

(36) Programs used in the solution and refinement of the structures included MULTAN (Germain, Main, Woolfson), ORFLS and ORFFE (Busing, Martin, Levy), and ORTEP (C. K. Johnson). Remaining programs were written by J. C. Calabrese.

(37) $R_1 = \frac{\sum |F_o|}{\sum |F_c|} - |F_c| / |\sum |F_o||$ and $R_2 = \frac{[\sum w_i |F_o| - |F_c|]^2}{\sum w_i |F_o|^2}^{1/2}$.

(38) All least-squares refinements were based on the minimization of $\sum w_i |F_o| - |F_c|$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040. Those for the hydrogen atoms are from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Specific Sequestering Agents for the Actinides. 2. A Ligand Field Effect in the Crystal and Molecular Structures of Tetrakis(catecholato)uranate(IV) and -thorate(IV)¹

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Abstract: The structures of the title compounds, $\text{Na}_4[\text{M}(\text{C}_6\text{H}_4\text{O}_2)_4] \cdot 21\text{H}_2\text{O}$, $\text{M} = \text{Th}, \text{U}$, have been determined by single-crystal X-ray diffraction methods using counter data. These isostructural tetrakis(catecholato) complexes are structural archetypes for actinide-specific macrocyclic sequestering agents. The complexes have D_{2d} molecular symmetry. The M-O bond lengths are 2.417 (3) and 2.421 (3) Å for Th and 2.362 (3) and 2.389 (4) Å for U. The ring O-M-O bond angles are 66.8 (1)° for Th and 67.7 (1)° for U. The difference in M-O bond lengths for the uranium complex [0.027 (5) Å] vs. a difference of 0.004 (4) Å in the thorium complex is attributed to a ligand field effect of the $5f^2$ electronic configuration of U(IV) vs. $5f^0$ for Th(IV). Green crystals of the uranium complex, obtained from basic aqueous solution, conform to the space group $I\bar{4}$ with $a = 14.659$ (3) and $c = 9.984$ (4) Å. For 3660 independent data with $F_o^2 > 3\sigma(F_o^2)$ full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms converged to unweighted and weighted R factors of 3.8 and 4.5%, respectively. The colorless thorium compound, also obtained from basic aqueous solution, has $a = 14.709$ (4) and $c = 9.978$ (3) Å. For 5038 independent data refinement as above converged to unweighted and weighted R factors of 4.3 and 5.3%, respectively.

Introduction

A continuing project in this laboratory has been the development of powerful chelating agents highly specific for tetravalent actinide ions. One application of such compounds is their use in treating accidental plutonium poisoning. Although treatment procedures have been developed for such poisoning, they are severely hampered by the lack of sequestering agents which are both relatively specific and very strong chelating agents for Pu(IV). Controlled experiments on animals as well as data from industrial accidents show that in mammals plutonium is moved and stored by the iron transport and storage compounds transferrin and ferritin.²⁻⁵ It is this analogy of the chemistry of Pu^{4+} to Fe^{3+} in biological systems that has been the guiding principle in the design of an actinide sequestering agent. Bacteria have developed very efficient iron sequestering agents for obtaining ferric ion from mammalian hosts.⁶ Typically, these siderophores employ three bidentate chelating moieties bound to a trimeric backbone. In particular, the iron transport agent enterobactin employs three catechol (*o*-dihydroxybenzene) ligands to octahedrally coordinate iron.⁷ In preparing an actinide-chelating analogue, four catechols are provided to take advantage of the higher coordination number found among these metals as well as to introduce specificity.¹ The complexes formed by actinide(IV) ions and the catecholate dianion, in which the steric restraints of a macrochelate are absent, serve as structural archetypes for designing the optimum actinide(IV) macrochelate. Therefore, as part of a continuing project directed toward the synthesis and characterization of chelating agents specific for actinide ions we report here the structure of tetrakis(catecholato)thorate(IV) and -uranate(IV), $\text{Na}_4[\text{M}(\text{C}_6\text{H}_4\text{O}_2)_4] \cdot 21\text{H}_2\text{O}$ ($\text{M} = \text{Th}, \text{U}$).

