)–C(1)–C(2)	108.5(5)	O(6)–C(4)–C(3)	108.4(5)	O(6)–C(5)–C(6)	109.1(5)
C(1)–C(2)–O(2)	118.7(6)	C(4)–C(3)–O(5)	119.0(6)	C(5)–C(6)–O(8)	119.0(8)
O(2)–C(2)–O(1)	123.9(6)	O(5)–C(3)–O(4)	124.7(6)	O(6)–C(6)–O(7)	124.3(6)
C(1)–C(2)–O(1)	117.4(5)	C(4)–C(3)–O(4)	116.4(5)	O(7)–C(6)–C(5)	116.7(5)
C(2)–O(1)–Th	129.8(4)	C(3)–C(4)–Th	130.3(4)	C(6)–C(7)–Th	129.6(4)
C(1)–O(3)–C(11)	115.4(7)	C(4)–C(6)–C(5)	114.6(5)		

Key for symmetry

none	x,	y.	z
II	½ – x,	–½ + y,	½ – z
III	x,	–1 + y,	z
IV	–½ + x,	–½ + y,	z
V	½ – x,	½ – y,	–z
VI	½ – x,	½ + y,	½ – z
VII	½ + x,	½ + y,	z
VIII	x,	½ + y,	z

[a] Atoms with the second figure 1 are those at 1 – x, y, ½ – z.

The thorium atom lies on a crystallographic two-fold axis and the asymmetric unit is constituted by half the molecule: half thorium, one oda ligand and five water molecules two of which are coordinated to the metal.

Despite the presence of a multidentate ligand which generally promotes the formation of polymeric species, the compound is a monomer, the oda ligand is tridentate to the metal through two carboxylic and one etheric oxygen atoms with the formation of two five membered rings. The coordination sphere to the metal is then formed by six oxygens belonging to two oda ligands and four oxygens of the coordinated water molecules with ten coordination of the thorium ion and an overall C_2 crystallographic symmetry.

Bond distances and angles in the oda ligands have values similar to those usually found in the literature in the limits of the errors and, because of the relatively high e.s.d.s on the bond distances (0.02 Å), the C–O bonds with the oxygen coordinated to the metal and the C–O uncoordinated bonds are not significantly different. The methylene carbon atoms present the expected tetrahedral geometry while the three angles subtended by C(1) and C(4) are, as expected, about 120°.

The two pentaatomic rings are inclined to each other at an angle of 10.7° indicating some distortion

TABLE VI. Contact Distances in the Coordination Polyhedron for (*1*) and Contact Distances Involving Water Molecules for (*1*).

a) Contact distances in the coordination polyhedron for (*1*)

O(1)···O(3)	2.81(1)	O(3)···O(5)	2.57(1)
O(1)···O(5)	3.04(1)	O(2)···O(4)	3.14(1)
O(1)···O(11)	2.80(1)	O(2)···O(21)	2.87(1)
O(1)···O(5)	2.75(1)	O(2)···O(5)	3.05(1)
O(1)···O(4)	3.04(1)	O(2)···O(41)	2.73(1)
O(3)···O(4)	2.55(1)	O(4)···O(51)	2.96(1)
O(2)···O(3)	2.74(1)		

*Atoms with the second figure 1 are those of symmetry y, x, –z

b) Contact distances involving water molecules for (*1*)

O(1)···O(7)$^{\mathrm{III}}$	2.68(2)	O(9)···O(2)$^{\mathrm{IV}}$	2.80(2)
O(8)···O(6)	2.74(1)	O(9)···O(6)$^{\mathrm{V}}$	2.77(2)
O(8)···O(2)$^{\mathrm{II}}$	2.71(1)	O(9)···O(10)$^{\mathrm{VII}}$	2.90(2)
O(8)···O(1)$^{\mathrm{III}}$	2.72(1)	O(9)···O(10)$^{\mathrm{VIII}}$	2.85(2)
O(8)···O(10)$^{\mathrm{VI}}$	2.83(2)	O(10)···O(7)$^{\mathrm{IX}}$	2.81(2)

