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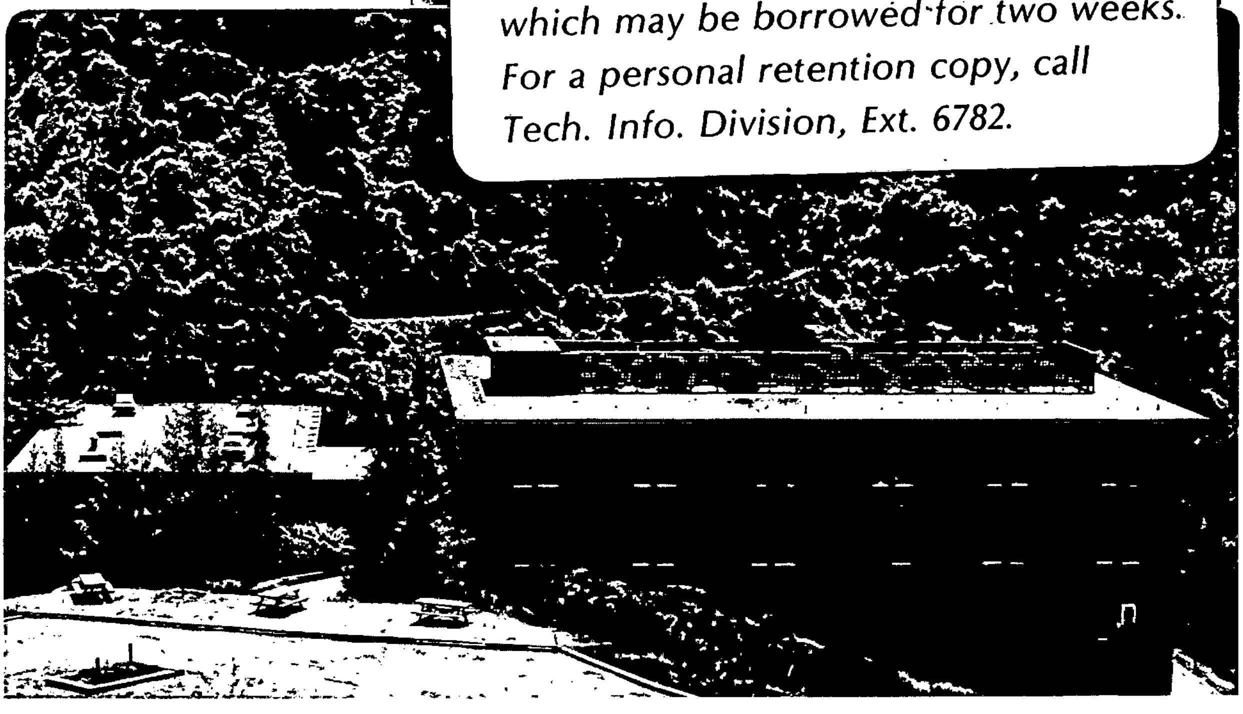
Paul E. Riley, Kamal Abu-Dari, and Kenneth N. Raymond

July 1982



LBL-15003 c.2

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DISCLAIMER

LBL-15003

Specific Sequestering Agents for the Actinides. 9. Synthesis of Metal Complexes of 1-Hydroxy-2(1H)-pyridinone and the Crystal Structure of Tetrakis(1-hydroxy-2(1H)-pyridinone)aquothorium(IV) Dihydrate[1]

By

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Received:

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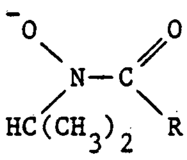
Abstract

