

**Table III.** Principal Electronic Absorption Bands<sup>a</sup> of Fe(III)-DA-BDHT[30]N<sub>6</sub> (Fe<sup>III</sup>(2)) as a Function of p[H]

p[H]	λ, nm	ε, M <sup>-1</sup> cm <sup>-1</sup>	λ, nm	ε, M <sup>-1</sup> cm <sup>-1</sup>	comments
2.90	440	2400	572	3500	a = 0, "MH <sub>3</sub> L"
4.09	442	2879	565	4070	a = 4, "ML <sub>2</sub> L"
9.03	448	4050	552	3680	a = 6, "ML"
10.60	440	4420	520	3500	a = 7, "MLOH"

<sup>a</sup> In H<sub>2</sub>O at 25.0 °C; μ = 0.100 M.

**Table IV.** Logarithms of the Formation Constants of Protonated Macrocylic Complexes of Fe(III)

formation equilibrium	DA-BDHT-[26]N <sub>6</sub> (1)	DA-BDHT-[30]N <sub>6</sub> (2)	TRIMER <sup>a</sup>
Fe <sup>3+</sup> + HL <sup>5-</sup> ⇌ FeHL <sup>2-</sup>	36.0	34.52	34.7
Fe <sup>3+</sup> + H <sub>2</sub> L <sup>4-</sup> ⇌ FeH <sub>2</sub> L <sup>-</sup>	32.8	31.34	28.7
Fe <sup>3+</sup> + H <sub>3</sub> L <sup>3-</sup> ⇌ FeH <sub>3</sub> L	27.1	25.09	

<sup>a</sup> TRIMER = ((*p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>)(CO)<sub>2</sub>)<sub>3</sub>(NHCH<sub>2</sub>CH<sub>2</sub>NH)<sub>3</sub>; see ref 9.

ligands, and greater metal binding by the protonated forms of the ligand that are predominant at physiological pH. Table IV shows the formation constants derived from the corresponding values of the equilibrium constants listed in Tables I and II.

The question has been raised<sup>9</sup> as to why the stability constant of the Fe(III) chelate of **17** turns out to be so much lower than that of enterobactin (log *K* ca. 52), in view of the fact that models show that Fe(III) coordination by all three catechol moieties can readily take place. The same questions might be raised for ligands **1** and **2**; however it should be pointed out that these sexadentate and octadentate ligands cannot conform to the octahedral coordination sphere of the metal ion without considerable distortion, involving twisting of the connecting bridges between the bidentate donor groups, which are made somewhat rigid by the trigonal amide pairs that extend the planarity of the aromatic rings. Such twisting would cost energy arising from the internal repulsions of the flexible ethylene groups of **17**, as well as **1**. The more flexible trimethylene bridge of **2** should provide some advantage in this respect. Another factor that would tend to lower the metal ion stability constants of **1**, **2**, and **17** would be the considerable

loss of entropy associated with the conversion of a flexible macrocyclic ring to a relatively rigid distorted conformation when it is completely coordinated to a central metal ion.

The stabilizing influence of the so-called "macrocyclic effect" does not seem to be operating effectively for the iron(III) chelates of ligands **1**, **2**, and **17**. It should be noted, however, that the macrocyclic effect applies only when the fit between the metal ion and the cavity of the macrocycle is reasonably close, and the macrocyclic stability increment falls off very rapidly when the ring is too large or too small. Presumably this is the situation for all three ligands discussed here.

Because of the fact that the use of CPK space-filling models indicates that the structure of the iron(III) chelate of **1** is somewhat crowded, it had been thought that its stability constant for Fe(III) would be somewhat lower than that of **2**. That such is not the case indicates that the macrocyclic ring of **2** may be too large, and that the optimum size may be somewhere in between (i.e., a ring with 28 atoms). The difference of four atoms between the ring sizes of **1** and **2** is seen to be a matter of convenience in synthesis. Nevertheless, an attempt should be made to devise a convenient synthetic scheme for a 28-membered macrocyclic ring containing two catechols and two additional donors, and work along these lines is currently being planned.

In order to design sexadentate ligands with six donor groups that closely conform to an octahedral structure without considerable twisting and distortion, cryptand type ligands similar in design to the one reported by Wolfgang and Vogtle<sup>8</sup> are needed. With the cryptates, however, the preciseness of fit between the metal ion and the cryptand cavity is even more important than for the simpler macrocyclic ligands. Thus the synthetic problems for such ligands may be more severe, but the rewards in terms of high stability and selectivity would seem to make the required synthetic efforts very worthwhile.

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**Registry No.** **1**, 105103-80-8; **2**, 105103-79-5; **3**, 111-42-2; **4**, 16695-22-0; **5**, 23538-91-2; **6**, 23539-15-3; **7**, 7169-12-2; **8**, 105139-38-6; **9**, 105103-82-0; **10**, 111-40-0; **11**, 56-18-8; **12**, 56642-94-5; **13**, 105103-83-1; **14**, 105103-84-2; **15**, 105103-85-3; **16**, 105103-81-9.

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## Thorium and Uranium Porphyrins. Synthesis and Crystal Structure of Bis(acetylacetonato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)thorium(IV)

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The action of thorium tetrachloride or uranium tetrachloride with porphyrins affords the dichloro complexes (Por)MCl<sub>2</sub> (M = Th or U). The latter derivatives react with sodium acetylacetonate giving rise to bis(acetylacetonato) complexes (Por)M(acac)<sub>2</sub>. The two series of complexes are characterized on the basis of mass spectral, IR, UV-visible, and NMR data. The crystal structure of the title compound has been determined by X-ray diffraction methods: (OEP)Th(acac)<sub>2</sub>, C<sub>46</sub>H<sub>58</sub>N<sub>4</sub>O<sub>4</sub>Th; *M<sub>r</sub>* = 963; triclinic, *P*1̄; *a* = 9.493 (7), *b* = 21.185 (5), *c* = 24.331 (7) Å; α = 104.18 (2), β = 96.11 (4), γ = 92.35 (4)°; *V* = 4705 Å<sup>3</sup>; *d*<sub>calc</sub> = 1.359 g cm<sup>-3</sup>; *Z* = 4; *T* = 298 K. A total of 9019 intensities were measured on a CAD 4 Enraf-Nonius diffractometer in the ω-2θ scan mode with monochromatized Mo Kα radiation (1.5 < θ < 20°). The crystal structure was refined to a conventional *R*(*F*) = 0.047 for 5323 reflections having σ(*I*)/*I* < 0.33. The thorium atom is octacoordinated by the four porphyrin nitrogen atoms and by the four oxygen atoms of the two acetylacetonato groups.