Key for symmetry

II	1 + y, x, –z
III	½ + x, ½ – y, –¼ – z
IV	½ + y, ½ – x, ¾ + z
V	–½ + x, ½ – y, ¾ – z
VI	x, –1 + y, –1 + z
VII	–½ + y, 1.5 – x, –¼ + z
VIII	1 – y, 1 – x, 1.5 – z
IX	1 – y, 1 – x, ½ – z

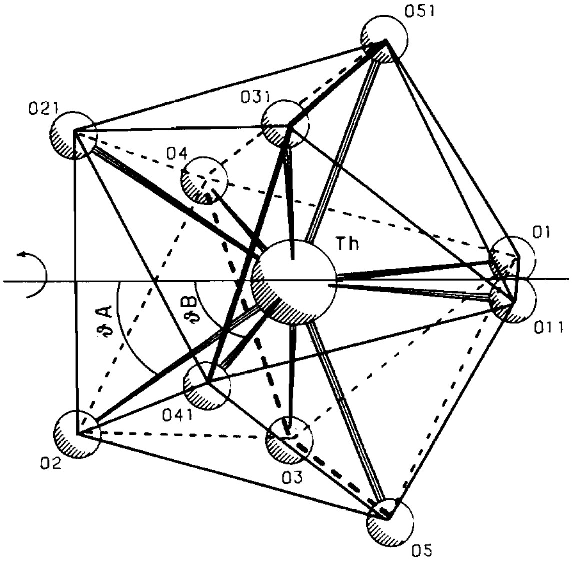


Fig. 2. Th(oda)$_2$(H$_2$O)$_4$ dodecahedron.

in the direction of the Th–O etheric bond and, in addition, the oda ligand is inclined with respect to the first one at an angle of about 47°.

An examination of the Th–O bond distances shows the differences between Th–O carboxylic (av. 2.413(9) Å), Th–O water (av. 2.483(9) Å) and Th–O etheric (2.697(9) Å).

As expected the carboxylic oxygens O(4) and O(5) are more strongly bound with respect to those of the water molecules, probably because the two negative charges of the pentadentate oda ligands are mainly located on them. The etheric oxygen represents the weakest bond and a significant difference between the My–O carboxylic and My–O etheric is present in actinide or lanthanide compounds with this ligand in spite of the differences in the metal oxidation state, coordination mode, or structure (monomeric or polymeric).

Thorium Coordination Polyhedron

A discussion of the 10-coordinate polyhedron is worthwhile due to the fact that while 10-coordinate actinides and lanthanides of the type M(bidentate)$_5$ or M(bidentate)$_x$(monodentate)$_y$ (where x and y have the correct value for a ten-coordinate

TABLE VII. Contact Distances in the Coordination Polyhedron for (*2*) and 'bite' of the Ligands for (*2*).

a) Contact distances in the coordination polyhedron for (*2*)

O(1)···O(3)	2.551(4)	O(3)···O(11)	2.551(4)
O(1)···O(4)	3.228(5)	O(1)···O(6)	3.019(5)
O(1)···O(41)	3.061(5)	O(1)···O(7)	3.095(5)
O(6)···O(71)	3.019(4)	O(6)···O(7)	2.554(5)
O(6)···O(4)	2.547(5)	O(7)···O(71)	3.191(4)
O(7)···O(41)	3.188(5)	O(3)···O(4)	2.959(5)

b) 'bite' of the ligands for (*2*)

O(1)···O(3)	2.551(4)	O(4)···O(6)	2.547(5)	O(6)···O(7)	2.554(5)
O(1)···O(2)	2.215(5)	O(4)···O(5)	2.220(6)	O(7)···O(8)	2.217(5)