The Zr(IV), Ce(IV), Th(IV) and U(IV) complexes of 1-hydroxy-2(1H)-pyridinone anion ($C_5H_4NO_2^-$) have been prepared and the crystal structure of the dihydrate of the nine-coordinate complex $(C_5H_4NO_2)_4(H_2O)Th$ has been determined by single crystal X-ray diffraction techniques with data obtained by counter methods. The compound crystallizes as colorless parallelepipeds in orthorhombic space group Pbcn with a = 12.880(1) Å, b = 8.812(2) Å, c = 20.826(2) Å. The calculated density of 2.041 g cm^{-3} agrees well with the measured value of 2.04 g cm^{-3} and is consistent with four formula units of the dihydrate per unit cell. Full-matrix least-squares refinement of the structure with use of the 2100 reflections with $F_o^2 > 3\sigma(F_o^2)$ has converged with R and R_w indices of 0.026. The Th(IV) complex consists of neutral molecules of rigorous C_2 symmetry in which Th(IV) and the coordinated water molecule lie along the C_2 axis parallel to b. The immediate coordination sphere about Th is completed by the eight oxygen atoms of the four bidentate $C_5H_4NO_2^-$ ligands, such that the resulting nine-coordinate complex resembles a D_{3h} tricapped trigonal prism.

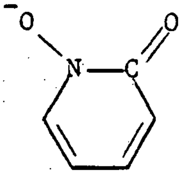
Introduction

The coordination chemistry of actinide(IV) ions is in some ways markedly similar to that of iron(III).[1,2] Hence, in our endeavors to design highly specific actinide(IV) sequestering agents, we have incorporated into our synthetic macrochelating ligands those groups, principally catecholate and hydroxamate, which are known to bind iron(III) strongly in the bacterial iron-transport and chelating agents called siderophores.

Clearly, detailed assessment of the architecture of the simple prototypical complexes formed between actinide(IV) ions and these small groups is particularly important if the desired synthetic macrochelating ligands are to be suitably designed to fulfill more satisfactorily — and hence more specifically — the coordination requirements of a particular actinide(IV) ion. Accordingly we have recently reported[2] the synthesis and the crystal structures of two eight-coordinate Th(IV) complexes of the bidentate hydroxamate ligand shown below (at left). We have now extended this work by preparing metal complexes of the related bidentate ligand 1-hydroxy-2(1H)-pyridinone ($C_5H_4NO_2^-$, above at right), which in one view represents a slight variation of the common hydroxamate ligand depicted above and in another is isoelectronic with the catecholate anion (N substituting for C in the ring). In this paper we report the synthesis of the Zr(IV), Ce(IV), Th(IV), and U(IV) complexes of this



R = $C(CH_3)_3$ or $CH_2C(CH_3)_3$



ligand and the crystal structure of the dihydrate of the $(C_5H_4NO_2)_4$-(H_2O)Th complex, the nuances of which will be used in our continuing design and refinement of actinide-specific macro-chelate sequestering agents.

Experimental Section

Materials. The ligand 1-hydroxy-2(1H)-pyridinone was purchased from Aldrich Chemical Company, anhydrous UCl_4 and $ThCl_4 \cdot 8H_2O$ from ROC-RIC Research Chemical Corporation, $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ from J. T. Baker Chemical Company, and aqueous $Zr(NO_3)_4$ from Alfa Products. All materials were used as supplied without further purification. The reaction with UCl_4 was conducted under dry argon using Schlenk line techniques with degassed aqueous solutions. However, unlike earlier work[2] with hydroxamate complexes of U(IV), the resulting complex was air-stable and decomposed to red UO_2^{2+} only after prolonged exposure to air.

Tetrakis(1-hydroxy-2(1H)-pyridinone)aquothorium(IV). A solution of 1.11 g (10 mmol) of 1-hydroxy-2(1H)-pyridinone in 10 mL of aqueous 1 M NaOH was added slowly with stirring to 20 mL of an aqueous solution of 1.30 g (2.5 mmol) of $ThCl_4 \cdot 8H_2O$. A clear solution was obtained which with additional stirring afforded a white precipitate. This white material was removed by filtration, washed several times with water to remove unreacted $ThCl_4 \cdot 8H_2O$ and ligand, and dried *in vacuo* over P_2O_5.

The preparations of the Zr(IV), Ce(IV), and U(IV) complexes were carried out as delineated for the Th(IV) species, except that the synthesis of the U(IV) complex was subject to the conditions cited above. All materials were recrystallized in air from a chloroform-ethanol mixture. Analytical data for all compounds are given in Table I.