### Introduction

There has recently been considerable work in metalloporphyrin chemistry because some complexes are of great interest as model compounds for understanding the function and relationships of

several biological macromolecules. The chemical reactivity of this family of compounds has also attracted interest from their potential use in the activation of small molecules.<sup>2-4</sup> However, complexes

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(2) Smith, K. M., Ed. *Porphyrins and Metalloporphyrins*; Elsevier: Amsterdam, 1975.

**Table I.** Characteristics of Reactions, Elemental Analyses, and Mass Spectral Data

complex	recrystn solvent <sup>a</sup>	yield, %	anal., % <sup>b</sup>					mass spectra			
			C	H	N	Cl	Th (or U)	<i>m/e</i>	rel intens, %	fragmentation pattern	
(OEP)ThCl <sub>2</sub> ·2C <sub>6</sub> H <sub>5</sub> CN ( <b>1a</b> )	4/2/0.5 A/B/C	82	57.3 (57.64)	5.2 (5.18)	7.8 (8.07)	6.6 (6.82)	22.0 (22.28)	834 799	100 15	[(OEP)ThCl <sub>2</sub> ] <sup>+</sup> [(OEP)ThCl] <sup>+</sup>	
(TPP)ThCl <sub>2</sub> ·2C <sub>6</sub> H <sub>5</sub> CN ( <b>1b</b> )	4/2/0.5 A/B/C	78	60.4 (61.39)	3.7 (3.54)	7.7 (7.82)	6.5 (6.61)	21.0 (21.62)	914 879 908	5 10 100	[(TPP)ThCl <sub>2</sub> ] <sup>+</sup> [(TPP)ThCl] <sup>+</sup> [(OEP)UCl(C <sub>6</sub> H <sub>5</sub> CN)] <sup>+</sup>	
(OEP)UCl <sub>2</sub> ·2C <sub>6</sub> H <sub>5</sub> CN ( <b>2a</b> )	4/1/0.5 A/B/C	79	57.0 (57.30)	5.3 (5.16)	7.8 (8.02)	6.5 (6.78)	21.0 (22.73)	840 805	2 54	[(OEP)UCl <sub>2</sub> ] <sup>+</sup> [(OEP)UCl] <sup>+</sup>	
(TPP)UCl <sub>2</sub> ·2C <sub>6</sub> H <sub>5</sub> CN ( <b>2b</b> )	4/1/0.5 A/B/C	75	59.9 (60.05)	3.3 (3.52)	7.7 (7.78)	6.4 (6.58)	21.3 (22.05)	920 885	48 48	[(TPP)UCl <sub>2</sub> ] <sup>+</sup> [(TPP)UCl] <sup>+</sup>	
(OEP)Th(acac) <sub>2</sub> ( <b>3a</b> )	4/1 D/E	70	57.4 (57.38)	6.2 (6.03)	5.8 (5.82)		23.7 (24.12)	962 863	60 100	[(OEP)Th(acac) <sub>2</sub> ] <sup>+</sup> [(OEP)Th(acac)] <sup>+</sup>	
(TPP)Th(acac) <sub>2</sub> ( <b>3b</b> )	4/1 D/E	67	62.1 (62.18)	4.1 (4.03)	5.5 (5.37)		21.4 (22.26)	943 872	71 15	[(TPP)Th(acac)] <sup>+</sup> [(TPP)ThCO] <sup>+</sup>	
(OEP)U(acac) <sub>2</sub> ( <b>4a</b> )	4/1 D/E	68	57.1 (57.02)	6.2 (5.99)	5.6 (5.78)		25.0 (24.59)	968 869	30 100	[(OEP)U(acac) <sub>2</sub> ] <sup>+</sup> [(OEP)U(acac)] <sup>+</sup>	
(TPP)U(acac) <sub>2</sub> ( <b>4b</b> )	4/1 D/E	65	62.0 (61.83)	4.0 (4.00)	5.4 (5.34)		22.1 (22.71)	949 878	40 10	[(TPP)U(acac)] <sup>+</sup> [(TPP)UCO] <sup>+</sup>	

<sup>a</sup>Key: A, toluene; B, tetrahydrofuran; C, pyridine; D, CHCl<sub>3</sub>; E, pentane. <sup>b</sup>Calculated values are given in parentheses.

**Table II.** <sup>1</sup>H NMR Data

complex	R <sup>1</sup>	R <sup>2</sup>	protons of R <sup>1</sup>		protons of R <sup>2</sup>		protons of acac	
			multiplicity <sup>a</sup> / intensity	δ	multiplicity/ intensity	δ	multiplicity/ intensity	δ
<b>1a</b>	H	C <sub>2</sub> H <sub>5</sub>	s/4	10.49	m/8 m/8 t/24	4.28 4.21 1.89		
<b>1b</b>	C <sub>6</sub> H <sub>5</sub>	H	m/12 m/8	7.64 8.08	s/8	8.84		
<b>2a</b>	H	C <sub>2</sub> H <sub>5</sub>	s/4 <sup>b</sup>	2.80	M/8 M/8 t/24	1.49 1.17 0.00		
<b>2b</b>	C <sub>6</sub> H <sub>5</sub>	H	m/8 m/8 m/4	4.7 5.7 6.1	s/8	4.88		
<b>3a</b>	H	C <sub>2</sub> H <sub>5</sub>	s/4	10.33	2q/16 t/24	4.19 1.95	s/2 s/12	4.22 1.37
<b>3b</b>	C <sub>6</sub> H <sub>5</sub>	H	m/12 m/8	7.86 8.35	s/8	8.95	s/2 s/12	4.27 1.24
<b>4a</b>	H	C <sub>2</sub> H <sub>5</sub>	s/4	-1.48	m/8 m/8 t/24	-0.31 -1.38 -0.85	s/2 s/12	9.87 -7.42
<b>4b</b>	C <sub>6</sub> H <sub>5</sub>	H	m/8 m/8 m/4	4.3 5.2 6.3	s/8	5.96	s/2 s/12	13.64 -5.65

