Crystal Structure and Normal Co-ordinate Analysis of Diaqua(oxydiacetato)sulphatothorium(IV) Monohydrate†

Rodolfo Graziani *
Itituto di Chimica Generale, Università di Padova, Via Loredan, 4, I-35100 Padova, Italy
Giovanni A. Battiston, Umberto Casellato, and Gino Sbrignadello *
Instituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Area di Ricerca, Corso Stati Uniti, I-35100 Padova, Italy

The structure of the title compound has been determined by single-crystal *X*-ray techniques, using diffractomer data. The compound crystallizes in the monoclinic space group *C*2 with $a = 10.67(1)$, $b = 8.35(1)$, $c = 6.73(1)$ Å, $Z = 2$, and $\beta = 110.96(2)°$. Refinement of the structure led to a final *R* value of 0.048 using 1 931 observed data. The thorium atom, which lies on a crystallographic two-fold axis, is nine-co-ordinate in the monocapped square antiprismatic geometry. Both the oxydiacetate and sulphate ligands are shared between different thorium atoms allowing the formation of a rather compact polymeric network. The length of the Th–O bond to the apical ether oxygen, 2.63(1) Å, is significantly greater than the average, 2.42 Å, for the other bonds to carboxylate or water oxygen. For this complex the fundamentals have been assigned on the basis of a normal co-ordinate analysis and potential-energy distribution obtained by use of a 48-parameter Urey–Bradley force field. The stretching force constant of the Th–O(ether) bond is greater than that of the corresponding U–O(ether) bond in the analogous uranium-containing compound (1.37×10^2 *versus* 1.10×10^2 N m^{-1} respectively).

The extraordinary versatility of α,ω-dicarboxylate ligands in binding metal ions in the crystalline state is well known. Various uranyl, neptunyl, and plutonyl complexes with oxydiacetate, iminodiacetate, or thiodiacetate have been studied in solution or in the solid state, and the observed tendency, at least for some of them, for the formation of polymeric species makes the structures of these compounds particularly interesting.[1-5]

Despite this and the possibility of different co-ordination modes, only relatively few complexes of these ligands with U^{IV} and Th^{IV} have been isolated.

With an intention to investigate the structural characteristics of carboxylate–metal ion interactions and to assign the fundamental vibrations on the basis of a normal co-ordinate analysis, we have determined the crystal structure of $\{[Th(oda)(SO_4)(H_2O)_2]\cdot H_2O\}_n$ (oda = oxydiacetate), in order to determine the nature of metal–ligand binding, as well as to obtain information concerning the Th^{IV} ion co-ordination geometry.

Experimental

The initial aim was to carry out an *X*-ray analysis of $[\{Th(oda)_2\}_n]$, whose preparation and characterization have been previously reported.[6] Unfortunately, the product obtained following the preparation mentioned above was unsuitable for *X*-ray work. Eventually, we added a dilute solution of an excess of $[Na_2(oda)]$, dissolved in aqueous sulphuric acid, to a solution of thorium nitrate. White crystals formed after several days which were filtered off and washed with water and methanol. These crystals were suitable for *X*-ray study and the resulting compound was identified, mainly by diffraction data, as $\{[Th(oda)(SO_4)(H_2O)_2]\cdot H_2O\}_n$.

Infrared spectra (CsI and polythene discs) were recorded with Perkin-Elmer 580B (4 000–180 cm^{-1}) and Beckman IR11 (300–50 cm^{-1}) spectrophotometers. The 580B model was equipped with Data Station 3500, and the spectra were optimized by ABEX, FLAT, and SMOOTHING software functions. No data were available from Raman spectra, owing to the decomposition of the compound under a laser beam.

The crystal chosen for data collection was coated with cyanoacrylate adhesive and mounted in a Lindemann glass capillary tube on the goniostat of a Philips PW 1100 diffractomer. Cell dimensions were determined by least-squares refinement from the measured setting angles of 25 reflections.

Crystal Data.—$C_4H_{10}O_{12}STh$, $M = 514$, Monoclinic, $a = 10.67(1)$, $b = 8.35(1)$, $c = 6.73(1)$ Å, $\beta = 110.96(2)°$, $U = 560$ Å^3, $D_m = 3.05(1)$, $Z = 2$, $D_c = 3.05$ g cm^{-3}, $F(000) = 472$, μ(Mo-K_α) = 200.7 cm^{-1}, space group *C*2 (from structure determination).

Data Collection.—Data were collected at room temperature by the θ—2θ step-scan method at a 2θ scan rate of 2° min^{-1} using Mo-K_α radiation. Two non-coplanar reflections measured at regular time intervals showed no significant variations in either intensity or position. A total of 1 931 contributing reflections [$I > 3\sigma(I)$] were collected to a maximum 2θ value of 50° and the resultant data were corrected for background, Lorentz, and polarization effects. Absorption corrections were also applied following the method of ref. 7.

Structure Determination.—Apart from the uncertainty about the exact chemical formula of the complex, the very high value of the crystal density requires only two molecules to be present in the unit cell with the heavy atom on a special position. Of the two possible equipoints 0, *y*, 0 and 0, *y*, ½, of space group *C*2, the latter is compatible with the observed maxima of the Patterson function if the *y* co-ordinate is assumed to be ½.