Attempts to obtain single crystals suitable for X-ray diffraction studies have so far been successful only for the Th(IV) complex, which was recrystallized from a 1:1 mixture of $CHCl_3$ and 95% C_2H_5OH. Precession photographs of colorless parallelepiped which had been wedged into a thin-walled capillary displayed orthorhombic symmetry and systematic absences consistent with space group Pbcn. Preliminary examination of the data crystal with an Enraf-Nonius CAD 4 automated diffractometer confirmed the space group and cell constants, and demonstrated that the crystal was of good quality. The crystal mosaicity (measured from peak widths at half peak heights), as determined by ω-scans with a receiving aperature of 1 mm width, is ∿ 0.20° for intense, low-angle reflections. Accurate cell constants were determined from the refinement of 25 accurately centered high angle reflections selected from diverse regions of reciprocal space; intensity data were collected in accordance with previously published procedures.[3,4] Crystal data and those variables of data collection which are peculiar to this study are presented in Table II. The measured intensities were reduced, corrected for absorption, and assigned standard deviations with $p = 0.02$.[4]

The structure was solved by standard heavy atom procedures and refined by full-matrix least-squares methods[5] using only reflections with $F_o^2 > 3\sigma(F_o^2)$. The function minimized in refinement was $\Sigma w(|F_o| - |F_c|)^2$.[6] Neutral atom scattering factors for Th, O, N, C, and H, corrected for the anomalous scattering of MoK_α radiation, were used in these calculations.[4] Full-matrix least-squares refinement of the structure, in which the thermal motion of nonhydrogen atoms was treated anisotropically, converged with $\underline{R} = 0.026$, $\underline{R}_{\underline{w}} = 0.026$, and an error in an observation of unit weight of 1.18[7] for 2100 reflections and 165 variable. Hydrogen atoms of the ligand (located from a difference electron density map) were fixed at idealized positions[8] and assigned fixed isotropic thermal parameters of 5.0 Å^2, while those of the water molecules were not located. Distinction of the N atoms of the pyridinone rings was initially made from thermal parameters (with all atoms assigned as carbon) and subsequently confirmed from the final structure. Comparison of $|\underline{F}_{\underline{o}}|$ vs $|\underline{F}_{\underline{c}}|$ indicated that the data were affected by secondary extinction; hence, a small correction [2.9(3) x 10^{-8} e^{-2}] for this effect was included in the concluding cycles of refinement. In the final cycle of refinement, all shifts in parameters were less than 0.07 of a corresponding estimated standard deviation (esd). The largest peaks on a final difference Fourier map were 0.3 - 0.5 e Å^{-3} and were within 0.8 Å of the Th position or the water molecule [O(1)] bonded to Th. For comparison, the water molecules of this structure had heights of 3.2 and 5.2 e Å^{-3} on a previous difference Fourier map. Examination of $|\underline{F}_{\underline{o}}|$ vs $|\underline{F}_{\underline{c}}|$ at the end of refinement showed no trends as a function of $|\underline{F}_{\underline{o}}|$, sin θ/λ, or Miller index.[9]

Table III presents the positional parameters of the nonhydrogen atoms with esd's as derived from the least-squares inverse matrix. Tabulations of anisotropic thermal parameters (Table IV), hydrogen atom parameters (Table V), and observed and calculated structure factor amplitudes (Table VI) are available.[10]

Discussion

Figure 1 provides a stereoscopic view of the molecule and indicates the atom numbering scheme used herein. Selected bond lengths and bond angles are given in Table VII, and selected mean planes in Table VIII.[10]

