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BIS(TETRAHYDROFURAN)URANIUM(VI)¹

W. L. Smith and K. N. Raymond

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The Oxidation of Uranium(IV) by N-phenylbenzohydroxamic
Acid and the Structure of the Reaction Product:
Chlorodioxo-N-phenylbenzohydroxamato-
bis(tetrahydrofuran) uranium(VI)¹

By

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Received:

Running Title:

Formation and Structure of $\text{UO}_2(\text{Cl})[\phi\text{C}(\text{O})\text{N}(\text{O})\phi](\text{THF})_2$

Abstract

Uranium tetrachloride has been quantitatively oxidized via an oxygen transfer reaction with two equivalents of N-phenylbenzohydroxamic acid anion (PBHA) in tetrahydrofuran (THF) to form benzanilide and $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$. The structure of the uranyl complex has been determined by x-ray diffraction data collected by counter methods. The linear uranyl ion has an average U-O distance of $1.75(3) \text{ \AA}$, and is surrounded by a planar pentagonal array composed of two hydroxamate oxygen atoms, a chloride ion and two THF oxygens, such that the chloride ion is opposite the hydroxamate group. That the THF and phenyl rings are twisted from this equatorial plane limits the molecular geometry to that of the Cl point group. The U-Cl length is $2.68(1) \text{ \AA}$ and the other U-O bonds average $2.40 \text{ \AA}$. Refinement fitting 88 parameters to 1248 reflections led to a R-factor of 6.9%. Unit cell dimensions in the space group C2 are $a = 28.45(4) \text{ \AA}$, $b = 7.991(6) \text{ \AA}$, $c = 10.535(7) \text{ \AA}$, $\beta = 96.46(7)^\circ$ and the calculated density is 1.85 g-cm^{-3} for $Z = 4$.

Introduction

Hydroxamic acids have been widely used in the analysis of metal ions due to their powerful coordination as bidentate ligands.²⁻⁷ The formation constants⁸⁻¹¹ of hydroxamic acids with actinide ions suggest that these ligands may serve as functional groups in synthetic sequestering agents designed specifically for the tetravalent actinides.¹² Although several actinide(IV) hydroxamates have been formed during solvent extraction¹³⁻¹⁸ or precipitated in gravimetric analyses,¹⁹⁻²¹ the few complexes which have been isolated involve Th(IV).²²⁻²⁴ In order to explore the feasibility of benzohydroxamic acids as sequestering agents for Pu(IV) and U(IV), the coordination properties of N-phenylbenzohydroxamic acid (PBHA) with U(IV) have been investigated. Instead of simple coordination, the hydroxamic acid oxidizes U(IV) to UO_2^{2+} forming the title compound and benzanilide.

Experimental

Apparatus. All reactions were performed under dry argon on a vacuum line. Solutions were manipulated using Schlenk techniques and solids were handled in a Dri-Lab HE-43 glove box under dry argon. Glassware was dried at 100°C before use.

Reagents. Anhydrous UCl_4 was purchased from ROC/RIC. N-phenylbenzohydroxamic acid (PBHA) was obtained from Eastman and its sodium salt was precipitated from methanol by the

addition of sodium methoxide. After washing with methanol, THF, and ether and drying under high vacuum, the IR spectrum of Na-PBHA showed no water absorption.

Pentane and THF were dried by reflux over sodium and benzophenone followed by distillation. Solvents were degassed under vacuum before use.

Physical Measurements. Infrared spectra were obtained as KBr pellets under a nitrogen purge on a Perkin Elmer 283 spectrophotometer. A Varian T-60 spectrophotometer was used to record proton NMR spectra and the electronic spectra were measured with a Cary 17 recording spectrophotometer. Thin layer chromatography (TLC) was performed on precoated silica gel 60 F-254 sheets and precoated aluminum oxide F-254 neutral type T sheets (E. Merck Darmstadt) which were developed in CHCl_3 . Spots were detected under UV light. Microanalyses were performed by Analytical Services, Chemistry Department, University of California, Berkeley.