<sup>a</sup>Key: s, singlet; q, quadruplet; t, triplet; m, multiplet; M, massive. <sup>b</sup>Very broad signal.

of uranium have never been reported and very few results regarding thorium porphyrins have been published.<sup>5,6</sup> In a preliminary note<sup>7</sup> we described the synthesis and spectroscopic characterization of thorium(IV) and uranium(IV) porphyrins (Por)MCl<sub>2</sub><sup>8</sup> (M = Th or U). The preparation of dichloro complexes was accomplished by treating porphyrins with thorium tetrachloride or uranium tetrachloride. We now report the complete synthesis and properties of (Por)MCl<sub>2</sub> and (Por)M(acac)<sub>2</sub>. The latter derivatives were synthesized by the reaction of sodium acetylacetonate with (Por)MCl<sub>2</sub>. Total characterizations of these compounds were obtained on the basis of elemental analysis and <sup>1</sup>H NMR, IR, UV-visible, and mass spectral data. An X-ray

study was carried out for the complex (OEP)Th(acac)<sub>2</sub>. Moreover, this latter derivative and uranium complex (OEP)U(acac)<sub>2</sub> are isomorphous. The presented structure provides the first X-ray data on a porphyrin coordinated to a metal of the actinide series.

### Experimental Section

The synthesis and handling of the metalloporphyrins and metal tetrachlorides were carried out under an atmosphere of argon. All common solvents were thoroughly dried in a manner appropriate to each and were distilled under argon prior to use. All operations were carried out in Schlenk tubes under purified argon and with oxygen-free solvents.

**Synthesis.** (Por)MCl<sub>2</sub> molecules (M = Th or U) were synthesized by the reaction of thorium tetrachloride or uranium tetrachloride with porphyrins. The reaction of Na(acac) with (Por)MCl<sub>2</sub> gave the corresponding complexes (Por)M(acac)<sub>2</sub>. Detailed procedures for the preparation of (OEP)ThCl<sub>2</sub> and (OEP)Th(acac)<sub>2</sub> are given below.

**Dichloro(2,3,7,8,12,13,17,18-octaethylporphyrinato)thorium(IV).** A mixture of 4.01 mmol of ThCl<sub>4</sub> and 1.31 mmol of (OEP)H<sub>2</sub> in 40 mL of benzonitrile was introduced in a reactor provided with magnetic stirring, and 10 mL of pyridine was added. The mixture was then heated at 150 °C during 4 h. The reaction was monitored by UV-visible spectroscopy, and after completion of the reaction, the solution was evaporated under reduced pressure. The crude material was recrystallized from 40 mL of toluene, 20 mL of tetrahydrofuran, and 5 mL of

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(5) Wong, L. P.; Horrocks, W. D., Jr. *Tetrahedron* **1975**, *31*, 2637.

(6) Gouterman, M., private communication.

(7) Dormond, A.; Belkalem, B.; Guillard, R. *Polyhedron* **1984**, *3*, 107.

(8) Abbreviations: Por = porphyrinate(2-); OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2-); TPP = 5,10,15,20-tetraphenylporphyrinate(2-); acac = acetylacetonate; AcO = acetate.

Table III. Characteristic IR and UV-Visible Data

complex	IR $\nu(\text{M-L}),^a \text{ cm}^{-1}$	Soret band, $\text{cm}^{-1}$	UV-vis $\lambda$ , nm	
1a	255	404	534	572
1b	263	424	512	550
2a	255	405	536	574
2b	266	428	512	553
3a	1577, 1524, 407, 392	408	535	573
3b	1565, 1521, 407, 390	418	509	553
4a	1572, 1516, 409, 392	407	536	574
4b	1567, 1524, 407, 390	420	510	553

<sup>a</sup>L = Cl or acac.

pyridine to give 82% yield of (OEP)ThCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN.

**Bis(acetylacetonato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)thorium(IV).** To 0.816 mmol of (OEP)ThCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN in 40 mL of THF was added a solution of 1.8 mmol of sodium acetylacetonate in 30 mL of THF. The reaction was stopped after 15 min, and the reaction medium was hydrolyzed with 200 mL of deoxygenated saturated sodium carbonate solution. The precipitate was filtered out and then dried. The crude product was recrystallized from CHCl<sub>3</sub> (40 mL)/pentane (10 mL), and the yield of the reaction was about 67%.

The conditions, yields, and spectroscopic data of the synthesized complexes are summarized in Tables I-III.

**Physical Measurements.** Elemental analyses were performed by the Service de Microanalyse du CNRS. Mass spectra were recorded in the electron-impact mode with a Finnigan 3330 spectrometer: ionizing energy, 70 eV; ionizing current, 0.4 mA; source temperature, 250-400 °C. <sup>1</sup>H NMR spectra were recorded on a JEOL FX 100 spectrometer or on a Bruker WM 400 of the Cerema (Centre de Résonance Magnétique of the University of Dijon). Spectra were measured for complex solutions in 0.5 mL of CDCl<sub>3</sub> with tetramethylsilane as internal reference. Twenty to two hundred scans over 16K points were accumulated for each spectrum at 21 ± 1 °C. Infrared spectra were achieved on a Perkin-Elmer 580 B instrument. Samples were 10% dispersions in Nujol mulls. Electronic absorption spectra were performed on a Perkin-Elmer 559 spectrophotometer using 5 × 10<sup>-3</sup> mol L<sup>-1</sup> tetrahydrofuran solutions.

**Determination of Crystal and Molecular Structure and Crystal Data.** The crystal data and the details of the crystal structure refinement are given in Table IV. Further experimental details are given in the supplementary material.

## Results and Discussion

Reaction of MCl<sub>4</sub> (M = Th or U) with porphyrins (Por)H<sub>2</sub> in benzonitrile affords the corresponding dichloro derivatives (Por)MCl<sub>2</sub>. The reaction is monitored by UV-visible spectroscopy. Elemental analyses, in conjunction with valency considerations, lead to the formulation (Por)MCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN. The yields are high (75-82%) and do not seem to depend on the nature of the metal. The bis(acetylacetonato) derivatives (Por)M(acac)<sub>2</sub> are prepared by reaction of the dichloro complexes (Por)MCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN with sodium acetylacetonate in THF. The yields are about 70%.