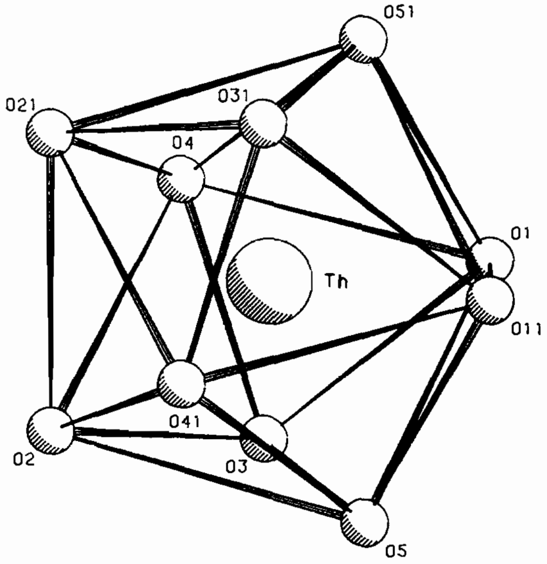


Fig. 3. $Th(oda)_2(H_2O)_4$ bicapped square antiprism.

compound) are known, that of the type M(tridentate)$_2$(monodentate)$_4$ is new.

The angular parameters $\theta_A = 35.5$, $\theta_B = 70.3°$ and $\theta_C = 55.4$ (θ_C is the angle between the planes O(5)–O(11)–O(1) and O(1)–O(11)–O(51)) (Fig. 2) approximate to the theoretical values $\theta_A = 32.8°$. $\theta_B = 77.0$ and $\theta_C = 60.0$ [12] for an ideal bicapped dodecahedron polyhedron with D_{4d} symmetry. The same polyhedron interpreted in terms of a bicapped square antiprism where the capping positions are represented by O(3) and O(31) gives the value for $\theta = 62.1$ (θ is the angle between the unique axis and the non axial bonds and in this case it represents the average of the values O(3)–Th–O(1) 65.7(3)°, O(2)–Th–O(3) 63.7(3)°, O(3)–Th–O(4) 59.6(3)° and O(3)–Th–O(5) 60.0(3)°) comparable with the theoretical value of 64.8° [12]. The averaged value for the ratio of axial antiprismatic bond distances is 1.1. In this case we have closer agreement with the theoretical value also if the twist angle between the square faces is 35° compared with the ideal value of 45°. In any case it is evident that the rigid geometry of the ligands does not allow the formation of a regular coordination polyhedron. If we consider the compound as having a bicapped square antiprism geometry we have at least four possible geometrical isomers (Fig. 4) depending on the respective positions of the two oda ligands and of the water molecules and taking into account the rigid geometry of the oda ligand. (The Akhtar and Smith nomenclature [13] is used to describe the polyhedron edges: p-pyramidal s-square and e-equatorial edges, *i.e.* those going from a square face to another). It appears that we are dealing with the isomer *1* structure which allows the bites of oda ligands on the pyramidal edges of the polyhedron.

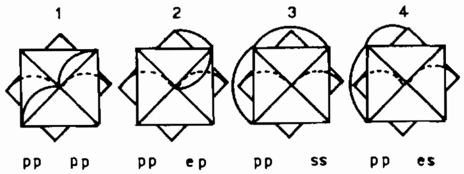


Fig. 4. Possible geometric isomers for (*1*).

Water Molecules and Hydrogen Bonding

The water molecules present in the structure are of two types, those coordinated to the Th atom *i.e.* O(1) and O(2) and those, O(8), O(9) and O(10), of crystallization. Both types interact both between themselves and with the carboxylic oxygens of the oda ligands suggesting the possibility of hydrogen bonds.