Preparation of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$; I. A suspension of 1.905 g (8.1 mmol) Na-PBHA and 0.760 g (2 mmol) UCl_4 in 50 mL THF was heated under reflux 25 h. The resulting NaCl was removed by filtration and the filtrate was diluted with an equal volume of pentane. After standing several days at 0°C , small, red, rectangular crystals of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$ were removed by filtration. This compound was soluble in most organic solvents except hydrocarbons such as pentane.

The electronic spectrum, which is summarized in Table I, was measured from 800 nm to 215 nm on a 9.016×10^{-5} M solution in THF employing 9.996 cm cells in the visible region and 5 mm cells in the UV.

Anal. Calc'd. for $\text{UC}_{21}\text{H}_{26}\text{NO}_6\text{Cl}$: C, 38.11%; H, 3.96%; N, 2.12%; Cl, 5.36%; U, 35.96%.

Found: C, 35.91%; H, 3.78%; N, 2.01%; Cl, 5.45%; U, 36.2%.

IR-(KBR pellet)-3063(w), 2970(m), 2900(m), 1530(vs), 1588(m), 1492(m), 1460(m), 1445(m), 1437(m), 1365(w), 1342(w), 1314(w), 1262(m), 1155(m), 1079(w), 1045(m), 1019(s), 934(m), 917(vs), 873(m), 859(s), 838(m), 825(w), 800(w), 780(s), 775(m), 765(m), 720(m), 698(s), 663(s), 612(w), 597(w), 530(m), 492(w), 470(m), 440(m), 382(w), 346(w), 262(m), 235(m) cm^{-1} .

Isolation of Benzanilide. The above filtrate was evaporated to dryness under vacuum and the residue dissolved in a small amount of CHCl_3 which was eluted from a basic alumina column (15 x 200 mm) with CHCl_3 . The eluant was evaporated to dryness to yield .80 g (4 mmol) benzanilide, which was single spot in TLC and had IR and NMR spectra identical to an authentic sample.

X-ray Diffraction Studies. Single crystals of $\text{UO}_2\text{Cl} \cdot (\text{PBHA})(\text{THF})_2$, obtained from the reaction mixture, were mounted in thin walled glass capillaries under argon. A red, rectangular crystal of dimensions 0.24 x 0.08 x 0.05 mm was used for data collection. Precession photographs and diffraction

data showed monoclinic symmetry and systematic absences $hk\ell$ with $h+k$ odd, consistent with the space groups $C2/m$, Cm , and $C2$. Graphite monochromatized $MoK\alpha$ radiation ($\lambda_{MoK\alpha_1} = 0.70930$ Å) was used for the precise measurement of the cell constants and for data collection on a Nonius Cad-4 automated four-circle diffractometer.²⁵ Cell parameters obtained by a least-squares fit to the measured coordinates of 24 reflections within the 2θ range of 15.9 – 27.4° are listed in Table II.

The intensities of all unique reflections, h , k , $\pm\ell$, with $2\theta < 50^\circ$ were measured and processed as previously described^{26,27} with a parameter p , introduced to prevent overweighting strong reflections, chosen as 0.0676 .²⁸ An analytical absorption correction,²⁹ ranging from 1.4 to 3.1 , was applied to the data, and its validity was checked by several azimuthal scans.

Structure Determination and Refinement. The uranium position found in the Patterson map narrowed the choice of space group to $C2/m$ or $C2$. Subsequent solution and refinement of the structure by standard difference Fourier and least-squares refinement techniques³⁰ established the space group as $C2$, with all the atoms in general positions. Figure 3 shows the orientation of the molecules in the unit cell. The uranyl groups related by centering are parallel and those related by a twofold rotation form an angle of 60° .

Some disorder was observed in the THF rings where the outermost carbon atoms appeared elongated perpendicular to the ring in the difference map more than could be accounted

for by anisotropic thermal motion. Consequently the THF's were refined as rigid groups, assuming C-C bond lengths of 1.54 Å, C-O bond lengths of 1.43 Å, and angles of 109.5°. ³¹ Each of the outermost carbons (C15, C16, C19, and C20), were given 1/4 occupancy at each of the four positions derived from the envelop and the twist conformations of the THF ring. ³² One combined isotropic temperature factor was varied for each of the outermost carbon atoms.