However, the choice of the space group was not a straightforward matter. In fact, the systematic absences *hkl*, $h + k = 2n + 1$, 0*k*0, $k = 2n + 1$, suggested space group *C*2 or *C*2/*m* and, on the basis of the Patterson peaks, the latter could be assumed to be correct, with the heavy metal atom in the equipoint 0, ½, ½ which has point symmetry 2/*m*. However, in this case, the Th atom would lie on both a two-fold axis and on a mirror plane and, according to the possible symmetry of the ligand, at least two oda units would be associated with each

†*Supplementary data available* (No. SUP 23411, 11 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Positional parameters with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Th	0.0000	0.5000	0.5000
S	0.0000	0.291 0(5)	1.0000
O(1)	0.345 8(8)	0.155 0(13)	0.610 4(20)
O(2)	0.212 1(8)	0.355 0(10)	0.623 9(20)
O(3)	0.0000	0.185 2(14)	0.5000
O(4)	0.008 8(25)	0.395 8(24)	0.833 5(25)
O(5)	0.116 8(14)	0.185 1(25)	1.074 9(40)
O(6)	−0.121 0(11)	0.694 7(21)	0.228 1(24)
O(7)	0.0000	0.867 9(22)	0.0000
C(1)	0.234 5(10)	0.209 3(14)	0.598 4(18)
C(2)	0.120 2(12)	0.093 2(14)	0.556 0(24)

the Fourier maps, calculated on the basis of the heavy-atom phases, have additional symmetry as compared to the true space group. In particular the Th position at 0, ½, ½, which corresponds to a special position of *C*2/*m*, results in a Fourier synthesis which belongs to *C*2/*m*. From this it was relatively easy to locate the atoms of one of the two images of the ligand oda. Addition of these atoms was not sufficient to produce an effect on the heights of the remaining peaks, but, because of the polymeric character of the structure, five co-ordination sites around Th were found occupied: three from oxygens of the same oda, and two from oxygens of oda groups of neighbouring units. Consideration of the possible geometry of the co-ordination polyhedron and of steric hindrance between the atoms, together with a laborious trial-and-error process, were needed to sort out the true structure from its image.

Table 2. Interatomic distances (Å) and interbond angles (°) with e.s.d.s in parentheses

(*a*) Co-ordination					
Th–O(1^{I})	2.41(1)	O(3)–Th–O(2)	60.2(2)	O(6)–Th–O(1^{I})	68.7(5)
Th–O(2)	2.44(1)	O(3)–Th–O(4)	68.5(5)	O(6)–Th–O(1^{III})	69.4(4)
Th–O(3)	2.63(1)	O(2)–Th–O(1^{III})	73.7(4)	O(6)–Th–O(6^{II})	96.6(5)
Th–O(6)	2.44(1)	O(2)–Th–O(4)	77.1(7)	O(6)–Th–O(4^{II})	72.8(6)
Th–O(4)	2.38(1)	O(2)–Th–O(6^{II})	84.1(4)	O(1^{I})–Th–O(4)	72.9(7)
		O(2)–Th–O(4^{II})	81.9(6)	O(1^{I})–Th–O(1^{III})	115.0(4)
(*b*) oda ligand					
C(1)–O(1)	1.25(1)	Th–O(1^{I})–C(1^{I})	156(1)	O(1)–C(1)–O(2)	124(1)
C(1)–O(2)	1.26(1)	Th–O(2)–C(1)	129(1)	O(1)–C(1)–C(2)	118(1)
C(1)–C(2)	1.50(2)	Th–O(3)–C(2)	123(1)	O(2)–C(1)–C(2)	118(1)
		C(2)–O(3)–C(2^{II})	115(1)	C(1)–C(2)–O(3)	107(1)
(*c*) Sulphate					
S–O(4)	1.45(2)	Th–O(4)–S	163(1)	O(4)–S–O(5^{IV})	112(1)
S–O(5)	1.46(2)	O(4)–S–O(4^{IV})	106(1)	O(5)–S–O(5^{IV})	106(1)
		O(4)–S–O(5)	110(1)		

Roman numeral superscripts refer to the following co-ordinate transformations: I $-\frac{1}{2}+x, \frac{1}{2}+y, z$; II $\bar{x}, y, 1-z$; III $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; IV $\bar{x}, y, 2-z$; V $-\frac{1}{2}+x, \frac{1}{2}+y, -1+z$; VI $x, 1+y, -1+z$; VII $\bar{x}, 1+y, 1-z$; VIII $\bar{x}, y, \bar{z}$; IX $x, y, -1+z$.