The crystal structure of $(C_5H_4NO_2)_4(H_2O)Th\cdot 2H_2O$ consists of neutral molecules of rigorous $\underline{C}_2$ symmetry in which the Th ions and the oxygen atoms of the coordinated H_2O molecules [O(1)] lie along the crystallographic twofold axes parallel to $\utilde{b}$. The immediate coordination sphere about Th is completed by the eight oxygen atoms of the four bidentate $C_5H_4NO_2^-$ ligands, such that the resulting nine-coordinate complex resembles a $\underline{D}_{3\underline{h}}$ tricapped trigonal prism (see below). Both hydrogen atoms of O(1) (which are equivalent by $\underline{C}_2$ symmetry) are hydrogen-bonded to water molecules O(2) which lie off the $\underline{C}_2$ axis. These molecules in turn are hydrogen-bonded to one of the two O(22) atoms which are related by the $\underline{C}_2$ axis and which define one of the polyhedral edges, which is approximately parallel to the pseudo $\underline{C}_3$ axis of the distorted $\underline{D}_{3\underline{h}}$ polyhedron (see Figure 2). In addition, each O(2) water molecule is hydrogen-bonded to an O(11) atom of an adjacent polyhedron, thereby linking all of the molecules of the structure together.

The Th-O(1) distance of 2.522(4) Å is slightly longer than the other Th-O distances of this complex, which average 2.44(2) Å[11] and thus compare favorably with the mean distance (2.445 Å) found in tetrakis(tropolonato)-N,N'-dimethylformamidethorium(IV).[12] This longer distance may be ascribed to the strength of the hydrogen bonds formed between O(1) and water molecules O(2) (2.65 Å) and/or the weaker interaction between the highly charged Th^{4+} ion and the uncharged H_2O

molecule O(1). In the structures of the two eight-coordinate hydroxamate complexes of Th^{4+} mentioned above,[2] the Th-O_N bonds are 0.10 and 0.14 Å shorter than the Th-O_C bonds. In the nine-coordinate complex reported here, this difference is less pronounced (∿ 0.07 Å, see Table VII) and thus is consistent with the greater delocalization of charge on this cyclic ligand compared with the more localized charge of the hydroxamate ligands.

An analysis[13] of the coordination polyhedron formed by the nine oxygen atoms bound to thorium is summarized in Table IX. The two most plausible polyhedra for a nine-coordinate complex are the tricapped trigonal prism (D_{3h}) and the monocapped square antiprism (C_{4v}). Although the geometry of this thorium complex is intermediate between these two idealized forms, it resembles a D_{3h} prism more closely than a C_{4v} antiprism (see Figure 2). Furthermore, despite possessing only C_2 symmetry, the deviations of this polyhedron from C_{2v} symmetry (a subgroup of both D_{3h} and C_{4v}) are small (see Table X). This arrangement of atoms, in which the lone monodentate ligand [O(1)] lies on a crystallographic C_2 axis, is in agreement with our view of the coordination polyhedron as a distorted D_{3h} polyhedron rather than a distorted C_{4v} polyhedron; although as the geometry and point symmetry indicate, this compound's structure lies on the reaction coordinate corresponding to the highest symmetry path between these polyhedra. In the C_{4v} structure, the unique monodentate ligand would not lie on what would have been the C_2 axis of the idealized polyhedron; that is, O(1) is not the capping atom of a distorted monocapped square antiprism. In addition, the values of the equatorial bond angles about Th (see Table VII) offer further support for the view that this polyhedron is closer to $\underline{D}_{3h}$ symmetry than to $\underline{C}_{4v}$. It is then of interest to note that the coordination geometry of the tropolonato complex of thorium-12 more nearly conforms to that of a $\underline{C}_{4v}$ polyhedron than to that of a $\underline{D}_{3h}$ polyhedron, despite the similarity of these unsaturated bidentate ligands.

Acknowledgment

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Supplementary Material

Listings of anisotropic thermal parameters (Table IV), idealized hydrogen atom parameters (Table V), observed and calculated structure factor amplitudes (Table VI, 23 pages), and selected least-squares planes (Table VIII). Ordering information is given on any current masthead.