In Table VI are reported the contacts that could be interpreted on this key. The O(1) water molecule is coordinated to the thorium atom and forms a short contact of 2.68(2) Å with the carboxylic oxygen O(7)^{III} of the oda ligand of an adjacent molecule, and symmetrically O(7) makes the same short contact with the O(1) at the position $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{4} - z$; this gives rise to a kind of dimeric molecule held together through the hydrogen bond system just described with the formation of ten membered rings (Fig. 5). Other contacts which exist between water molecules coordinated and uncoordinated suggest the presence of a three-dimensional framework of hydrogen bonds connecting together all the 'dimeric' units.

$Na_2[Th(oda)_3] \cdot 2NaNO_3$

In the complex anion $[Th(oda)_3]^{2-}$ the thorium is nine-coordinated, and in Fig. 6 a view down *a* of the anion with the atom numbering scheme is shown.

The anion has C_2 crystallographic symmetry with the thorium and the etheric oxygen O(3) lying on the binary axis. The asymmetric unit is constituted by one and one half oda ligands and half of a thorium atom, one sodium and one sodium nitrate molecule. The rigidity of the oda ligand allows only the *mer* isomer [14], in the tricapped trigonal prism coordination geometry around the thorium atom, (Fig. 7) where the oda ligands behave as tridentate with the fomation of five membered rings; the triangular faces of the prism are formed by carboxylic oxygens. The distance between the two triangular planes is 3.16 Å. The three independent Th–O (carboxylic) bond distances are equal within the limit of error, (Th–O(1) 2.384(3), Th–O(4) 2.402(4) and Th–O(7) 2.402(4) Å), and as expected are significantly shorter with respect to the Th–O etheric bonds (Th–O(3) 2.559(5) and Th–O(6) 2.562(4).