Table 3. Contact distances and possible hydrogen bonds (Å)

(*a*) Contact distances			
O(2) · · · O(3)	2.54(1)	O(4) · · · O(4^{IV})	2.31(2)
O(2) · · · O(1)	2.22(1)	O(4) · · · O(5)	2.39(2)
O(2) · · · O(1^{III})	2.91(1)	O(4) · · · O(5^{IV})	2.42(2)
O(2) · · · O(4)	3.00(2)	O(4) · · · O(3)	2.82(1)
O(2) · · · O(4^{II})	3.16(2)	O(5) · · · O(5^{IV})	2.33(2)
O(2) · · · O(6^{II})	3.27(2)	O(6) · · · O(6^{II})	3.65(2)
O(1) · · · O(5^{IX})	3.57(2)	O(1^{I}) · · · O(1^{III})	4.07(2)
(*b*) Possible hydrogen bonds			
O(1^{I}) · · · O(6)	2.74(2)	O(1^{III}) · · · O(7)	3.11(2)
O(1^{III}) · · · O(6)	2.76(2)	O(1^{V}) · · · O(7)	3.11(2)
O(5^{V}) · · · O(6)	2.61(2)	O(5^{VI}) · · · O(7)	2.89(2)
O(7) · · · O(6)	2.74(2)	O(5^{VII}) · · · O(7)	2.89(2)
O(6^{II}) · · · O(4)	2.86(2)	O(6^{VIII}) · · · O(7)	2.74(2)

For definition of Roman numeral superscripts see Table 2.

metal atom. This possibility was taken into account but it was subsequently discarded when it was clear, from the maxima of the Fourier electron-density map, that two oda ligands per molecule were sterically incompatible with the corresponding ligands of adjacent molecules in the crystal lattice and that the reciprocal positions of the bonded atoms in the co-ordination polyhedron were chemically unlikely. This fact indicated that the correct choice is *C*2 with only one oda bonded to the thorium atom. Although the ambiguity of space group was solved, further elucidation of the structure proved difficult because

The presence of three water molecules and of the unexpected sulphate group was unequivocally determined on the basis of the relative sizes and positions of the peaks, of bond lengths, and of the requirement of the overall charge neutrality, and was confirmed by the successive refinement. All atomic positions were refined anisotropically by full-matrix least squares and at convergence the final *R* was 0.048 when the last maximum shift was *ca.* 6% of the e.s.d. on co-ordinates and 20% of the e.s.d. in the thermal parameters. A difference-Fourier map computed at the end of the refinement showed no significant residual features other than small residuals near the Th sites, probably due to inadequacies in the absorption corrections, but gave no clear indications on the positions of the hydrogen atoms.

Neutral atom scattering factors were used throughout, that for thorium being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[8,9] All calculations were carried out using the *X*-RAY program system.[10] Non-hydrogen atomic co-ordinates, bond lengths and angles, contact distances, and the equations of selected mean planes are given in Tables 1—4.

Results and Discussion

The crystal structure determination shows the complex to be $\{[Th(oda)(SO_4)(H_2O)_2]\cdot H_2O\}_n$, the thorium atom being nine-co-ordinate. A view of portions of the polymeric units occurring in the unit cell, showing the co-ordination polyhedron around thorium, the mode of thorium binding by oxydiacetate, and the atom-labelling scheme, is presented in Figure