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1. Previous paper in this series: Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 1676.
2. Smith, W. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 3341 and references therein.
3. Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* **1980**, *19*, 2034.
4. Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 0000.
5. The computer program package used in this work is cited in Ref. 4.
6. The weight w used in refinement is $4F_o^2/\sigma^2(F_o^2)$ (the reciprocal square of the standard deviation of each observation $|F_o|$).
7. The error indices are: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, and the error in the observation of unit weight $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations $|F_o|$ and N_v is the number of variables in refinement.
8. The C-H bond lengths were constrained to 0.95 Å in accordance with a previous study: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.
9. This analysis was made with the FORTRAN program REVAL, written locally by F. J. Hollander.
10. Supplementary material.
11. A mean bond length $\bar{\ell}$ and its estimated standard deviation $\sigma(\bar{\ell})$ are given by $\bar{\ell} = \sum_i^n \ell_i/n$ and $\sigma(\bar{\ell}) = \left[\frac{\sum_i (\ell_i - \bar{\ell})^2}{n(n-1)}\right]^{1/2}$.
12. Day, V. W.; Hoard, J. L. *J. Am. Chem. Soc.* **1976**, *92*, 3626.
13. Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 7221.

Table I. Analytical results[a]

Complex	Color	% Calculated				% Found			
		C	H	N	Metal	C	H	N	Metal
$(C_5H_4NO_2)_4Zr\cdot CHCl_3$	white	38.75	2.63	8.60	14.0	40.51	3.00	8.63	16.0
$(C_5H_4NO_2)_4Ce\cdot H_2O$	red	39.83	2.77	9.13	-	40.13	3.00	9.36	-
$(C_5H_4NO_2)_4Th\cdot H_2O$	colorless	34.79	2.62	8.11	-	35.00	2.54	7.85	-
$(C_5H_4NO_2)_4U\cdot CHCl_3$	blue-green	31.62	2.15	7.02	29.8	32.25	2.24	7.25	31.2

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[a] Microanalyses were performed by Analytical Services, Department of Chemistry, University of California, Berkeley. Analyses for metal content were carried out locally by atomic absorption spectroscopy.

Table II. Crystallographic summary for $(C_5H_4NO_2)_4(H_2O)Th\cdot 2H_2O$[a]

a, Å	12.880(1)	Space group	*Pbcn* (no. 60)
b, Å	8.812(2)	Mol. formula	$C_{20}H_{18}N_4O_9Th$
c, Å	20.826(2)	Fw of complex	690.42
V, Å^3	2363.7(4)	Z	4
2θ range for cell constants, deg	18.2-20.5	d_{measd}^{b} g cm^{-3}	2.04
Crystal system	orthorhombic	d_{calcd} g cm^{-3}	2.041
Systematic reflection absences	0kℓ, k = 2n+1, h0ℓ, ℓ = 2n+1; hk0, h+k = 2n+1	F(000), electrons	1392
2θ range for data collection, deg	3.0-70.0	Data crystal faces	(100), $(\bar{1}00)$, (011), $(0\bar{1}\bar{1})$, $(01\bar{1})$, $(01\bar{1})$
Total reflections measured	5188	Absorption coeff., (μMoK_α), cm^{-1}	65.8
Check reflections	no decay over 95 h of data collection	Transmission factor range[c]	0.39-0.63
Data crystal dimensions, mm	0.08 x 0.18 x 0.18		

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[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Flotation at 20°C in a $CHBr_3/CCl_4$ mixture.

[c] Examination of six reflections with $\chi = 90 \pm 10°$ at approximately regular intervals ($\Delta 2\theta = 5°$) in reciprocal space for $10 < 2\theta < 37°$ by the psi scan technique revealed an appreciable variation in normalized transmission factors (0.64 - 1.00), thereby suggesting the need for an absorption correction.