The proposed formulas (Por)MCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN and (Por)M(acac)<sub>2</sub> are in accordance with the mass spectral data (Table I). In the mass spectra of the dichloro derivatives the molecular peak [(Por)MCl<sub>2</sub>]<sup>+</sup> appears. The parent peak is either the ion [(Por)MCl<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>CN]<sup>+</sup> (uranium series) resulting from the fission of a chlorine atom and one solvent molecule or the molecular peak [(Por)MCl<sub>2</sub>]<sup>+</sup>. In the mass spectra of the bis(acetylacetonato) complexes the parent peak corresponds to the fragment [(Por)M(acac)]<sup>+</sup> if Por = OEP. For the two latter compounds the molecular peak is observed. Curiously, when Por = TPP, the ion [(TPP)M(CO)]<sup>+</sup> is present.

The morphology and the chemical shifts of the macrocycle protons of thorium complexes (Table II) are similar to those observed for diamagnetic metalloporphyrins. Meso proton resonance signals of octaethylporphyrins appear at 10.33-10.49 ppm; methylene and methyl protons are normally located around 4.20 and 1.90 ppm. The protons of the two latter sites give an ABR<sub>3</sub> multiplet, which can be explained only by the presence of a nonoctahedral structure.<sup>9</sup> This morphology resulting from the magnetic nonequivalence between the two sides of the porphyrin

Table IV. Crystal Data

formula	C <sub>46</sub> H <sub>58</sub> N <sub>4</sub> O <sub>4</sub> Th
fw	963
crystn solvent	CHCl <sub>3</sub> /pentane (4/1)
cryst syst	triclinic
space group, conditions	P $\bar{1}$ , none
cryst habit and dimens, nm	prismatic, 0.20 × 0.14 × 0.09
cryst color	purple
lattice parameters	
a, Å	9.493 (7)
b, Å	21.185 (5)
c, Å	24.331 (7)
$\alpha$ , deg	104.18 (2)
$\beta$ , deg	96.11 (4)
$\gamma$ , deg	92.35 (4)
Z	2
V, Å <sup>3</sup>	4705
$d_{\text{calcd}}$ , g cm <sup>-3</sup>	1.359
radiation	Mo K $\alpha$ ( $\lambda$ = 0.7107 Å), graphite monochromator
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	33.19 (no abs cor)
temp, K	293
instrument	Enraf-Nonius CAD 4
$\omega$ range, deg	1.5-20
octants	$\pm h, \pm k, l$ (-9 + 9, -20 + 20, 0 + 23)
no. of collected data	9019
no. of data for $\sigma(I)/I < 0.33$	5323
no. of params	451
data/variable ratio	12.6
resolution programs	SDP 80 program package, Enraf-Nonius, Delft
scattering factor ( $f'$ , $f''$ ) sources	International Tables for X-ray Crystallography, Vol. IV, Tables 2-2B and 2-3-1
structure soln	heavy-atom method
R(F)	0.047
R <sub>w</sub> (F)	0.077
w	4F <sub>o</sub> <sup>2</sup> /[( $\sigma(I)$ ) <sup>2</sup> + ( $pF_o$ ) <sup>2</sup> ] with $p$ = 0.04
function used in the least-squares refinement	$\sum w( F_o  -  F_c )^2$

ligand may be due to both an out-of-plane displacement of the metal atom and a cis coordination of the two axial ligands. The <sup>1</sup>H NMR characteristics of tetraphenylporphyrins 1b and 3b are in good agreement with this deduction since splittings are observed for the ortho and meta protons.<sup>10</sup>

Uranium porphyrins exhibit typical <sup>1</sup>H NMR features of paramagnetic species.<sup>11</sup> Meso protons of uranium octaethylporphyrins appear as very broad signals (line width ~ 30 Hz) around 2.8 ppm downfield from Me<sub>4</sub>Si for dichloro derivative 2a and 1.48 ppm upfield vs. Me<sub>4</sub>Si for bis(acetylacetonato) complex 4a. The methyl protons of 2a exhibit a triplet around 0 ppm while the  $\alpha$ -CH<sub>2</sub> protons present two well-resolved signals at 1.49 and 1.17 ppm. If the morphology of the ethyl protons of (OEP)U(acac)<sub>2</sub> is similar to that observed for the dichloro complex, the ethyl proton signals of the latter are observed at higher field. This result is in accordance with the upfield shift of the meso protons when the two chlorine ligands are replaced by two acetylacetonato ligands.

Other observations are made for uranium tetraphenylporphyrins: the resonance of the pyrrole protons is located at 4.88 ppm for 2b and 5.98 ppm for 4b, and the positions of the phenyl proton resonance signals are not significantly different. For these latter signals, both the out of the porphyrin plane displacement of the uranium atom and the cis coordination of the ligands render the two sides of the macrocycle magnetically nonequivalent so that the ortho and meta protons are anisotropic in the limit of slow phenyl group rotation.

Electronic spectra (Table III) of thorium and uranium porphyrins are similar to those of the metalloporphyrins belonging