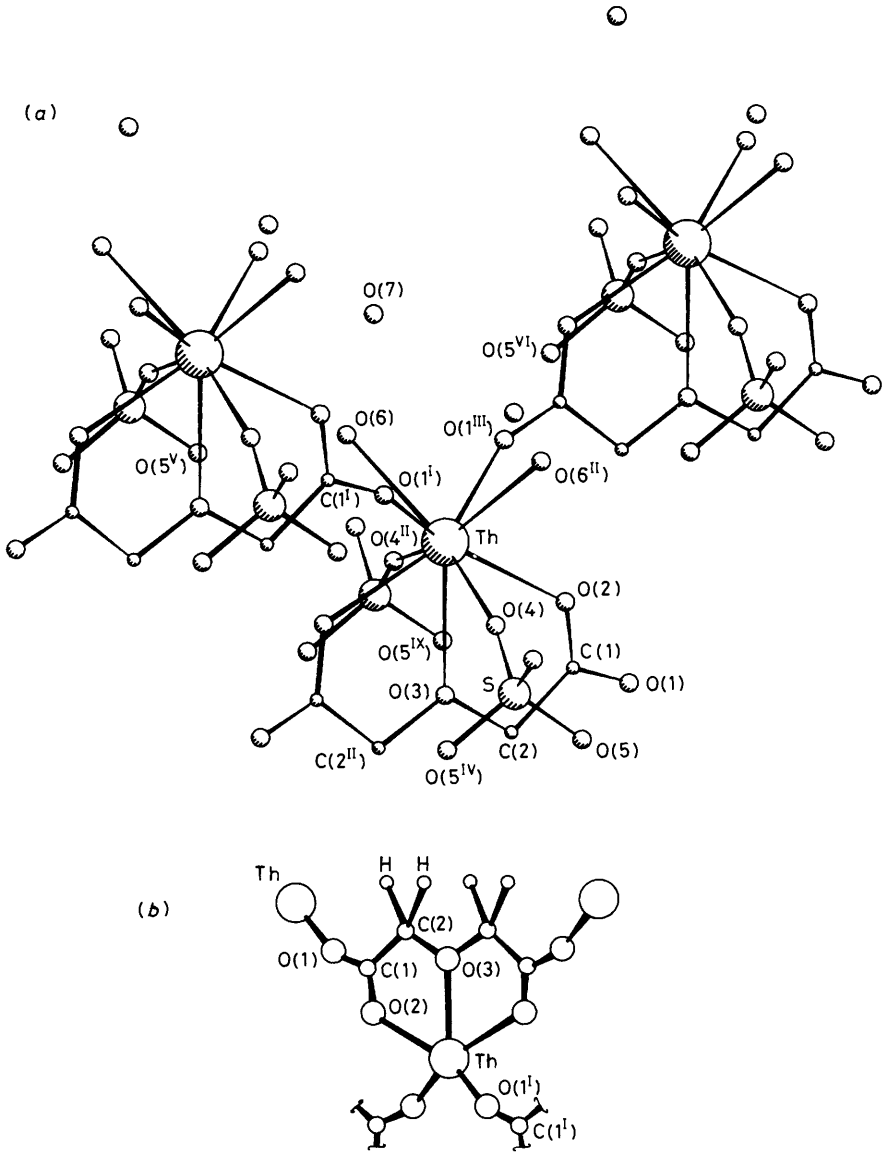

Figure 1 (*a*) Crystal structure of {[Th(oda)(SO_4)(H_2O_2)$_n$[·H_2O} showing the atomic numbering. (*b*) Molecular model of the repeating unit Th(oda) used for normal co-ordinate analysis

1(*a*). Each oxydiacetate ion is chelated to the same Th atom through the ether oxygen and two carboxylate oxygens, and links two different Th atoms by unidentate bridging bonds with the two remaining carboxylate oxygens. Both the ether oxygen O(3) and the metal atom lie on the same crystallographic two-fold axis, so that the oda group as well as the entire molecule has imposed *C*2 symmetry. The oda ligand provides, directly or indirectly, linkage of one Th atom to four adjacent Th atoms with the same *z* co-ordinate. As shown in Figure 2 the Th atoms are also bridged by the sulphate groups in the direction of the *c* axis, so that each repeating unit of the resulting polymeric structure is octahedrally surrounded by six similar units. Two of the three formula H_2O molecules are also directly bonded to Th. The stereochemistry around the Th atom is a monocapped square antiprism with the two square faces normal to *b* and O(3) in the apical position, as shown in Figures 3 and 4. The angle of twist between the two square faces (39°) approaches the ideal value and the co-ordination polyhedron has approximately local C_{4v} symmetry, where the symmetry axis coincides with the Th–O(3) bond. The mean planes for the atoms O(1^{I}), O(1^{III}), O(6), and O(6^{II}) comprising the ' square ' base of the co-ordination polyhedron and for the atoms O(2), O(2^{II}), O(4), and O(4^{II}) comprising the ' square ' base of the pyramidal cap [with O(3) at the apex] are given in Table 4 with the displacements from these planes. It is seen that each of these ' square ' arrays displays a quasi-S_4 ruffling from its mean plane, averaging 0.17 Å for both the lower and upper squares.

In addition, as expected for an anisotropic compound, the ' squares ' are slightly distorted towards parallelograms because of small differences in metal–ligand bond distances. The presence of the square antiprismatic co-ordination group requires a substantial spreading of the polyhedral face thus capped.

Consequently, the average length of the four O · · · O edges delineating the base of the pyramidal cap is 3.08 Å, as compared with 2.89 Å for the other 12 interligand O · · · O edges and 2.75 Å for the corresponding edges of the opposite face. The Th atom lies 1.59 Å below the base of the pyramidal cap and 1.46 Å above the base of the co-ordination poly-