Little is known about the coordination chemistry of catechol with the actinides. There are old reports of isolable compounds with formulas assigned from analytical data alone. These include apparently polymeric materials such as $\text{K}_2\text{Th}_3(\text{C}_6\text{H}_4\text{O}_2)_7 \cdot 20\text{H}_2\text{O}$ and $[\text{C}_5\text{H}_5\text{NH}]_2[\text{Th}_2(\text{C}_6\text{H}_4\text{O}_2)_3(\text{OH})_4] \cdot 10\text{H}_2\text{O}$ as well as the presumably monomeric salts, $[\text{NH}_4]_2[\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot \text{C}_6\text{H}_6\text{O}_2$, $[\text{NH}_4]_2[\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 5\text{H}_2\text{O}$, and $\text{H}_4\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_4$.⁸⁻¹¹ Similar compounds have been reported for uranium.¹² In addition, solution studies of actinide catecholates led to the conclusion that polymeric compounds were prominent.^{13,14} This work, then, reports the first structural information for these materials.

Considering the long and intense interest in actinides for their various applications, it is surprising how little structural information is available for eight-coordinate actinide compounds. For such compounds two limiting geometries are prevalent: square antiprisms (D_{4d}) and trigonal-faced dodecahedra (D_{2d}).¹⁵ The structure of β -tetrakis(acetylacetonato)uranium(IV) consists of a uranium atom coordinated by eight oxygen atoms in the form of a square antiprism.¹⁶ Trigonal-faced dodecahedral coordination is observed in the Th(salicylaldehydato)₄ complex.¹⁷ The uranium and thorium catecholates reported here have coordination polyhedra which are very close to the idealized trigonal-faced dodecahedron.

Experimental Section

All experimental manipulations with catechol were carried out under an inert atmosphere free of O_2 either on a Schlenk line or in a recirculating atmosphere glovebox. Thorium tetrachloride (ROC-RIC), catechol (a generous gift of Crown-Zellerbach Corp.), sodium hydroxide (Mallinckrodt), and uranium tetrachloride (ROC-RIC) were used without further purification. The compounds were characterized using a Perkin-Elmer Model 337 infrared spectrophotom-

Table I. Summary of Crystal Data for $\text{Na}_4[\text{M}(\text{C}_6\text{H}_4\text{O}_2)_4]\cdot 21\text{H}_2\text{O}$, $\text{M} = \text{Th}, \text{U}$

complex	Th	U
mol wt, g/mol	1134.8	1140.8
space group	$I\bar{4}$	$I\bar{4}$
cell constants ^a		
<i>a</i> , Å	14.709 (4)	14.659 (3)
<i>c</i> , Å	9.978 (3)	9.984 (4)
cell volume, Å ³	2158.8	2145.4
formula units/cell	2	2
calcd density	1.75	1.77
obsd density	1.74	1.76
$\mu_{\text{MoK}\alpha}$, cm ⁻¹	37.00	37.26
crystal shape	approximate sphere radius = 0.315 mm	capped rectangular solid with 8 faces: 010, 0 $\bar{1}$ 0, 100, $\bar{1}$ 00, $\bar{1}$ 01, 101, 01 $\bar{1}$, 0 $\bar{1}$ $\bar{1}$; 023 × 0.27 × 0.52 mm

^a Ambient temperature of 26 °C; Mo K α radiation, $\lambda = 0.70930$ Å.

eter, a Varian T-60 NMR spectrometer, and a Varian-Cary Model 118 or 17 spectrophotometer. Elemental analysis for thorium was carried out by EDTA titration.¹⁸ Carbon, hydrogen, and sodium were analyzed by the Microanalytical Laboratory, University of California, Berkeley.

Synthesis of $\text{Na}_4[\text{M}(\text{C}_6\text{H}_4\text{O}_2)_4]\cdot 21\text{H}_2\text{O}$ ($\text{M} = \text{Th}, \text{U}$). The low solubility of the tetrakis(catecholato) complexes permits their direct synthesis and isolation from aqueous solutions of the metal chlorides. Sodium hydroxide pellets, 4.8 g (0.12 mol), were dissolved in 10 mL of O₂-free water and then 6.6 g of catechol (0.06 mol) was added to this solution. To the alkaline catechol solution was added a filtered, O₂-free solution of the metal salt in 15–50 mL of water. Soon thereafter, the crystalline product formed. The reaction mixture was filtered and by slow cooling of the filtrate crystals suitable for X-ray diffraction were obtained.