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Table V. Positional and Thermal Parameters of Non-Hydrogen Atoms<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Th(1)	0.20821 (9)	0.24163 (4)	0.13188 (3)	3.81 (2)	C(118)	-0.053 (3)	0.243 (1)	0.240 (1)	6.4 (6)*
Th(2)	0.58332 (9)	0.75847 (4)	0.37522 (3)	3.79 (2)	C(119)	-0.091 (3)	0.281 (1)	0.200 (1)	6.5 (6)*
C(11)	0.400 (1)	0.2485 (6)	0.0770 (6)	4.7 (3)*	C(120)	-0.197 (3)	0.329 (1)	0.207 (1)	8.6 (8)*
O(12)	0.417 (1)	0.2018 (7)	0.1726 (6)	4.8 (3)*	C(121)	-0.322 (4)	0.338 (2)	0.259 (2)	15 (1)*
O(13)	0.254 (2)	0.3105 (7)	0.2274 (6)	5.8 (4)*	C(122)	-0.229 (4)	0.384 (2)	0.288 (2)	14 (1)*
O(14)	0.239 (2)	0.3544 (7)	0.1309 (6)	5.8 (4)*	C(123)	-0.205 (3)	0.352 (1)	0.160 (1)	8.1 (8)*
O(21)	0.784 (1)	0.7944 (7)	0.3366 (6)	4.9 (3)*	C(124)	-0.320 (4)	0.403 (2)	0.145 (1)	10.0 (9)
O(22)	0.798 (1)	0.7500 (7)	0.4335 (6)	5.1 (3)*	C(125)	-0.237 (4)	0.460 (2)	0.157 (2)	12 (1)*
O(23)	0.574 (2)	0.6929 (7)	0.2786 (6)	5.9 (4)*	C(126)	-0.107 (3)	0.318 (1)	0.123 (1)	6.5 (6)*
O(24)	0.579 (2)	0.6449 (8)	0.3734 (7)	6.5 (4)*	C(127)	-0.092 (2)	0.324 (1)	0.068 (1)	5.8 (6)*
N(11)	0.196 (2)	0.1267 (7)	0.0712 (6)	3.8 (4)*	C(128)	-0.016 (2)	0.286 (1)	0.0285 (9)	4.8 (5)*
N(12)	0.100 (2)	0.1669 (8)	0.1823 (7)	4.1 (4)*	C(129)	-0.018 (2)	0.289 (1)	-0.0308 (9)	5.1 (5)*
N(13)	-0.037 (2)	0.2743 (9)	0.1497 (8)	5.2 (4)*	C(130)	-0.102 (3)	0.337 (1)	-0.057 (1)	6.7 (6)*
N(14)	0.065 (2)	0.2364 (8)	0.0374 (7)	4.2 (4)*	C(131)	-0.013 (4)	0.404 (2)	-0.042 (1)	9.9 (9)*
N(21)	0.487 (2)	0.7650 (8)	0.4677 (7)	4.1 (4)*	C(132)	0.057 (2)	0.241 (1)	-0.0570 (9)	4.8 (5)*
N(22)	0.631 (2)	0.8727 (8)	0.4359 (7)	4.0 (4)*	C(133)	0.084 (3)	0.220 (1)	-0.119 (1)	6.1 (6)*
N(23)	0.472 (2)	0.8354 (8)	0.3236 (7)	4.0 (4)*	C(134)	0.231 (3)	0.248 (1)	-0.127 (1)	9.0 (8)*
N(24)	0.320 (2)	0.7302 (8)	0.3554 (7)	4.6 (4)*	C(135)	0.110 (2)	0.206 (1)	-0.0141 (9)	4.5 (5)*
C(10)	0.512 (2)	0.219 (1)	0.069 (1)	5.4 (5)*	C(136)	0.184 (2)	0.1501 (9)	-0.0247 (8)	3.9 (4)*
C(11)	0.577 (3)	0.225 (1)	0.014 (1)	7.2 (7)*	C(201)	0.391 (1)	0.719 (1)	0.4762 (9)	5.0 (5)*
C(12)	0.580 (3)	0.184 (1)	0.105 (1)	6.2 (6)*	C(202)	0.418 (2)	0.716 (1)	0.536 (1)	5.7 (6)*
C(13)	0.527 (2)	0.176 (1)	0.1539 (9)	5.2 (5)*	O(203)	0.323 (3)	0.673 (1)	0.566 (1)	8.9 (8)*
C(14)	0.604 (3)	0.136 (1)	0.189 (1)	7.2 (7)*	C(204)	0.384 (5)	0.613 (2)	0.555 (2)	16 (2)*
C(15)	0.232 (3)	0.371 (1)	0.251 (1)	6.6 (6)*	C(205)	0.521 (2)	0.763 (1)	0.562 (1)	5.4 (5)*
C(16)	0.231 (3)	0.383 (1)	0.317 (1)	8.9 (8)*	C(206)	0.595 (3)	0.774 (1)	0.627 (1)	7.9 (7)*
C(17)	0.220 (3)	0.419 (1)	0.224 (1)	7.2 (7)*	C(207)	0.522 (4)	0.826 (2)	0.658 (2)	12 (1)*
C(18)	0.223 (3)	0.410 (1)	0.166 (1)	7.0 (7)*	C(208)	0.562 (2)	0.795 (1)	0.5201 (8)	3.9 (4)*
C(19)	0.210 (3)	0.468 (1)	0.139 (1)	9.1 (7)*	C(209)	0.656 (2)	0.851 (1)	0.5320 (8)	4.0 (5)*
C(20)	0.912 (3)	0.820 (1)	0.358 (1)	5.9 (6)*	C(210)	0.681 (2)	0.8885 (9)	0.4941 (8)	3.9 (4)*
C(21)	0.984 (3)	0.858 (1)	0.321 (1)	7.1 (7)*	C(211)	0.756 (2)	0.953 (1)	0.5098 (8)	4.0 (5)*
C(22)	0.977 (3)	0.815 (1)	0.410 (1)	6.7 (6)*	C(212)	0.820 (2)	0.988 (1)	0.5710 (9)	4.3 (5)*
C(23)	0.920 (3)	0.780 (1)	0.445 (1)	5.8 (6)*	C(213)	0.704 (2)	1.021 (1)	0.605 (1)	5.7 (6)*
C(24)	1.002 (3)	0.777 (1)	0.502 (1)	8.4 (8)*	C(214)	0.754 (2)	0.976 (1)	0.4624 (9)	4.3 (5)*
C(25)	0.531 (3)	0.633 (1)	0.251 (1)	7.3 (7)*	C(215)	0.808 (2)	1.042 (1)	0.4573 (9)	4.3 (5)*
C(26)	0.511 (3)	0.621 (2)	0.186 (1)	9.7 (9)*	C(216)	0.687 (3)	1.089 (1)	0.463 (1)	6.3 (6)*
C(27)	0.515 (3)	0.582 (1)	0.277 (1)	8.0 (7)*	C(217)	0.673 (2)	0.9257 (9)	0.4161 (8)	3.5 (4)*
C(28)	0.538 (3)	0.590 (1)	0.333 (1)	7.5 (7)*	C(218)	0.637 (2)	0.933 (1)	0.3610 (9)	4.2 (5)*
C(29)	0.520 (4)	0.531 (2)	0.363 (1)	10.0 (9)*	C(219)	0.541 (2)	0.8917 (9)	0.3188 (8)	3.6 (4)*
C(101)	0.217 (2)	0.1108 (9)	0.0137 (8)	3.8 (4)*	C(220)	0.490 (2)	0.905 (1)	0.2638 (9)	4.3 (5)*
C(102)	0.267 (2)	0.0461 (9)	-0.018 (8)	3.8 (4)*	C(221)	0.545 (2)	0.962 (1)	0.2430 (9)	5.2 (5)*
C(103)	0.292 (2)	0.010 (1)	-0.0618 (9)	4.5 (5)*	C(222)	0.679 (3)	0.945 (2)	0.215 (1)	9.1 (8)*
C(104)	0.149 (3)	0.124 (1)	-0.098 (1)	6.1 (6)*	C(223)	0.390 (2)	0.857 (1)	0.2379 (8)	4.1 (5)*
C(105)	0.277 (2)	0.223 (9)	0.0462 (8)	3.8 (4)*	C(224)	0.305 (2)	0.849 (1)	0.178 (1)	5.4 (5)*
C(106)	0.315 (2)	-0.044 (1)	0.0513 (9)	4.5 (5)*	C(225)	0.366 (3)	0.796 (1)	0.134 (1)	7.9 (7)*
C(107)	0.180 (3)	-0.090 (1)	0.045 (1)	5.8 (6)	C(226)	0.373 (2)	0.815 (1)	0.2750 (9)	4.5 (5)*
C(108)	0.233 (2)	0.0739 (9)	0.0918 (8)	3.5 (4)*	C(227)	0.273 (2)	0.764 (1)	0.266 (1)	5.4 (5)*
C(109)	0.219 (2)	0.0680 (9)	0.1474 (8)	3.6 (4)*	C(228)	0.244 (2)	0.724 (1)	0.302 (1)	5.8 (6)*
C(110)	0.152 (2)	0.110 (1)	0.1880 (9)	4.3 (5)*	C(229)	0.117 (3)	0.681 (2)	0.295 (1)	9.3 (8)*
C(111)	0.126 (2)	0.096 (1)	0.2421 (9)	4.8 (5)*	C(230)	-0.037 (4)	0.675 (2)	0.243 (1)	11 (1)*
C(112)	0.179 (2)	0.040 (1)	0.265 (1)	5.7 (6)*	C(231)	0.031 (4)	0.621 (2)	0.210 (2)	12 (1)*
C(113)	0.079 (3)	-0.021 (1)	0.240 (1)	7.5 (7)*	C(232)	0.120 (3)	0.656 (2)	0.342 (1)	9.5 (9)*
C(114)	0.052 (2)	0.146 (1)	0.2679 (1)	5.0 (5)*	C(233)	-0.025 (4)	0.615 (2)	0.360 (2)	11 (1)*
C(115)	-0.002 (3)	0.158 (1)	0.328 (1)	6.9 (7)*	C(234)	0.047 (4)	0.558 (2)	0.341 (1)	11 (1)*
C(116)	-0.143 (3)	0.119 (2)	0.322 (1)	9.6 (9)*	C(235)	0.251 (3)	0.688 (1)	0.381 (1)	6.1 (6)*
C(117)	0.029 (2)	0.189 (1)	0.2314 (9)	5.2 (5)*	C(236)	0.287 (3)	0.680 (1)	0.437 (1)	5.9 (6)*