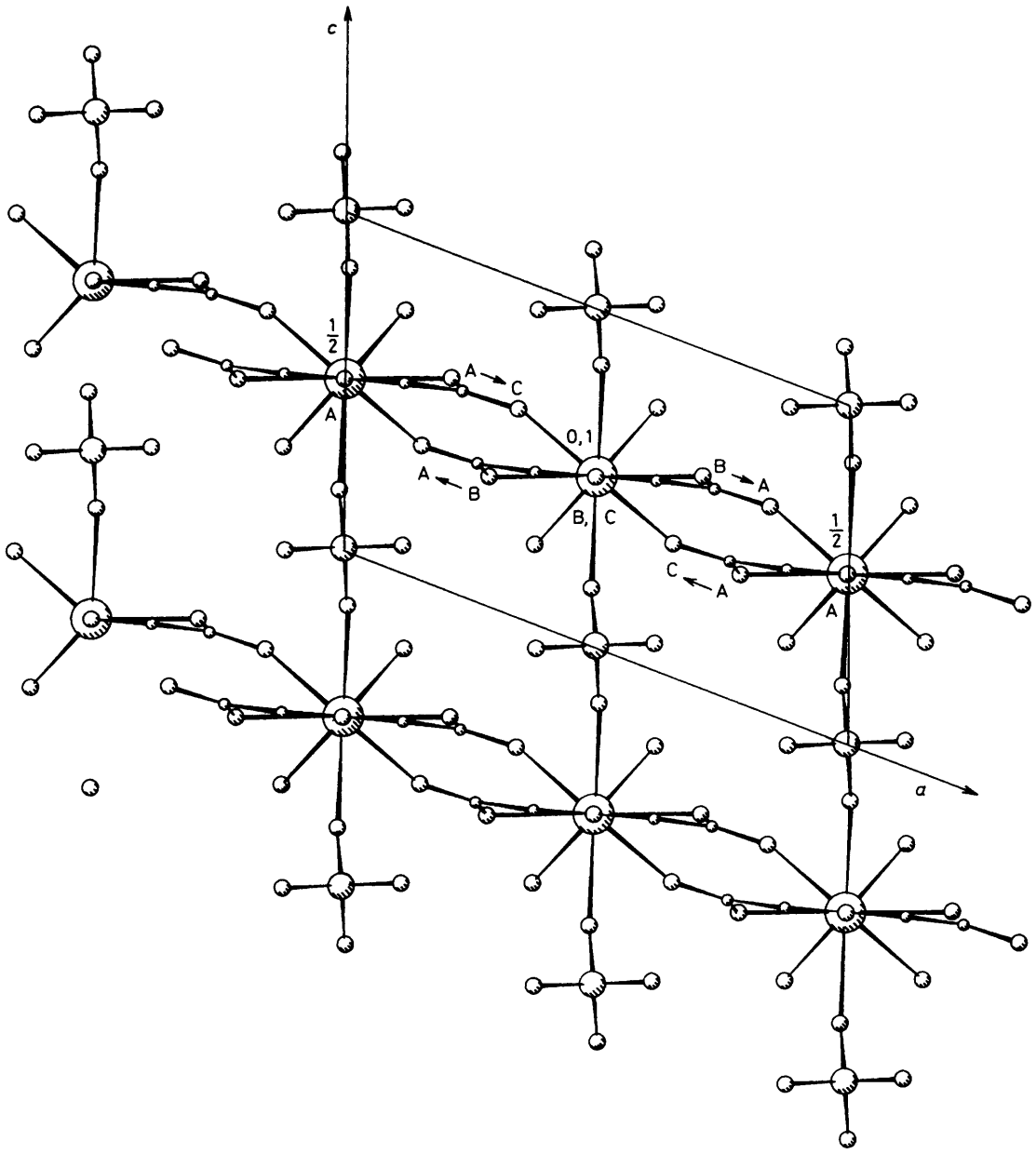

Figure 2. Bonding scheme: projection along the *b* axis. Thorium atoms at $y = \frac{1}{2}$ (A) are bridged to Th at $y = 0$ (B) and $y = 1$ (C) along the *a* axis. Thorium atoms B and C are superimposed in this Figure. The ligand oda of B bridges A and that of A bridges C, thus each Th is linked through the oda ligands to four Th at $z = \frac{1}{2}$ along *a* and through the sulphate groups to the two other Th atoms along the *x* axis of the cell

hedron. The angles subtended at the thorium atom within the co-ordination polyhedron are listed in Table 2.

It can be noted that the angles subtended by O · · · O edges at the base of the polyhedron are appreciably smaller (mean 69.0°) than the corresponding angles relative to the base of the pyramidal cap (mean 79.5°). Moreover, three of the four independent angles subtended by the lateral edges connecting the base of the polyhedron with the base of the pyramidal cap range from 72.8 to 73.7, averaging 73.1°, whereas the fourth is significantly larger (84.1°) because of the observed departure of the angle of twist of the square faces from the ideal value of 45°. The radius of the co-ordination polyhedron, that is the average of the nine Th–O bond lengths, is 2.44 Å, but eight of these bonds lie between 2.38 and 2.44 Å, with a mean of 2.42 Å, whereas the apical Th–O(3) bond of 2.63 Å is significantly larger. This is not surprising if one considers that O(3) is an ether oxygen. A comparable difference between the U–O(ether) and U–O(carboxylate) bonds has been observed in $[\{UO_2(oda)\}_n]$.[3]

It is worthwhile to note that, in spite of the differences in metal oxidation state and co-ordination geometry and of the metal–oxygen bond lengths, the internal O(3) · · · O(2) contact distance of 2.54(1) Å in oda is the same, within the estimated error, as found in $[\{UO_2(oda)\}_n]$ [2.54(2) Å], which could be reasonably attributed to some geometrical rigidity of the bonded ligand.[8] The Th–O(2) (carboxylate) and Th–O(6) (water) bonds have the same length of 2.44 Å, only slightly longer than the Th–O(1^1) bond length of 2.41 Å. This small but significant difference could suggest that the negative charges of the quinquedentate ligand are mainly located on the

Table 4. Least-squares planes. Deviations (Å) of atoms from the planes are given in square brackets; X, Y, and Z are fractional co-ordinates in the direct cell. Atoms not used in the plane calculation are marked with an asterisk

Plane 1: O(1), O(2), O(3), O(1^{II}), O(2^{II})

$-2.610X + 0.000Y + 6.683Z = 3.341$

[O(1) −0.165, O(2) 0.274, O(3) −0.000, O(1^{II}) 0.165, O(2^{II}) −0.274, Th * 0.000, C(1) * 0.045, C(2) * 0.060]

Plane 2: O(2), O(2^{II}), Th

$-3.931X + 0.000Y + 6.730Z = 3.365$

Plane 3: O(6), O(6^{II}), Th

$10.107X + 0.000Y - 0.267Z = -0.133$

Plane 4: O(2), O(2^{II}), O(4), O(4^{II})

$0.000X + 8.350Y + 0.000Z = 3.134$

[O(2) −0.171, O(2^{II}) −0.171, O(4) 0.171, O(4^{II}) 0.171, Th * 1.041, O(3) * −1.588]