The phenyl rings of the complexed PBHA were also refined as rigid groups, using bond lengths of 1.395 Å and angles of 120.0°, ³⁰ since the non-rigid phenyl rings were not justified at the 75% level by the R-factor ratio test. ³³ The identities of the N and Cl atoms were correctly assigned at the 99% level. ³³ This assignment gives more plausible temperature factors than the alternate arrangement.

Final full-matrix, least-squares refinement ³⁴ on 1248 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 88 variables led to convergence with $R = .0689$, $R_w = .0816$ and an error in an observation of unit weight of 1.63. ³⁵ The uranium and chlorine atoms were given anisotropic temperature factors and all other atoms, including those in rigid groups, were refined isotropically. Hydrogen atoms were not located nor was any attempt made to account for them. Atomic scattering factors were those of Cromer and Mann ³⁶ and those for uranium and chlorine were corrected for anomalous dispersion. ³⁷ Refinement of the alternate enantiomorph caused a marked deviation

from linearity of the O-U-O moiety and a large inequivalence in the U-O bond lengths. A list of observed and calculated structure factors are available from the authors.

Results and Discussion

The addition of a 4:1 mole excess of PBHA anion with U(IV) led to the formation of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$, I, via the reaction:

The uranyl complex has been identified by elemental analysis, electronic and vibrational spectra and x-ray diffraction. Other 1:1 uranyl hydroxamates have been seen spectrophotometrically³⁸⁻⁴⁰ and potentiometrically^{41,42} but have not been isolated. Several bis complexes have been precipitated from aqueous solution.^{38,43-46} Bis complexes are also obtained by the procedure for I if a larger excess of NaPBHA is used. As exemplified by I, the electronic spectra of uranyl aryl-hydroxamates are characterized by two bands in the visible region;^{38,47,48} one near 500-520 nm and a much stronger band between 360 and 430 nm. The UV spectra are dominated by $\pi-\pi^*$ transitions of the phenyl rings.

The presence of complexed PBHA, THF and the uranyl ion was found in the infrared spectrum of I. The very strong carbonyl stretch was shifted from 1635 cm^{-1} found in free

PBHA to 1530 cm^{-1} . The weak C-H stretch at 3063 cm^{-1} and the strong N-O stretch at 917 cm^{-1} were unshifted. Similar shifts have been reported for other actinide PBHA complexes.^{23,44} The presence of THF was shown by C-H stretches at 2970 and 2900 cm^{-1} , a medium band at 1460 cm^{-1} and strong C-O stretches at 1019 and 859 cm^{-1} . That the C-O stretches were shifted from 1064 and 904 cm^{-1} indicates complexation to the ether oxygen. Peaks at 934 and 873 cm^{-1} were assigned as ν_3 and ν_1 of the uranyl ion. These are similar to the uranyl stretching frequencies found in bis-hydroxamic acid complexes.⁴⁴

The molecular structure of I is shown in Figures 1 and 2. The uranyl ion is surrounded by an approximate pentagonal array composed of two hydroxamate oxygen atoms, a chloride ion, and two THF oxygens such that the chloride is opposite the hydroxamate group. This pentagonal array, along with the uranium atom, have an average deviation of $0.045\text{ \AA}$ from the calculated least-squares plane, which forms an angle of 90.4° with the uranyl group. The THF's form dihedral angles of $64(1)^\circ$ and $124(1)^\circ$ with this equatorial plane. Atoms O3, O4, N and Cl are coplanar with an average deviation of $0.032\text{ \AA}$ from the calculated plane which is itself 6.3° from the equatorial plane. The N-phenyl ring is twisted $37(2)^\circ$ from the hydroxamate plane while the C-phenyl is twisted $58(2)^\circ$. The twist of the phenyl rings, which minimizes the repulsive energy, limits the symmetry of the molecule to that of the Cl point group.