<sup>a</sup>Starred values indicate that atoms were refined isotropically.

to the normal class:<sup>12</sup> the octaethylporphyrin complexes show a Soret band near 405 nm and two extra bands between 534 and 574 nm while the tetraphenylporphyrin derivatives exhibit a Soret band near 418–428 nm and three extra bands in the range 509–594 nm.

The IR spectra of the dichloro isolated complexes (Por)MCl<sub>2</sub> show one absorption at 255 cm<sup>-1</sup> for the thorium series and one near 265 cm<sup>-1</sup> for the uranium series attributable to the M–Cl stretching. Such characteristic absorptions have already been reported for several organochlorides (near 230–250 cm<sup>-1</sup>) for uranium<sup>13,14</sup> and thorium<sup>14</sup> compounds. The complexes (Por)M-

(acac)<sub>2</sub> show typical vibrational spectra of acetylacetonato complexes that have been studied extensively.<sup>15</sup> On the basis of the previous data, the bands near 1570 and 1520 cm<sup>-1</sup> can be assigned to a  $\nu(\text{C}=\text{O})$  and a  $\nu(\text{C}=\text{C})$ , respectively. The M–O stretching band of the studied acetylacetonato complexes appears in the range 390–410 cm<sup>-1</sup>. The presence of the  $\nu(\text{M}-\text{O})$  in the low-frequency region agrees well with a cis coordination of the two acac ligands.<sup>16,17</sup> This affirmation is fully confirmed by X-ray diffraction methods.

The molecular stereochemistry of the compounds 1–4 was definitely established by X-ray diffraction results obtained for the

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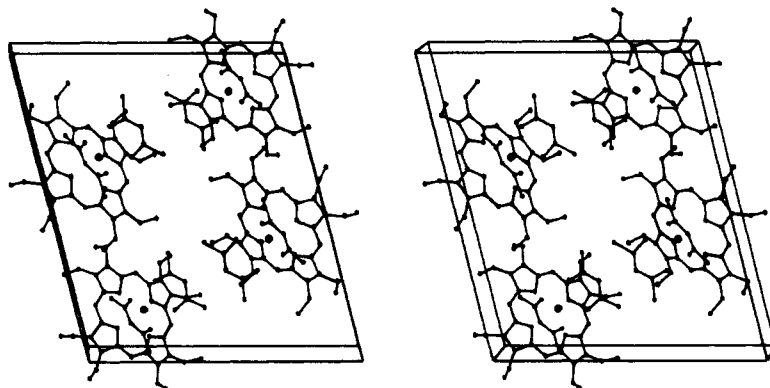