Plane 5: O(1^{I}), O(1^{III}), O(6), O(6^{II})

$0.000X + 8.350Y + 0.000Z = 5.635$

[O(1^{I}) −0.166, O(1^{III}) −0.166, O(6) 0.166, O(6^{II}) 0.166, Th * −1.460]

Angles (°) between planes: 1–2 7.5, 1–3 85.5, 1–4 90.0, 1–5 90.0, 2–3 87.1, 2–4 90.0, 2–5 90.0, 3–4 90.0, 3–5 90.0, 4–5 0.0.

two crystallographically equivalent O(1) atoms. However, the C–O bond lengths of 1.25 and 1.26 Å indicate that these bonds are chemically equivalent with a statistical distribution of the electron density and, therefore, the observed differences in the Th–O(oda) lengths can best be attributed to packing constraints imposed by the crystalline arrangement or to other trivial factors.

Apart from the long Th–O(3) (ether) bond, the thorium–oxygen bond distances observed in this compound agree well with those generally found in other nine-co-ordinated thorium complexes with different ligands,[11-15] irrespective of the possibility that the co-ordination polyhedron is a monocapped square antiprism or a tricapped trigonal prism. Bond parameters of the oda moiety have the expected values [C(1)–O(1) 1.25 Å and C(1)–O(2) 1.26 Å] and are intermediate between C–O single and double bonds; the O(1)–C(1)–O(2) angle of 124° is consequently larger than the adjacent C(2)–C(1)–O ones (118°).

The sulphur atom, which lies on a two-fold symmetry axis, and the two pairs of O(4) and O(5) oxygens form the tetrahedral SO_4^{2-} ion. The lengths of the S–O bonds are equivalent, and apparently unaffected by co-ordination of O(4) and O(4^{IV}) to Th. The O–S–O angles subtended by symmetry-related oxygens (106°) are slightly smaller than those subtended by the non-symmetry-related ones (110° and 112°). Both the co-ordinated O(6) and O(6^{II}) and the free O(7) water molecule, which also lies on the two-fold axis, are involved in a rather complicated network of intra- and inter-molecular hydrogen bonds, lending additional stability to a very compact crystal packing.

The X-ray analysis has shown a C_2 crystal site symmetry for the title compound. The vibrational analysis was performed on the Th(oda) entity by neglecting intermolecular effects, except for the carboxylic-thorium ones, using our computer program UBATOR.[16] In the C_2 point group there are 48 non-redundant fundamentals, for this fragment, which are classified into 24(A) and 24(B) modes, all i.r. and Raman active. A Urey–Bradley force field (U.B.f.f.) was employed as

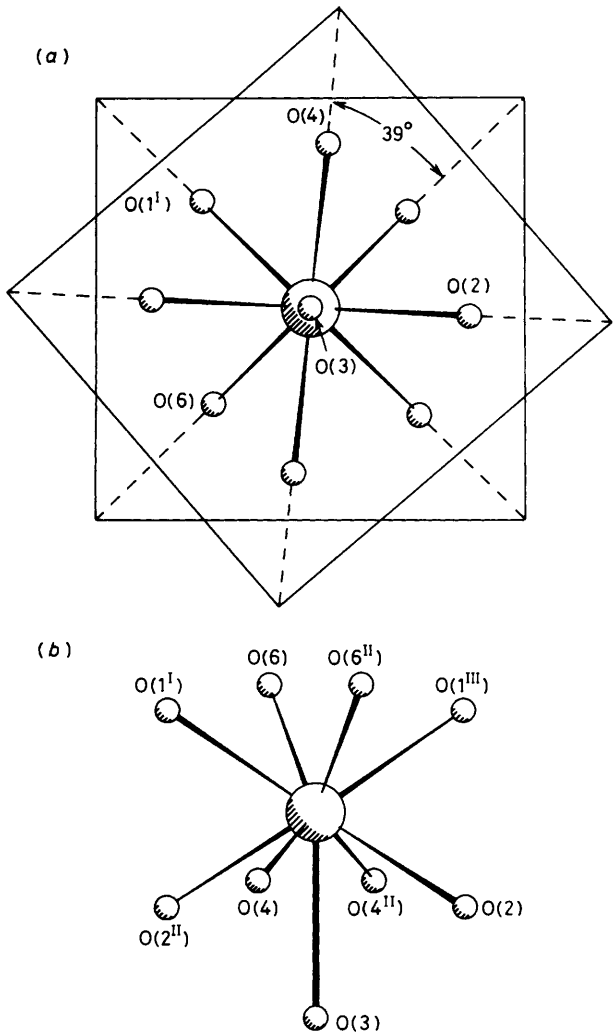

Figure 3. Nine-co-ordination of thorium. (*a*) Projection along the Th–O(3) bond direction; (*b*) projection perpendicular to the Th–O(3) bond direction