The uranyl group is linear with a normal³¹ average U-O bond length of 1.75(3) Å and an angle of 180(1)°. The U-Cl distance of 2.68(1) is similar to the average U-Cl bond in $\text{UO}_2\text{Cl}_4^{2-}$ [2.668(5)].⁴⁹ The distances from the uranium atom to the charged hydroxamate oxygens [avg = 2.35 (3) Å] are slightly shorter than those to the THF oxygens [avg = 2.45(3) Å]. These are in good agreement with an U-O distance of 2.35 Å for a five-coordinate uranyl complex,³¹ while the THF oxygens were found 2.42 Å and 2.47 Å from the uranium in other uranyl compounds.^{50,51} Due to the molecular disorder and the domination of the uranium atom, the details of the PBHA ligand are not precise. However, the overall configuration is similar to that found in other complexes.^{52,53}

The oxidation of uranium(IV) to uranyl occurred under anhydrous, anaerobic conditions. The isolation of benzanilide established that PBHA was reduced to its corresponding amide, to complete the redox couple. Reduction of hydroxamic acids to amides is known to occur with phosphines^{54,55} and nitroso compounds,⁵⁶ which undergo oxygen transfer to form phosphine oxides and nitro compounds. Reduction with zinc,⁵⁴ also yields amides and ZnO. Other reducing agents reduce hydroxamic acids all the way to amines.^{57,58} The stoichiometry required by Eq. (1) was confirmed by the isolation of two equivalents of benzanilide per mole of uranyl complex.

The elevated temperatures of the refluxing THF used in the synthesis of I are not required for the oxidation to

occur; U(IV) was rapidly oxidized when base was added to a solution of UCl_4 and PBHA in THF or acetonitrile at room temperature. The solution of UCl_4 and PBHA is stable and the anion of PBHA must be formed before the oxidation occurs. When benzohydroxamic acid is reacted with UCl_4 under similar conditions, tetrakis(benzohydroxamato)uranium(IV) is isolated as the major product. The N-substituent is known to play an important role in the oxidation of hydroxamic acids:⁵⁹⁻⁶³ it is not surprising to find it also influences the reduction of hydroxamic acids.

No other reductions of hydroxamic acids by metal ions have been characterized. Lutwick and Ryan observed the oxidation of V(II) to V(IV), Ti(III) to Ti(IV) and Sn(II) to Sn(IV) by several hydroxamic acids in dilute aqueous solution.⁶⁴ However, they did not take special precautions against oxygen and it was later shown that oxygen was responsible for the oxidation of Sn(II) and not the hydroxamic acids.⁶⁵ Considering the following aqueous reduction potentials;⁶⁶

and that all are oxidized to oxo-cations, it seems likely that Ti(III) and V(III) would also reduce PBHA anion in THF via an oxygen transfer reaction.

Acknowledgment

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a height of 4 mm was located 173 mm from the crystal. An attenuator was employed when the intensity exceeded 5×10^4 cps. The orientation was checked every 100 reflections and recalculated if any of the setting angles changed more than 0.1%. Three intensity standards were measured every 3600s.

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 $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$ and the error in an observation in unit weight = $[\Sigma w(F_o - F_c)^2 / (N_{obs} - N_{var})]^{1/2}$.
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Table I
Electronic Spectrum of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$

λ (nm)	ϵ ($\ell\text{-cm}^{-1}\text{-mol}^{-1}$)
502	220
394	776
292 (sh)	7280
237 (sh)	15700

Table II

Crystal Data for $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$

Molecular Formula	$\text{UC}_{21}\text{H}_{26}\text{NO}_6\text{Cl}$
Molecular Weight	661.93 g-mol ⁻¹
Space Group	C2 (C_2^3)
Cell Constants	
a	28.45(4) Å
b	7.991(6) Å
c	10.535(7) Å
β	96.46(7)°
V	2379(4) Å ³
Z	4
Calculated Density ^a	1.85 g cm ⁻³
Linear Absorption	
Coefficient, $\mu_{\text{MoK}\alpha}$	66.13 cm ⁻¹

^aDensity measured by flotation in $\text{CCl}_3\text{Br-CCl}_4 = 1.89\text{g cm}^{-3}$.