Anal. Calcd for $\text{Na}_4[\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_4]\cdot 21\text{H}_2\text{O}$ (mol wt 1134.8): C, 25.40; H, 5.16; Na, 8.11; Th, 20.45. Found: C, 25.62; H, 4.44; Na, 7.52; Th, 19.1.

Magnetic Susceptibility. Magnetic susceptibility measurements on the uranium complex were obtained with a PAR Model 155 vibrating sample magnetometer used with an homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet. Measurements were made at field strengths of 12.5, 10.0, 7.5, and 5.0 kG. In a glovebox, approximately 100-mg samples were carefully loaded into tared, diamagnetic, calibrated sample holders machined from Kel-F rod. Immediately after measurement of the susceptibility the

sample holder and sample were weighed. A variable-temperature liquid helium Dewar was used to vary the sample temperature in the range 4–80 K. Temperatures were measured using a calibrated GaAs diode placed approximately 0.5 in. above the sample. The magnetometer was calibrated with $\text{HgCo}(\text{CNS})_4$.¹⁹ The resulting susceptibilities were corrected for underlying diamagnetism²⁰ and found to be independent of temperature and field strength with a molar susceptibility of 870×10^{-6} cgs mol⁻¹.

Unit Cell and Diffraction Data. Precession photographs showed the two compounds to be isomorphous with tetragonal symmetry and systematic absences hkl , $h + k + l \neq 2n$, consistent with a body-centered tetragonal space group. Chemical and crystallographic evidence confirmed that the space group is $I\bar{4}$. Crystal data obtained by a least-squares fit to 25 high-angle reflections are in Table I.

Intensity data were collected on a Nonius CAD-4 automated diffractometer using monochromatic Mo K α radiation.^{21–23} The data were processed as previously described with a parameter, p , introduced to prevent overweighting strong reflections, chosen as 0.04.²⁴ Given the size of the crystals used, absorption effects were considered significant; therefore, a spherical absorption correction was calculated for the thorium complex and an analytical correction for the uranium complex.²⁵ The crystal densities were determined by the flotation technique in dibromomethane/heptane solutions. The measured densities are 1.74 and 1.76 g/cm³; those calculated for two formula units per cell are 1.75 and 1.77 g/cm³ for the thorium and uranium complexes, respectively.

Solution and Refinement of the Structures. Thorium. Positions for the thorium, chelate ring, and sodium were deduced from a sharpened Patterson map, and these led to completion of the structure by standard difference Fourier and least-squares techniques. Full-matrix refinements were employed using the 5038 reflections with $F_o^2 > 3\sigma(F_o^2)$.^{26–29} None of the hydrogen atoms could be located. Positions for the four ligand hydrogens were calculated assuming that the C–H bond bisects the C–C–C angle of the ring and the C–H bond distance is 0.95 Å. These hydrogens were assigned isotropic temperature factors of 5.0 Å² and were put in as fixed atoms. Examination of the final difference Fourier showed no peak greater than 2.6 e/Å³ (approximately 50% of a carbon atom), and several of the highest peaks were located near the thorium atom. The remaining peaks were located near the water oxygens; however, water hydrogen atoms could not be located. The final unweighted (R) and weighted (R_w) agreement factors are 4.3 and 5.3%, respectively,³⁰ and the error in an observation of unit weight is 2.0. Table II gives the positional and thermal parameters of the nonhydrogen atoms. Table III gives the final positional parameters for the fixed hydrogen atoms and Table IV lists the amplitudes of vibration derived from the thermal parameters.³¹

Uranium. Precession photographs revealed that the unit cells of the compounds are nearly identical. Structures based upon refined positional and thermal parameters from the Th structure afforded an R factor of 15% when compared to the U data. Catechol hydrogens were included as described above. The largest peaks in the final difference