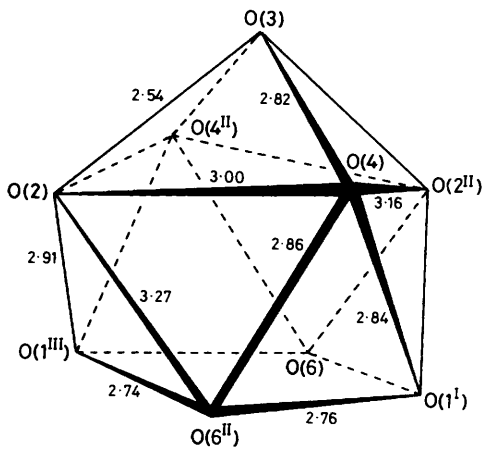

Figure 4. Schematic drawing of the monocapped square antiprismatic co-ordination polyhedron with the observed O · · · O edge contact distances (Å)

Table 5. Urey–Bradley force constants (10^2 N m^{-1})

Stretching			Bending			Repulsive		
K_1	Th–O(2)	1.63	H_1	Th–O(2)–C(1)	0.06	F_1	Th · · · C(1)	0.05
K_2	O(2)–C(1)	8.98	H_2	O(2)–Th–O(3)	0.07	F_2	O(2) · · · O(3)	0.08
K_3	C(1)–C(2)	2.77	H_3	O(2)–Th–O(2^{II})	0.08	F_3	O(2) · · · O(2^{II})	0.08
K_4	C(1)–O(1)	8.81	H_4	O(1)–C(1)–C(2)	0.28	F_4	O(1) · · · C(2)	0.54
K_5	C(2)–O(3)	3.98	H_5	O(1)–C(1)–O(2)	0.21	F_5	O(1) · · · O(2)	2.39
K_6	C(2)–H	4.02	H_6	O(2)–C(1)–C(2)	0.68	F_6	O(2) · · · C(2)	0.73
K_7	Th–O(3)	1.37	H_7	C(1)–C(2)–O(3)	0.85	F_7	C(1) · · · O(3)	0.15
K_8	Th–O(1^I)	1.30	H_8	C(1)–C(2)–H	0.30	F_8	C(1) · · · H	0.29
			H_9	C(1)–O(1)–Th^I	0.06	F_9	C(1) · · · Th	0.07
			H_{10}	H–C(2)–O(3)	0.22	F_{10}	H · · · O(3)	0.77
			H_{11}	C(2)–O(3)–Th	0.05	F_{11}	C(2) · · · Th	0.03
			H_{12}	C(2)–O(3)–C(2^{II})	0.31	F_{12}	C(2) · · · C(2^{II})	0.43
			H_{13}	H–C(2)–H	0.38	F_{13}	H · · · H	0.14

Table 6. Calculated and observed frequencies (cm^{-1}) and potential-energy distribution (%) *

Species	Calc.	Obs.	Description	Species	Calc.	Obs.	Description
A	2 934	2 935	$\nu_{sym}(CH_2)$ (99)	*B*	2 934	2 935	$\nu_{sym}(CH_2)$ (99)
	2 867	2 870	$\nu_{asym}(CH_2)$ (99)		2 870	2 870	$\nu_{asym}(CH_2)$ (100)
	1 592	1 590	$\nu_{asym}(COO)$ (82)		1 588	1 590	$\nu_{asym}(COO)$ (84)
	1 472	1 470	$\delta(CH_2)$ (75), $\nu_{sym}(COO)$ (19)		1 471	1 470	$\delta(CH_2)$ (78), $\nu_{sym}(COO)$ (15)
	1 430	1 435	$\nu_{sym}(COO)$ (52), $\delta(CH_2)$ (37)		1 423	1 422	$\nu_{sym}(COO)$ (68), $\delta(CH_2)$ (19)
	1 368	1 365	$\omega(CH_2)$ (55), $\nu_{asym}(COO)$ (20)		1 310	1 315	$\omega(CH_2)$ (77)
	1 250	1 242	$\tau(CH_2)$ (95)		1 272	1 265	$\tau(CH_2)$ (94)
	1 113	1 118	ν_{sym}[CO(3)] (41), $\omega(CH_2)$ (26), δ[CCO(3)] (10)		1 041	1 045	ν_{asym}[CO(3)] (62), $\omega(CH_2)$ (20)
	1 006	1 005	ν(CC) (66)		970	972	ν(CC) (58), δ(COO) (15)
	890	888	$\rho(CH_2)$ (88), $\nu_{asym}(CH_2)$ (11)		915	940	$\rho(CH_2)$ (88), $\nu_{asym}(CH_2)$ (10)
	751	747	δ(COO) (65), ν_{sym}(COO) (11)		734	728	δ(COO) (56), δ[CCO(3)] (18), ν_{sym}(COO) (10)
	570	555	δ(COO) (46), ν[ThO(3)] (15), ν_{sym}[CO(3)] (9)		638	620	δ(COO) (35), ν_{asym}[CO(3)] (19), ν(CC) (11)
	435	470	ν_{sym}[ThO(2)] (38), ν_{sym}[ThO(1)] (24), ν_{sym}[CO(3)] (14)		398	361	ν_{asym}[ThO(2)] (39), δ(COO) (22)
	328	363	ν[ThO(3)] (35), ν_{sym}[ThO(2)] (13), δ[CO(3)C] (12)		319	325	ν_{asym}[ThO(1)] (32), ν_{asym}[ThO(2)] (20), δ[CCO(3)] (12)
	226	236	ν[ThO(3)] (20), ν[ThO(1)] (13)		185	200	δ[ThO(2)] (63), δ(ring) (20)
	167	177	δ[ThO(2)C] (31), δ(ring) (53)		121	120	ν_{asym}[ThO(2)] (43), ν_{asym}[ThO(1)] (21), δ[ThO(2)C] (15)
	112	108	ν_{sym}[ThO(2)] (41), δ(ring) (23)				

* The rounded percentage potential-energy distribution values are shown in parentheses; small values have been neglected. Abbreviations: ν = stretching, δ = scissoring, ω = wagging, τ = twisting, ρ = rocking; and as subscripts, sym = symmetric and asym = asymmetric.

previously reported.[5,16] The best set of force constants is shown in Table 5, the measured and calculated frequencies (mean deviation less than 1%) and the relative assignment with the potential energy distribution are given in Table 6.