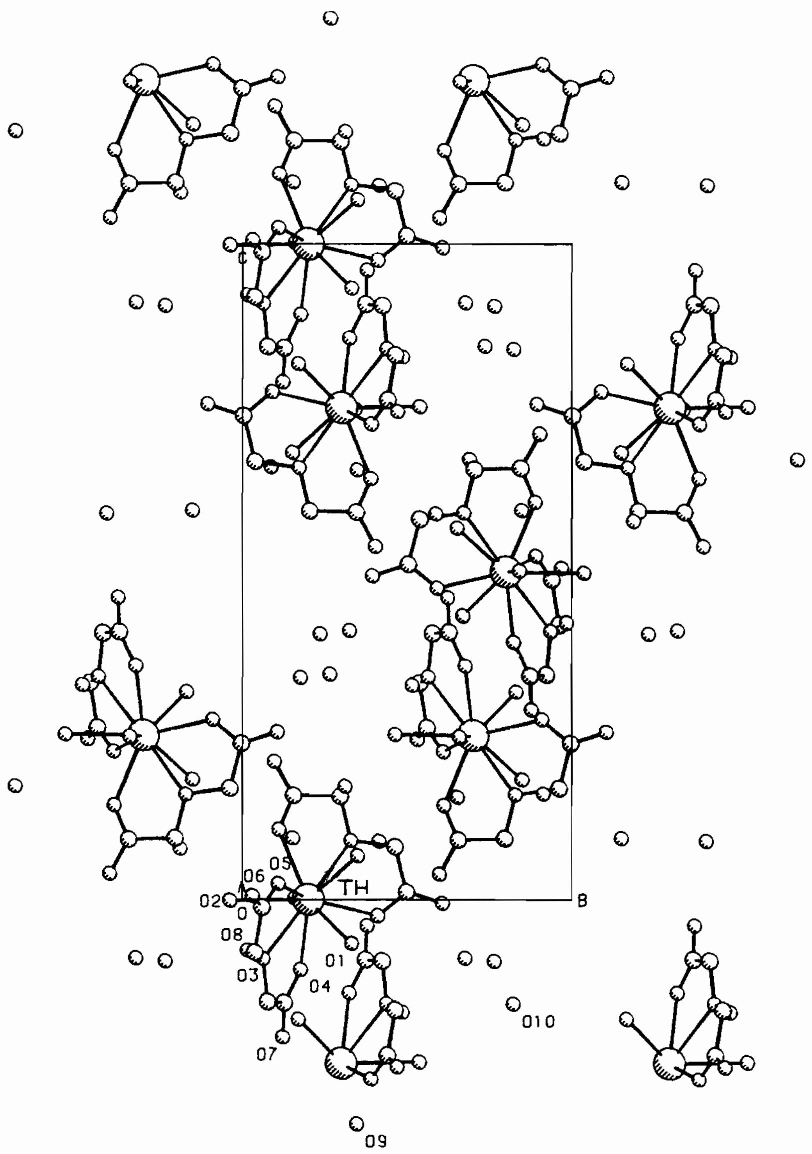


Fig. 5. Unit cell content viewed down *a* for (*1*).

The planes calculated through the oxygens of the two halves of O(4)···O(6) and O(6)···O(7) of one oda ligand make an angle of 2.3°; the carbon atoms are coplanar with the respective oxygen's mean plane except for the methylenic carbon C(4) which deviates by 0.09 Å. The second oda ligand is planar for reasons of symmetry. The oda ligands are rotated around each other by an angle of 83°.

This kind of coordination geometry is typical for complexes of the type $M(oda)_3$ (M is either a lanthanide or an actinide).

The rigidity of the oda ligand causes a twist of the triangular faces of the prism. Here the twist angle is 12.6° and can be compared with the value of 13.3° found in $Na_3[Yb(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ [15] while it is smaller with respect to the values of 18.8° found in $Na_3[Nd(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ [15] and of 20.5° found in $[Ce(oda)_3]^{3-}$ [16].

An examination of different compounds of lanthanides or actinides with the same ligand and also with different coordination geometries, shows that the bite of the oda ligand is not significantly different from the value of 2.55 Å found here and that this value is shorter with respect to the van der Waals diameter (2.80 Å) while the other O···O contacts have values in the range 3.019···3.228 Å. The distances in the oda ligand can be shown to be distances involving oxygens coordinate to the thorium ($C–O_{av.}$ 1.284(8) Å) and oxygens uncoordinated (C–O 1.224(7) Å). The second value is significantly shorter than the first one. This allows in this case the assignment of the negative charges of the oda ligands to the coordi-

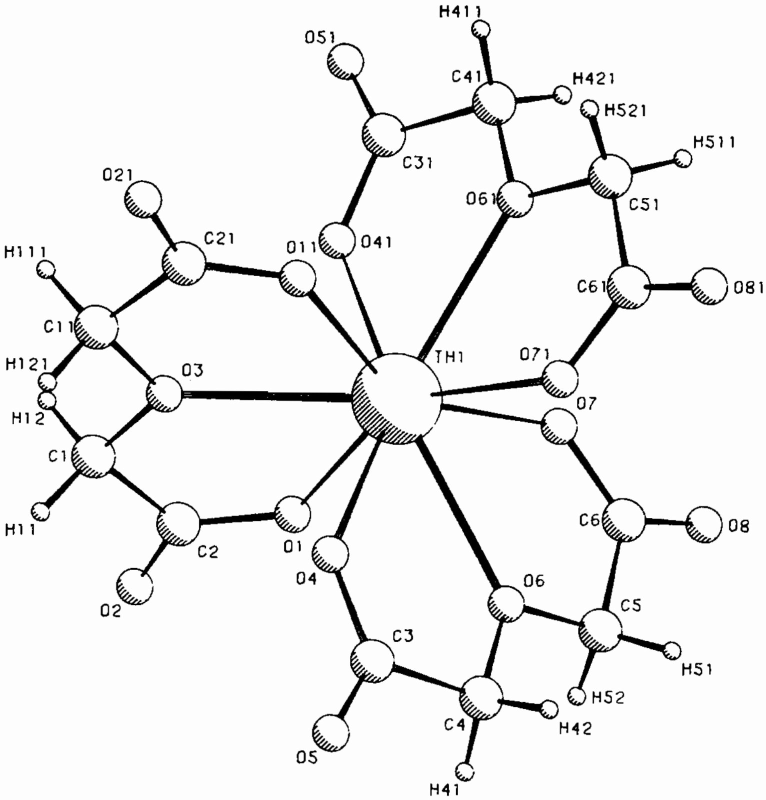


Fig. 6. View down *a* of the $[Th(oda)_3]^{2-}$ anion.