Table II. Positional and Thermal Parameters ($\times 10^4$) for the Nonhydrogen Atoms in $\text{Na}_4[\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_4]\cdot 21\text{H}_2\text{O}$

atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} ^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th ^b	0	0	0	20.10 (7) ^c	20.10 (7)	47.5 (2)	0	0	0
Na	0.18742 (18)	0.04120 (18)	0.7376 (3)	45.4 (11)	44.4 (11)	88 (2)	−3.7 (9)	6.1 (13)	7.6 (13)
O ₁	0.0384 (3)	0.1544 (2)	0.0610 (4)	42.9 (16)	26.8 (12)	64 (3)	−7.0 (11)	4.6 (18)	0.6 (15)
O ₂	0.0305 (3)	0.0963 (2)	0.8084 (4)	41.5 (15)	23.9 (11)	62 (3)	−2.5 (10)	0.1 (17)	2.4 (14)
O ₃ ^d	0.0620 (4)	0.0923 (5)	0.6086 (6)	58 (3)	66 (3)	107 (5)	1 (2)	1 (3)	20 (3)
O ₄	0.3269 (4)	0.9681 (5)	0.6394 (7)	54 (3)	63 (3)	131 (7)	7 (2)	2 (4)	−3 (4)
O ₅	0.2227 (4)	0.1320 (5)	0.5434 (7)	48 (2)	84 (4)	126 (6)	−7 (2)	−5 (3)	24 (4)
O ₆	0.2729 (5)	0.1662 (4)	0.8515 (8)	57 (3)	58 (3)	152 (8)	−5 (2)	5 (4)	−12 (4)
O ₇	0.2824 (4)	0.3161 (4)	0.6428 (8)	42 (2)	48 (2)	203 (10)	−2.9 (18)	17 (4)	−11 (4)
O ₈ ^e	0	1/2	1/4	49 (3)	49 (3)	213 (22)	0	0	0
C ₁	0.0455 (3)	0.2171 (3)	0.9629 (5)	29.1 (14)	24.6 (13)	75 (4)	−2.6 (11)	1.0 (17)	0.6 (16)
C ₂	0.0430 (3)	0.1854 (3)	0.8290 (5)	25.5 (13)	25.0 (14)	71 (4)	0 (11)	0.7 (18)	4.9 (18)
C ₃	0.0557 (3)	0.2482 (4)	0.7252 (6)	34.2 (18)	34.8 (18)	87 (5)	0.2 (15)	−4 (2)	19 (2)
C ₄	0.0703 (4)	0.3395 (4)	0.7514 (7)	37 (2)	32.8 (19)	119 (6)	−2.9 (16)	−6 (3)	24 (3)
C ₅	0.0694 (4)	0.3702 (3)	0.8838 (8)	45 (2)	26.1 (17)	142 (8)	−6.3 (16)	−9 (4)	12 (3)
C ₆	0.0569 (4)	0.3091 (3)	0.9926 (19)	47.6 (19)	24.6 (12)	122 (8)	−5.1 (12)	−1 (7)	−5 (5)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Located on the crystallographic $\bar{4}$ axis at 0, 0, 0. ^c Standard deviations of the least significant figures are given here and elsewhere in parentheses. ^d Atoms O₃–O₈ are water oxygens. ^e Located on the crystallographic $\bar{4}$ axis at 0, 1/2, 1/4.

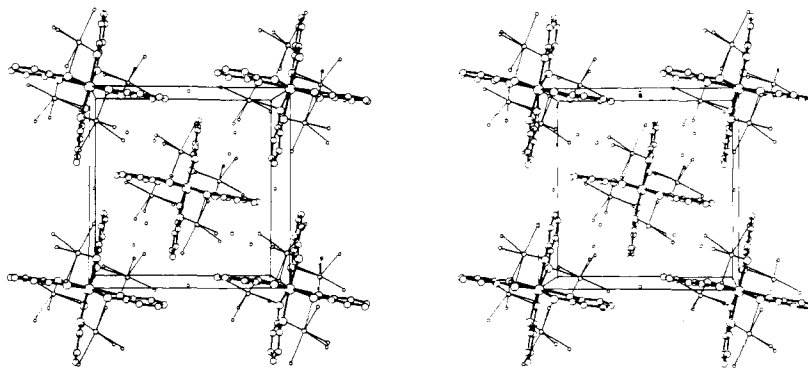


Figure 1. A stereoscopic packing diagram of the $\text{Na}_4[\text{M}(\text{C}_6\text{H}_4\text{O}_2)_4] \cdot 21\text{H}_2\text{O}$. $\text{M} = \text{Th}, \text{U}$, structures viewed down the crystallographic c axis.