Table III
Positional and Thermal^a Parameters for $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	.65479(5)	.5	.80287(11)	10.16(19)	149(2)	32.8(10)	6(2)	3.5(3)	-21(5)
Cl	.6835(4)	.6010(17)	.5816(10)	17(2)	273(27)	83(11)	6(7)	15(4)	51(15)

Atom	x	y	z	B	Atom	x	y	z	B
O1	.6075(10)	.392(4)	.718(3)	4.4(7)	Cl14	.6161(12)	.902(4)	.863(3)	4.7(10)
O2	.7015(10)	.607(4)	.888(3)	4.4(7)	Cl15A	.5790(15)	.037(4)	.821(4)	8.4(16)
O3	.6584(10)	.293(4)	.960(3)	4.3(6)	Cl15B	.5727(15)	.017(4)	.837(4)	8.4(16)
O4	.6049(9)	.556(3)	.964(2)	4.2(7)	Cl15C	.5700(15)	.005(5)	.847(4)	8.4(16)
O5	.6134(10)	.771(3)	.771(3)	5.3(7)	Cl15D	.5832(16)	.046(4)	.814(4)	8.4(16)
O6	.7071(9)	.273(3)	.759(3)	4.7(6)	Cl16A	.5454(12)	.950(5)	.717(4)	6.7(18)
N	.6111(11)	.452(3)	.069(3)	3.3(8)	Cl16B	.5517(13)	.971(5)	.701(4)	6.7(18)
Cl	.6329(14)	.318(5)	.069(3)	2.9(8)	Cl16C	.5422(11)	.937(6)	.724(4)	6.7(18)
C2	.6343(10)	.186(3)	.157(2)	3.7(9)	Cl16D	.5553(14)	.979(5)	.691(4)	6.7(18)
C3	.5943(7)	.106(4)	.193(3)	4.9(10)	Cl17	.5739(13)	.799(5)	.677(3)	7.8(15)
C4	.5993(8)	.982(4)	.287(3)	5.5(11)	Cl18	.7447(12)	.213(4)	.849(2)	4.8(10)
C5	.6442(11)	.938(4)	.344(3)	6.1(14)	Cl19A	.7699(11)	.067(5)	.790(3)	9.5(22)
C6	.6842(7)	.018(5)	.308(2)	5.0(8)	Cl19B	.7589(14)	.036(4)	.811(3)	9.5(22)
C7	.6792(8)	.142(4)	.214(3)	3.6(8)	Cl19C	.7628(13)	.045(4)	.802(3)	9.5(22)
C8	.5792(8)	.504(4)	.1690(17)	3.5(6)	Cl19D	.7735(10)	.081(5)	.785(4)	9.5(22)
C9	.5354(9)	.580(4)	.1334(17)	3.6(8)	C20A	.7425(13)	.037(4)	.661(3)	4.3(10)
Cl10	.5068(8)	.627(4)	.226(3)	6.0(12)	C20B	.7355(13)	.015(4)	.673(3)	4.3(10)
Cl11	.5219(9)	.598(5)	.355(2)	5.0(10)	C20C	.7456(13)	.050(5)	.653(3)	4.3(10)
Cl12	.5656(9)	.523(5)	.3909(15)	4.3(8)	C20D	.7310(13)	.005(4)	.679(3)	4.3(10)
Cl13	.5942(7)	.476(4)	.2978(19)	2.8(8)	C21	.7023(11)	.167(4)	.649(2)	5.9(12)

^aThe form of the anisotropic temperature factor is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$, anisotropic temperature factors are reported $\times 10^4$.

Table III
Positional and Thermal^a Parameters for $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	.65479(5)	.5	.80287(11)	10.16(19)	149(2)	32.8(10)	6(2)	3.5(3)	-21(5)
Cl	.6835(4)	.6010(17)	.5816(10)	17(2)	273(27)	83(11)	6(7)	15(4)	51(15)