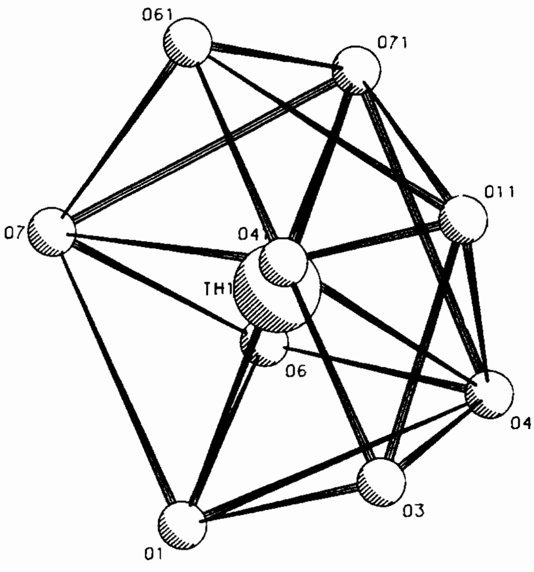


Fig. 7 $[Th(oda)_3]^{2-}$ tricapped trigonal prism geometry.

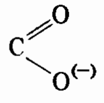
nated oxygens and it also shows that with this ligand there is little tendency to an electronic delocalization within the system  $\mathrm{C}\begin{matrix} /\!\!/\mathrm{O} \\ \backslash\mathrm{O}^{(-)} \end{matrix}$ either when both oxygens are chelated to the metal or when only one is coordinated; a significant example is the polymeric structure $[UO_2(oda)]_n$ [1] where the two carboxylic distances C–O(2) 1.29(2) and C–O(1) 1.23(2) Å are significantly different also if both oxygens are coordinated to the metal atoms in a polymeric structure.

Table VIII shows a comparison between the different Th–O bond distances in Th compounds with oda ligands. It appears that Th–O (carboxylic) bonds and Th–O (water) bonds are comparable in the three quoted compounds independently from the coordination number and from the number of oda ligands.

In fact the compounds have 1, 2, or 3 oda ligands, two structures are monomeric and one is polymeric. The coordination geometries are different and the coordination number is 9 in two and 10 in one. The Th–O etheric bonds are in three cases longer with respect to the other types of Th–O bonds but the amount of difference depends on the examined compound: Th–O etheric is 2.560(1) in $[Th(oda)_3]^{2-}$, 2.63(1) in $Th(oda)(SO_4)(H_2O)$, and 2.697(9) Å in $Th(oda)_2(H_2O)_4 \cdot 6H_2O$. It is evident that only the weaker Th–O bond is affected by all the factors just described and that the other stronger bonds Th–O (water) and Th–O (carboxylic) are not influenced.

The different coordination numbers and polyhedra found for the complexes with 2 and 3 oda ligands

TABLE VIII. Significant Geometrical Parameters in Th(IV) Compounds with the oda Ligands.

	Th–$O_{carboxylic}$	Th–$O_{etheric}$	Th–O_{water}	CN	Coordination
Th(oda)(SO_4)(H_2O)·(H_2O) [2] (polymer)	2.44(1) 2.41(1)	2.63(1)	2.44(1) 2.38(1)[a]	9	monocapped square antiprism
Th(oda)$_3$Na$_2$·NaNO$_3$ (monomer)	2.384(3) 2.402(4) 2.402(4)	2.559(5) 2.562(4) Av. 2.560		9	tricapped trigonal prism
Th(oda)$_2$(H_2O)$_4$·6H_2O (monomer)	2.411(8) 2.414(9)	2.697(9)	2.479(10) 2.486(8)	10	bicapped square antiprism

[a] O(SO_4).