Table III. Fractional Coordinates of Nonhydrogen Atoms[a]

ATOM	X	Y	Z
TH	0.0000(0)	0.09845(2)	0.2500(0)
O(11)	0.1570(2)	-0.0015(4)	0.2017(2)
O(12)	-0.0143(2)	0.0143(4)	0.1372(2)
O(21)	0.1552(2)	0.2146(4)	0.2882(2)
O(22)	-0.0237(2)	0.3241(4)	0.3198(2)
O(1)	0.0000(0)	-0.1878(5)	0.2500(0)
O(2)	0.1342(3)	-0.4086(4)	0.2268(2)
N(1)	0.1502(3)	-0.0772(4)	0.1452(2)
N(2)	0.1515(3)	0.3236(5)	0.3328(2)
C(11)	0.0587(4)	-0.0644(6)	0.1121(3)
C(12)	0.0542(5)	-0.1390(7)	0.0526(3)
C(13)	0.1362(6)	-0.2233(7)	0.0299(3)
C(14)	0.2249(5)	-0.2373(7)	0.0666(3)
C(15)	0.2306(4)	-0.1629(6)	0.1231(3)
C(21)	0.0570(4)	0.3790(5)	0.3496(3)
C(22)	0.0522(4)	0.4938(7)	0.3952(3)
C(23)	0.1404(6)	0.5488(7)	0.4219(3)
C(24)	0.2373(5)	0.4922(7)	0.4038(3)
C(25)	0.2410(4)	0.3804(6)	0.3592(3)

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[a] See Figure 1 for identity of the atoms. Numbers in parentheses are the estimated standard deviations in the least significant digits.

Table VII. Selected bond lengths (Å) and bond angles (deg) for $(C_5H_4NO_2)_4(H_2O)Th\cdot 2H_2O$[a]

Th-O(11)	2.424(3)	Th-O(22)	2.482(4)
Th-O(12)	2.469(4)	O(21)-N(2)	1.336(5)
O(11)-N(1)	1.356(5)	O(22)-C(21)	1.303(6)
O(12)-C(11)	1.281(6)	N(2)-C(21)	1.358(6)
N(1)-C(11)	1.371(6)	C(21)-C(22)	1.390(7)
C(11)-C(12)	1.403(8)	C(22)-C(23)	1.354(8)
C(12)-C(13)	1.375(8)	C(23)-C(24)	1.396(9)
C(13)-C(14)	1.380(9)	C(24)-C(25)	1.355(7)
C(14)-C(15)	1.348(9)	C(25)-N(2)	1.372(6)
C(15)-N(1)	1.361(7)	O(11)···O(12)	2.587(5)
Th-O(1)	2.522(4)	O(21)···O(22)	2.582(4)
Th-O(21)	2.382(3)		

O(11)-Th-O(12)	63.8(1)	O(1)-Th-O(21)	115.4(1)
O(11)-Th-O(22)'	86.9(1)	O(21)-Th-O(21)'	129.1(2)
O(12)-Th-O(22)'	72.1(1)		

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[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. Coordinates of primed atoms are related to the correspondingly numbered atoms of Table III by the C_2 transformation $\bar{x}$, y, $1/2 - z$.

Table IX. Comparison of dihedral angles δ (deg) of $(C_5H_4NO_2)_4(H_2O)Th$ to those of the idealized D_{3h} and C_{4v} polyhedra[a]

Type of faces	Position	Idealized δ	Face 1[b]	Face 2[b]	Determined δ
		D_{3h} tricapped trigonal prism			
Opposed (⊥)	⊥ threefold axis	180	O(11), O(22)', O(12)	O(12)', O(22), O(11)'	159.2
Opposed (‖)	‖ threefold axis	146.4	O(21), O(22)', O(22)	O(1)', O(11)', O(12)	149.5
			O(21), O(12)', O(11)	O(21)', O(11)', O(12)	130.8
			O(1), O(12)', O(11)	O(21)', O(22), O(22)'	149.5
Vicinal (‖)	‖ threefold axis	26.4	O(21), O(22)', O(22)	O(21)', O(22), O(22)'	49.0
			O(21)', O(11)', O(12)	O(1), O(11)', O(12)	12.5
			O(1), O(12)', O(11)	O(21), O(12)', O(11)	12.5
		C_{4v} monocapped square antiprism			
Opposed	1 vertex on square face	163.5	O(1), O(11)', O(12)	O(21), O(22)', O(22)	149.5
			O(12)', O(11)', O(22)	O(11), O(12), O(22)'	159.2
Opposed	2 vertices on square face	138.2	O(1), O(12)', O(11)'	O(21), O(11), O(22)'	144.2
			O(21), O(12)', O(22)	O(1), O(11), O(12)	129.9
Vicinal (⊥)	⊥ fourfold axis	0	O(12)', O(1), O(11)	O(12)', O(21), O(11)	12.5
			O(1), O(12)', O(21)	O(1), O(11), O(21)	13.6