Four of the observed frequencies are assigned to superimposed or overlapping or negligibly split components of both *A* and *B* vibrational species, owing to internal motions of the isolated groups with a little contribution from intergroup coupling. As a result, we expect similar molecular vibrations for corresponding *A* and *B* modes which occur above 1 300 cm^{-1}, being those stretching and bending modes mainly due to CH_2 and COO groups. At lower frequencies, modes involving Th–O, C–C, C–O–C stretching and C–O–O, C–O–C, and O–Th–O angle bendings become more predominant and some of these vibrations contain appreciable intergroup coupling and pronounced splitting effects.

Only the assignment of the absorption bands associated with the co-ordinated groups will be briefly discussed, the other vibrations being generally unchanged if compared with those of analogous compounds.[5,16]

The spectrum shows a strong broad absorption at *ca.* 3 400 cm^{-1}, assigned to the water O–H stretching; the broadness of this band indicates the presence of hydrogen bonds. The asymmetric and symmetric stretching frequencies of the carboxylic groups occur at 1 590 and 1 435—1 422 cm^{-1} respectively, in agreement with the bidentate behaviour of the carboxylate groups, and the symmetric and asymmetric stretching frequencies of the ether group are shifted towards lower wavenumbers, by 21 and 9 cm^{-1} respectively, in comparison with the anionic ligand, confirming the co-ordination to the metal atom. The complex exhibits five bands between 560 and 170 cm^{-1}, due to metal–oxygen stretching modes plus ring deformation and breathing of the molecule in- and out-of-plane. The Th–O(ether) stretching mode is extensively coupled to a complicated mixed vibration between 555 and 236 cm^{-1}, as is the U–O(ether) one, in the [{UO_2(oda)}$_n$] complex, but at higher wavenumbers, and this agrees well with the relative stretching force constants (1.37×10^2 *versus* 1.10×10^2 N m^{-1} respectively). The values obtained for the force constants are consistent, generally, with those expected from structural and chemical considerations.

The sulphate ion belongs to the C_{2v} point group, owing to the lowering of symmetry caused by co-ordination, but only the ν_3 fundamental is observed split in the spectrum at 1 140, 1 115, and 1 040 cm^{-1}.

As for the correlation between the i.r. data and stability

constants measured in solution (~40 kJ mol^{-1}),[17] the thorium-containing compound has an intermediate behaviour between $[\{UO_2(ida)\}_n]$ (ida = iminodiacetate) and $[\{UO_2(oda)\}_n]$ complexes.

Acknowledgements

We thank Mr. V. Corrado for helpful technical assistance.

References

1 A. Cassol, P. DiBernardo, R. Portanova, and L. Magon, *Inorg. Chim. Acta*, 1973, **7**, 353.
2 G. Bombieri, R. Graziani, and E. Forsellini, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 551.
3 G. Bombieri, U. Croatto, R. Graziani, E. Forsellini, and L. Magon, *Acta Crystallogr., Sect. B*, 1974, **30**, 407.
4 G. Bombieri, E. Forsellini, G. Tomat, L. Magon, and R. Graziani, *Acta Crystallogr., Sect. B*, 1974, **30**, 2659.
5 G. A. Battiston, G. Sbrignadello, G. Bandoli, D. A. Clemente, and G. Tomat, *J. Chem. Soc., Dalton Trans.*, 1979, 1965.
6 G. Sbrignadello, G. Tomat, G. A. Battiston, G. DePaoli, and L. Magon, *Inorg. Chim. Acta*, 1976, **18**, 195.
7 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
8 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
9 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.
10 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *X*-RAY System of Crystallographic Programs, University of Maryland, U.S.A., 1972.
11 T. W. Hambley, D. L. Kepert, C. L. Raston, and A. H. White, *Aust. J. Chem.*, 1978, **31**, 2635.
12 J. G. Leipoldt, G. F. S. Wessels, and L. D. C. Bok, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2487.
13 V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, 1977, **92**, 3626.
14 R. J. Hill and C. E. F. Rickard, *J. Inorg. Nucl. Chem.*, 1975, **37**, 2481.
15 E. Huber-Buser, *Cryst. Struct. Commun.*, 1975, **4**, 731.
16 G. A. Battiston and G. Sbrignadello, *Inorg. Chim. Acta*, 1978, **26**, 145.
17 A. Bismondo, P. DiBernardo, G. Tomat, and A. Cassol, unpublished work.

Received 19*th April* 1982; *Paper* 2/650