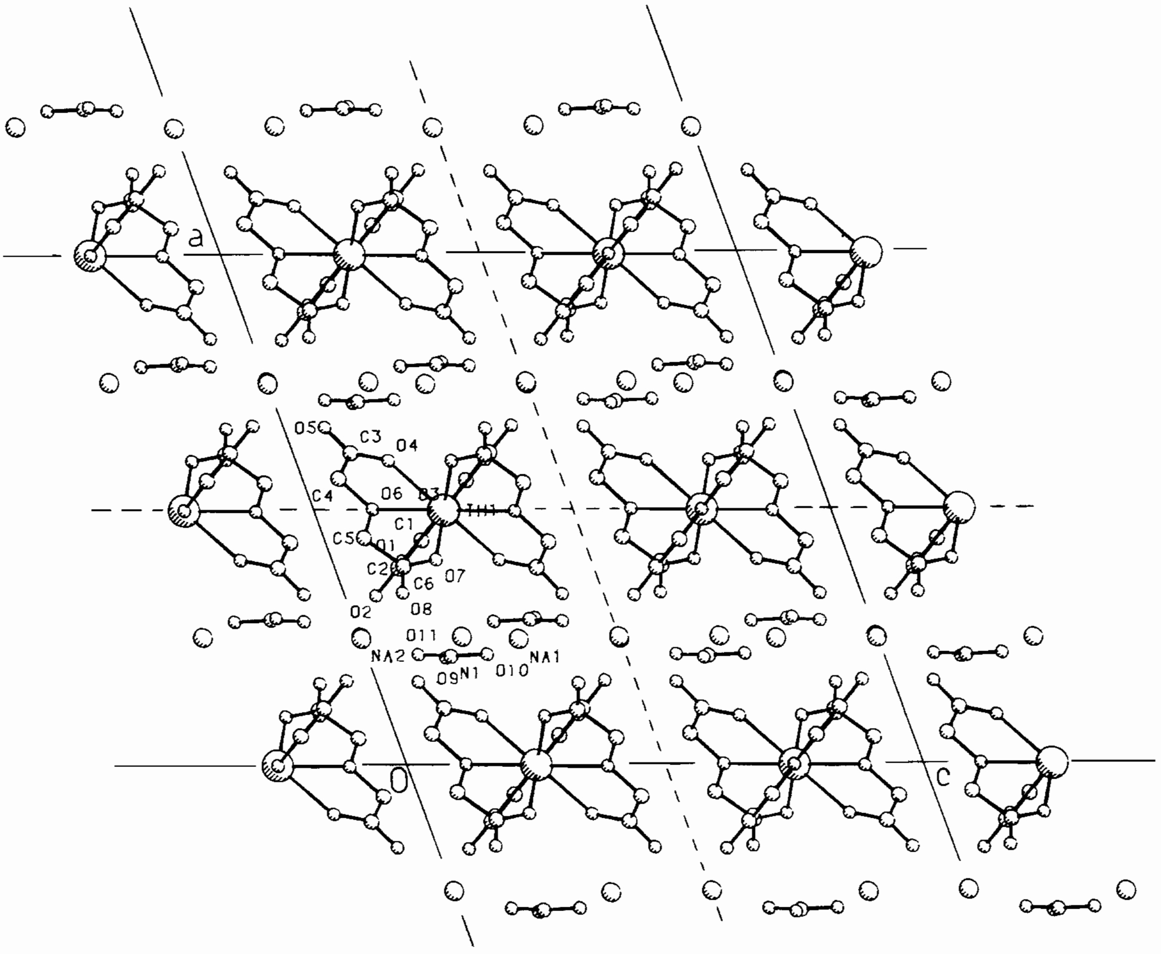


Fig. 8. Unit cell content viewed down *b* for (*2*).

might well be indicative of a similar abrupt change in the coordination geometry accompanying the formation of the tris complex, in aqueous solution, as postulated on the grounds of thermodynamic parameters [7].