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[a] Shape-determining dihedral angles for these idealized polyhedra and definition of face type are given in Ref. 13. [b] See Figure 1 for identity of atoms. Primed atoms are related to the positions of the correspondingly numbered unprimed atoms of Table III by the C_2 transformation $\bar{x}$, y, $1/2 - z$.

Table X. Deviations from the symmetry plane of an idealized $\underline{C}_{2\underline{v}}$ polyhedron[a]

Atom	Displacement (A)	Atom	Displacement (A)
O(11)	-1.269(4)	O(12)	1.313(4)
O(22)	-0.447(4)	O(22)'	0.447(4)

Atoms[b]	Dihedral angle (deg)
O(12)', MID2, MID1, O(11)	2.6
O(11)', MID2, MID1, O(12)	2.6
O(22), MID2, MID1, O(22)'	19.1

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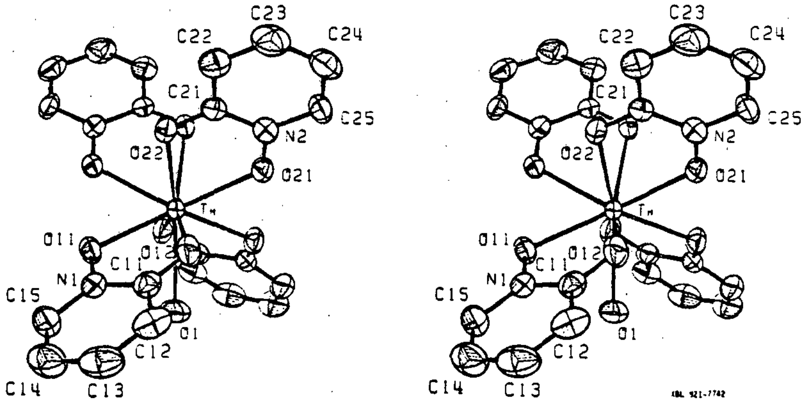
[a] Pseudo symmetry plane formed by atoms Th and O(1) and the point between O(11) and O(12) which yields the plane which is normal to the O(11), O(12), O(11)', O(12)' least-squares plane. Coordinates of primed atoms are related to the correspondingly numbered atoms of Table III by the $\underline{C}_2$ transformation $\bar{\underline{x}}$, $\underline{y}$, $1/2 - \underline{z}$.