Atom	x	y	z	B	Atom	x	y	z	B
O1	.6075(10)	.392(4)	.718(3)	4.4(7)	Cl14	.6161(12)	.902(4)	.863(3)	4.7(10)
O2	.7015(10)	.607(4)	.888(3)	4.4(7)	Cl15A	.5790(15)	.037(4)	.821(4)	8.4(16)
O3	.6584(10)	.293(4)	.960(3)	4.3(6)	Cl15B	.5727(15)	.017(4)	.837(4)	8.4(16)
O4	.6049(9)	.556(3)	.964(2)	4.2(7)	Cl15C	.5700(15)	.005(5)	.847(4)	8.4(16)
O5	.6134(10)	.771(3)	.771(3)	5.3(7)	Cl15D	.5832(16)	.046(4)	.814(4)	8.4(16)
O6	.7071(9)	.273(3)	.759(3)	4.7(6)	Cl16A	.5454(12)	.950(5)	.717(4)	6.7(18)
N	.6111(11)	.452(3)	.069(3)	3.3(8)	Cl16B	.5517(13)	.971(5)	.701(4)	6.7(18)
Cl	.6329(14)	.318(5)	.069(3)	2.9(8)	Cl16C	.5422(11)	.937(6)	.724(4)	6.7(18)
C2	.6343(10)	.186(3)	.157(2)	3.7(9)	Cl16D	.5553(14)	.979(5)	.691(4)	6.7(18)
C3	.5943(7)	.106(4)	.193(3)	4.9(10)	Cl17	.5739(13)	.799(5)	.677(3)	7.8(15)
C4	.5993(8)	.982(4)	.287(3)	5.5(11)	Cl18	.7447(12)	.213(4)	.849(2)	4.8(10)
C5	.6442(11)	.938(4)	.344(3)	6.1(14)	Cl19A	.7699(11)	.067(5)	.790(3)	9.5(22)
C6	.6842(7)	.018(5)	.308(2)	5.0(8)	Cl19B	.7589(14)	.036(4)	.811(3)	9.5(22)
C7	.6792(8)	.142(4)	.214(3)	3.6(8)	Cl19C	.7628(13)	.045(4)	.802(3)	9.5(22)
C8	.5792(8)	.504(4)	.1690(17)	3.5(6)	Cl19D	.7735(10)	.081(5)	.785(4)	9.5(22)
C9	.5354(9)	.580(4)	.1334(17)	3.6(8)	C20A	.7425(13)	.037(4)	.661(3)	4.3(10)
Cl10	.5068(8)	.627(4)	.226(3)	6.0(12)	C20B	.7355(13)	.015(4)	.673(3)	4.3(10)
Cl11	.5219(9)	.598(5)	.355(2)	5.0(10)	C20C	.7456(13)	.050(5)	.653(3)	4.3(10)
Cl12	.5656(9)	.523(5)	.3909(15)	4.3(8)	C20D	.7310(13)	.005(4)	.679(3)	4.3(10)
Cl13	.5942(7)	.476(4)	.2978(19)	2.8(8)	C21	.7023(11)	.167(4)	.649(2)	5.9(12)

^aThe form of the anisotropic temperature factor is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$, anisotropic temperature factors are reported $\times 10^4$.

Table III
Positional and Thermal^a Parameters for $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	.65479(5)	.5	.80287(11)	10.16(19)	149(2)	32.8(10)	6(2)	3.5(3)	-21(5)
Cl	.6835(4)	.6010(17)	.5816(10)	17(2)	273(27)	83(11)	6(7)	15(4)	51(15)