Sodium Coordination Polyhedra

There are short distances between the nitrate ion and sodium atoms (Table V), O(9) is shared between Na(1) and Na(2)^{VI}, O(10) between Na(1) and Na(1)^{VI} and O(11) between Na(1)^{VI} and Na-

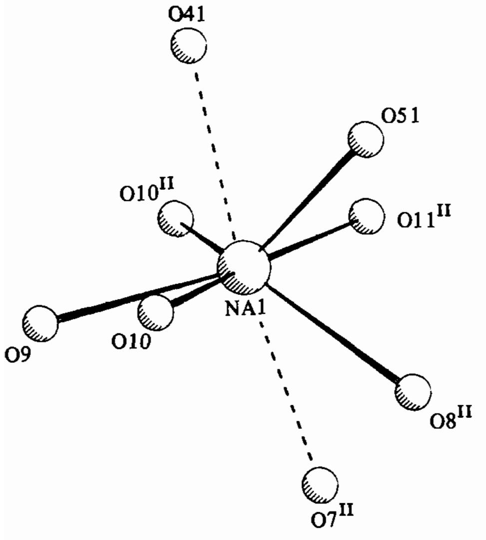


Fig. 9. Na(1) polyhedron.

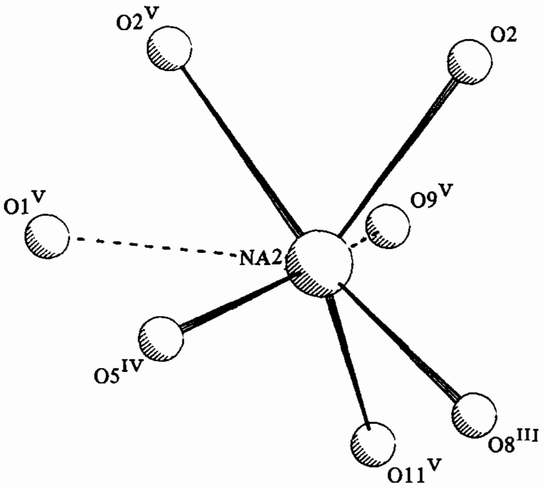


Fig. 10. Na(2) polyhedron.

(2)^{V}. The carboxylic oxygens uncoordinated to the thorium atom are linked to the sodium atoms: O(2) is bridging between Na(2) and Na(2)^{V}, O(5) between Na(11) and Na(2)^{VII} and O(8) between Na(1)^{VI} and Na(2)^{VIII}.

The different $[Th(oda)_3]^{2-}$ units are connected to each other in a three-dimensional framework through the carboxylic oxygens coordinated to the sodium atoms which are also interconnected *via* nitrate groups. The unit cell content viewed down *b* is reported in Fig. 8.

Around Na(1) there are six oxygens at a distance ranging between 2.403(6) Å and 2.651(6)° and for Na(2) the six Na–O distances vary from 2.334(4) Å to 2.730(7) Å.

The coordination polyhedron about Na(1) is a distorted octahedron (Fig. 9), while that about Na(2) could be described as a trigonal bipyramid (Fig. 10) if the distance Na(2)···O(9)^{V} of 2.730 Å is considered as a non bonded distance; in this case the upper limit for bond distances for Na(2) is 2.478(6) Å.

In $Na_3[Ce(oda)_3]\cdot 9H_2O$ [16] are present similar polyhedra with a range of Na–O bond distances of 2.35–2.52 Å, and also in $Na_3[M(oda)_3]\cdot 2NaClO_4\cdot 6H_2O$ with comparable Na–O bond distances (M = Nd, Gd, Yb) [15].

Acknowledgement

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