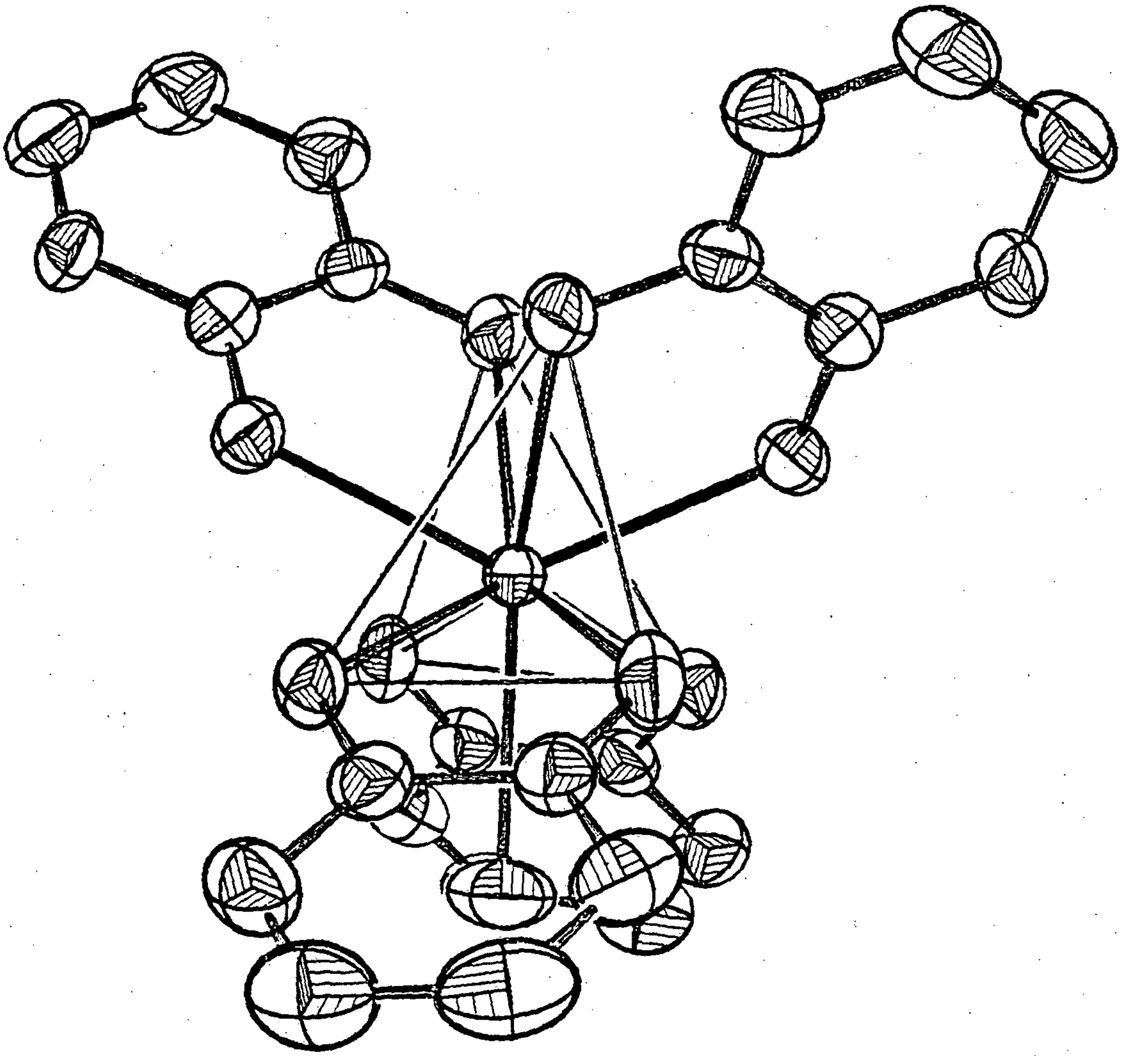
[b] MID1 and MID2 represent the centroids of the opposing faces formed by [O(11), O(12), O(12)'] and [O(12)', O(11)', O(22)].

Figure Captions

Figure 1. Stereoscopic view of $(C_5H_4NO_2)_4(H_2O)Th$, illustrating the atom-numbering scheme. Atoms are drawn as ellipsoids of 50% probability; hydrogen atoms have been omitted for clarity. A crystallographic $\underline{C}_2$ axis is coincident with the Th-O(1) bond and thus carries the left and right halves of the molecule into each other. For sake of clarity, the atoms labeled O(11), N(1), ···, O(12) are related to the correspondingly named atoms of Table III by the operation $\bar{\underline{x}}$, $\underline{y}$, $1/2 - \bar{\underline{z}}$.

Figure 2. Projection normal to the plane formed by the vectors along the Th-O(1) bond and the O(21) to O(21)' direction; i.e., approximately along the pseudo-$\underline{C}_3$ axis of the molecule. Atoms are drawn as ellipsoids of 50% probability and hydrogen atoms have been excluded for clarity.


C23
C22
C24
C21
C25
N2
O22
O21
Tm
O11
O12
C11
N1
C15
O1
C12
C14
C13
C23
C22
C24
C21
C25
N2
O22
O21
Tm
O11
O12
C11
N1
C15
O1
C12
C14
C13
XBL 821-7742



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