Atom	x	y	z	B	Atom	x	y	z	B
O1	.6075(10)	.392(4)	.718(3)	4.4(7)	Cl14	.6161(12)	.902(4)	.863(3)	4.7(10)
O2	.7015(10)	.607(4)	.888(3)	4.4(7)	Cl15A	.5790(15)	.037(4)	.821(4)	8.4(16)
O3	.6584(10)	.293(4)	.960(3)	4.3(6)	Cl15B	.5727(15)	.017(4)	.837(4)	8.4(16)
O4	.6049(9)	.556(3)	.964(2)	4.2(7)	Cl15C	.5700(15)	.005(5)	.847(4)	8.4(16)
O5	.6134(10)	.771(3)	.771(3)	5.3(7)	Cl15D	.5832(16)	.046(4)	.814(4)	8.4(16)
O6	.7071(9)	.273(3)	.759(3)	4.7(6)	Cl16A	.5454(12)	.950(5)	.717(4)	6.7(18)
N	.6111(11)	.452(3)	.069(3)	3.3(8)	Cl16B	.5517(13)	.971(5)	.701(4)	6.7(18)
Cl1	.6329(14)	.318(5)	.069(3)	2.9(8)	Cl16C	.5422(11)	.937(6)	.724(4)	6.7(18)
Cl2	.6343(10)	.186(3)	.157(2)	3.7(9)	Cl16D	.5553(14)	.979(5)	.691(4)	6.7(18)
Cl3	.5943(7)	.106(4)	.193(3)	4.9(10)	Cl17	.5739(13)	.799(5)	.677(3)	7.8(15)
Cl4	.5993(8)	.982(4)	.287(3)	5.5(11)	Cl18	.7447(12)	.213(4)	.849(2)	4.8(10)
Cl5	.6442(11)	.938(4)	.344(3)	6.1(14)	Cl19A	.7699(11)	.067(5)	.790(3)	9.5(22)
Cl6	.6842(7)	.018(5)	.308(2)	5.0(8)	Cl19B	.7589(14)	.036(4)	.811(3)	9.5(22)
Cl7	.6792(8)	.142(4)	.214(3)	3.6(8)	Cl19C	.7628(13)	.045(4)	.802(3)	9.5(22)
Cl8	.5792(8)	.504(4)	.1690(17)	3.5(6)	Cl19D	.7735(10)	.081(5)	.785(4)	9.5(22)
Cl9	.5354(9)	.580(4)	.1334(17)	3.6(8)	Cl20A	.7425(13)	.037(4)	.661(3)	4.3(10)
Cl10	.5068(8)	.627(4)	.226(3)	6.0(12)	Cl20B	.7355(13)	.015(4)	.673(3)	4.3(10)
Cl11	.5219(9)	.598(5)	.355(2)	5.0(10)	Cl20C	.7456(13)	.050(5)	.653(3)	4.3(10)
Cl12	.5656(9)	.523(5)	.3909(15)	4.3(8)	Cl20D	.7310(13)	.005(4)	.679(3)	4.3(10)
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^aThe form of the anisotropic temperature factor is $\exp[-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]$, anisotropic temperature factors are reported $\times 10^4$.

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positional and Thermal^a Parameters for $\text{UO}_2\text{Cl}_2(\text{PBHA})(\text{THF})_2$

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Atom	x	y	z	B	Atom	x	y	z	B
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O5	.6134(10)	.771(3)	.771(3)	5.3(7)	Cl15D	.5832(16)	.046(4)	.814(4)	8.4(16)
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C5	.6442(11)	.938(4)	.344(3)	6.1(14)	Cl19A	.7699(11)	.067(5)	.790(3)	9.5(22)
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Cl12	.5656(9)	.523(5)	.3909(15)	4.3(8)	C20D	.7310(13)	.005(4)	.679(3)	4.3(10)
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^aThe form of the anisotropic temperature factor is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$, anisotropic temperature factors are reported $\times 10^4$.

Table IV
Selected Interatomic Distances ($\text{\AA}$)

U-Cl	2.68(1)	Cl-O5	3.27(3)
U-O1	1.76(3)	Cl-O6	3.24(3)
U-O2	1.74(3)	O3-O6	2.67(4)
U-O3	2.34(3)	O4-O5	2.69(4)
U-O4	2.37(3)	O3-O4	2.59(4)
U-O5	2.47(3)	Cl-N	1.24(5)
U-O6	2.42(3)	N-C8	1.53(4)
O3-Cl	1.44(4)	Cl-C2	1.40(5)
O4-N	1.38(4)		

Figure Captions

Figure 1. Molecular geometry of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$.

Figure 2. Stereopair of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$ with thermal ellipsoids at the 30% probability level.

Figure 3. Contents of two unit cells of $\text{UO}_2\text{Cl}(\text{PBHA})(\text{THF})_2$ viewed down the b axis, with the a axis horizontal.

XBL 783-7435

Figure 1.

XBL 782-7191

Figure 2.

Figure 3.

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