Figure 1. Stereoview of the molecular packing (ORTEP, 1976).<sup>18</sup>

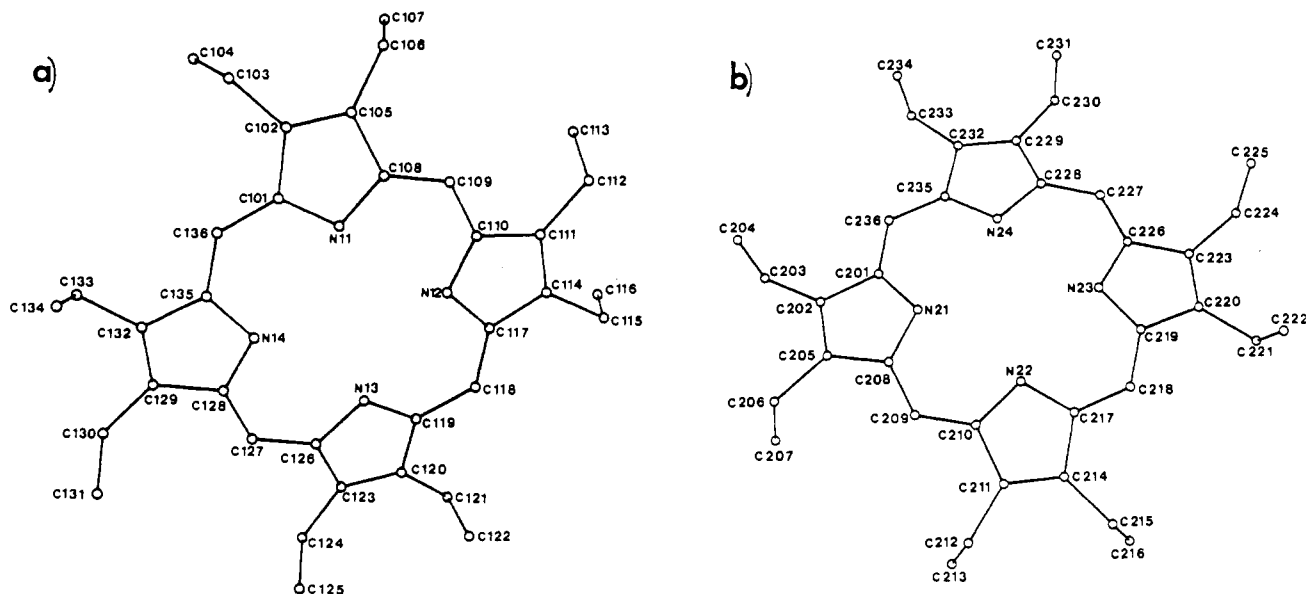


Figure 2. Atomic labeling scheme for the two independent porphyrin macrocycles.

Table VI. Characteristics of the Coordination Polyhedron of Thorium Atoms (Distances in Å, Angles in deg)

Th(1)		Th(2)	
Th(1)-O(11)	2.386 (5)	Th(2)-O(21)	2.386 (6)
Th(1)-O(12)	2.397 (6)	Th(2)-O(22)	2.391 (6)
Th(1)-O(13)	2.407 (6)	Th(2)-O(23)	2.410 (6)
Th(1)-O(14)	2.402 (6)	Th(2)-O(24)	2.394 (7)
Th(1)-N(11)	2.510 (6)	Th(2)-N(21)	2.493 (6)
Th(1)-N(12)	2.479 (6)	Th(2)-N(22)	2.502 (6)
Th(1)-N(13)	2.502 (3)	Th(2)-N(23)	2.492 (6)
Th(1)-N(14)	2.518 (6)	Th(2)-N(24)	2.511 (7)
O(11)-Th(1)-O(12)	69.7 (2)	O(21)-Th(2)-O(22)	68.9 (2)
O(13)-Th(1)-O(14)	68.9 (2)	O(23)-Th(2)-O(24)	69.4 (2)
N(11)-Th(1)-N(12)	70.6 (2)	N(21)-Th(2)-N(22)	71.5 (2)
N(12)-Th(1)-N(13)	71.4 (2)	N(22)-Th(2)-N(23)	70.7 (2)
N(13)-Th(1)-N(14)	71.1 (2)	N(23)-Th(2)-N(24)	71.1 (2)
N(14)-Th(2)-N(11)	71.3 (2)	N(24)-Th(2)-N(21)	71.3 (2)

complex (OEP)Th(acac)<sub>2</sub> (4a). Final positional and thermal parameters are given in Table V with their estimated standard deviations. Figure 1 represents the four molecular units along the [100] axis (the [010] axis being horizontal). The two independent Th(1) and Th(2) atoms show identical coordination spheres formed by an octaethylporphyrin unit and two acetylacetonato ligands. The angles between the [100] plane and the macrocyclic planes bound to Th(1) and Th(2) are 32.8 and -45.7°, respectively, while the dihedral angle between the macrocyclic ligands is 102°. The coordination number, polyhedron type, and

Table VII. Bond Distances (Å) and Angles (deg) of the acac Ligands

1A		2A	
O(11)-C(10)	1.267 (9)	O(21)-C(20)	1.317 (10)
C(10)-C(11)	1.577 (13)	C(20)-C(21)	1.537 (13)
C(10)-C(12)	1.416 (12)	C(20)-C(22)	1.356 (12)
C(12)-C(13)	1.378 (12)	C(22)-C(23)	1.392 (12)
C(13)-C(14)	1.500 (3)	C(23)-C(24)	1.539 (11)
C(13)-O(12)	1.273 (9)	C(23)-O(22)	1.274 (10)
O(11)-C(10)-C(12)	125.8 (9)	O(21)-C(20)-C(22)	123.6 (9)
C(10)-C(12)-C(13)	122.3 (9)	C(20)-C(22)-C(23)	125.3 (1.0)
C(12)-C(13)-O(12)	124.7 (9)	C(22)-C(23)-O(22)	124.2 (9)
1B		2B	
O(13)-C(15)	1.303 (11)	O(23)-C(25)	1.305 (11)
C(15)-C(16)	1.562 (15)	C(25)-C(26)	1.541 (15)
C(15)-C(17)	1.3452 (13)	C(25)-C(27)	1.370 (14)
C(17)-C(18)	1.377 (13)	C(27)-C(28)	1.341 (14)
C(18)-C(19)	1.524 (15)	C(28)-C(29)	1.609 (16)
C(18)-O(14)	1.305 (11)	C(28)-O(24)	1.334 (12)
O(13)-C(15)-C(17)	125.2 (1.0)	O(23)-C(25)-C(27)	124.9 (1.1)
C(15)-C(17)-C(18)	124.9 (1.1)	C(25)-C(27)-C(28)	122.9 (1.2)
C(17)-C(18)-O(14)	123.6 (1.1)	C(27)-C(28)-O(24)	127.6 (1.1)

the domed shape of the macrocycle toward the uranium are essentially the same as those of Hf(IV) and Zr(IV) in (OEP)M(acac)<sub>2</sub><sup>19</sup> and related (OEP)M(AcO)<sub>2</sub>.<sup>20</sup>

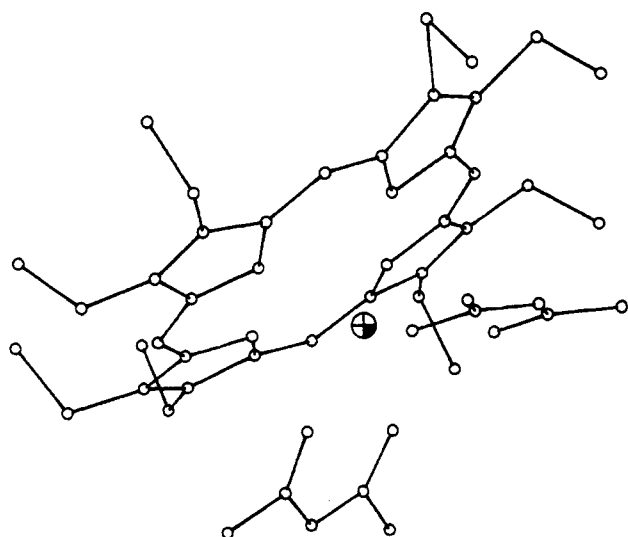
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**Table VIII.** Selected Bond Distances (C–C and C–N, Å) and Angles (C–N–C, deg)

N(11)–C(101)	1.394 (9)	N(21)–C(201)	1.353 (10)
C(101)–C(136)	1.414 (10)	C(201)–C(236)	1.406 (12)
C(136)–C(135)	1.395 (11)	C(236)–C(235)	1.415 (12)
C(135)–N(14)	1.377 (10)	C(235)–N(24)	1.389 (11)
N(14)–C(128)	1.370 (10)	N(24)–C(228)	1.388 (10)
C(128)–C(127)	1.383 (12)	C(228)–C(227)	1.393 (12)
C(127)–C(126)	1.408 (12)	C(227)–C(226)	1.372 (11)
C(126)–N(13)	1.392 (11)	C(226)–N(23)	1.395 (9)
N(13)–C(119)	1.379 (11)	N(23)–C(219)	1.370 (9)
C(119)–C(118)	1.427 (13)	C(219)–C(218)	1.397 (10)
C(118)–C(117)	1.403 (12)	C(218)–C(217)	1.392 (10)
C(117)–N(12)	1.423 (10)	C(217)–N(22)	1.386 (9)
N(12)–C(110)	1.343 (9)	N(22)–C(210)	1.398 (9)
C(110)–C(109)	1.391 (10)	C(210)–C(209)	1.387 (10)
C(109)–C(108)	1.410 (10)	C(209)–C(208)	1.405 (10)
C(108)–N(11)	1.373 (9)	C(208)–N(21)	1.385 (9)
C(101)–N(11)–C(108)	106.5 (6)	C(201)–N(21)–C(208)	107.3 (7)
C(110)–N(12)–C(117)	104.8 (7)	C(210)–N(22)–C(217)	106.0 (6)
C(119)–N(13)–C(126)	104.7 (8)	C(219)–N(23)–C(226)	106.2 (6)
C(128)–N(14)–C(135)	107.4 (7)	C(228)–N(24)–C(235)	106.9 (8)

**Figure 3.** ORTEP drawing of the coordination sphere of Th(1) (for clarity only the inner porphyrin cycle has been drawn and the square faces of the antiprism are outlined).

The closest neighbors of the metal are the four nitrogen atoms of the macrocycle and the four oxygen atoms of the acetylacetonato ligands. These bounded atoms define a nearly perfect Archimedean antiprism: the angles between the planes of the four nitrogen atoms and the planes of the four oxygen atoms are 1.5 and 1.7°, respectively with the faces rigorously planar within the estimated error (0.015 Å). The thorium atoms are closer to the oxygen atom planes (1.34 Å for Th(1) and 1.31 Å for Th(2)) than those of the nitrogen atoms (1.44 and 1.41 Å being the corresponding distances). These results are in good agreement with the observed Th–O and Th–N distances, which are significantly

different (mean values are 2.40 Å for Th–O and 2.50 Å for Th–N). Table VI gives the main characteristics of the coordination sphere.

The geometry of the bidentate acetylacetonato ligands is in good accordance with that of known acetylacetonato complexes. The characteristic distances and angles of the four independent acac ligands are given in Table VII. The acac–thorium ring is normally folded along the O–O axis by 17.7, 18.5, 19.9, and 15.3° for the cycles 1A and 1B (Th(1)) and 2A and 2B (Th(2)), respectively. The angles between Th(1)–O(11)–O(12) and Th(1)–O(13)–O(14), on the one hand, and between Th(2)–O(21)–O(22) and Th(2)–O(23)–O(24), on the other hand, are both equal to 95.5°.

The two independent porphyrin macrocycles are very similar and each possesses an approximate twofold axis perpendicular to its mean plane. All the atoms of the inner chain define a dish, the four nitrogen atoms forming the bottom with its convexity directed to the heavy atom. The pyrrole rings increase this geometry for the N(11)/N(13) and N(22)/N(24) atoms, respectively. Figure 2 gives the labeling used for the two porphyrin molecules. The thermal parameters of the terminal CH<sub>3</sub> carbon atoms are high; this is particularly the case for C(122), C(125), C(204), C(207), C(231), and C(234): steric hindrance at the sites of these carbon atoms could induce such results. The main values of the C–N and C–C distances are reported in Table VIII as well as the C–N–C angles, and Figure 3 shows the coordination sphere of Th(1).

The X-ray powder diffraction patterns of (OEP)U(acac)<sub>2</sub> (**4a**) demonstrate that **4a** is isomorphous with the studied thorium complex (OEP)Th(acac)<sub>2</sub>.

**Supplementary Material Available:** Tables of calculated and nonrefined positions of the hydrogen atoms included in the refinement process and calculated positions of the methyl hydrogen atoms (2 pages); a listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.