Table III. Positional Parameters for the Fixed Hydrogen Atoms^a

atom	x		y		z	
	Th	U	Th	U	Th	U
H ₃	0.0541	0.0524	0.2280	0.2266	0.6349	0.6346
H ₄	0.0806	0.0787	0.3810	0.3803	0.6804	0.6820
H ₅	0.0772	0.0764	0.4328	0.4318	0.9018	0.9033
H ₆	0.0563	0.0566	0.3306	0.3284	0.0826	0.0834

^a The subscript of each hydrogen atom is chosen to be the same as the carbon atom to which it is bonded. The isotropic temperature factor for all the hydrogen atoms is 5.0 \AA^2 .

Fourier were $1.4 e/\text{\AA}^3$. The water hydrogens were not located. The final unweighted (R) and weighted (R_w) agreement factors from full-matrix least-squares refinement of the 3660 independent data with $F_o^2 > 3\sigma(F_o^2)$ are 3.8 and 4.5%, respectively,³⁰ and the error in an observation of unit weight is 1.46. Table V gives the positional and thermal parameters for the fixed hydrogen atoms and Table IV lists the amplitudes of vibration derived from the thermal parameters.³¹

Description of the Structures. The crystal structure consists of discrete $[\text{M}(\text{cat})_4]^{4-}$ units, sodium ion, and waters of crystallization, as shown in Figure 1. Each metal lies in a position of $\bar{4}$ crystallographic symmetry (the cell origin) generating the dodecahedral geometry for the complex. In addition to four water oxygens, each sodium is coordinated to a nonequivalent oxygen from each of two catechol ligands resulting in a very distorted six-coordinate cluster. Although the water hydrogens could not be located, all of the water oxygens are within a reasonable distance to form a hydrogen-bonded network through the crystal. The "21st" water is also located at a special position of $\bar{4}$ symmetry and apparently fills in a hole in the cell; it is hydrogen bonded to O-6 and O-4. It is 7.8 \AA from the nearest thorium

ion. This is therefore a true eight-coordinate complex in contrast to the related nine-coordinate monocapped antiprism of $\text{Th}(\text{tropolonato})_4\text{DMF}$.³² The coordination of the sodium ion is quite distorted from any common ideal six-coordinate geometry owing to the steric constraints imposed by coordination to the catecholate oxygens. The structure of the chelate complex is shown in Figures 2 and 3. The O-M-O angle is $66.8 (1)^\circ$ for Th and $67.7 (1)^\circ$ for U.

Bond lengths and angles for both complexes are shown in Figure 4 and listed in Tables VI and VII. The M-O bond length averages $2.419 (3) \text{ \AA}$ for Th and $2.375 (3) \text{ \AA}$ for U. These distances are not unusual. Other known Th-O distances include 2.315 and 2.520 \AA in tetrakis(salicylaldehydato)thorium(IV), 2.445 \AA in tetrakis(tropolonato)thorium(IV) DMF, 2.41 \AA in β -tetrakis(acetylacetonato)thorium(IV), and 2.39 \AA in the trifluoroacetylacetonato thorium complex.^{16,17,33} For uranium complexes of carbonate, acetate, and acetylacetonates U-O distances range from 2.23 to 2.80 \AA .³⁴⁻³⁶ As shown in Figure 1, the catecholate ligands are only slightly distorted from planarity by bending of the rings at the oxygen. In the thorium complex the average deviation from planarity for catecholate atoms is 0.023 \AA while for the phenyl ring atoms alone the deviation is 0.010 \AA (see Table VIII). The angle between the plane formed by O-1, O-2, C-1, and C-2 with the plane of the phenyl ring carbons is 2.6° . These slight deviations may be caused by the sodium-water clusters coordinated to the catechols but do not appreciably affect the coordination polyhedron.

Discussion

The infrared spectrum of catechol exhibits shifts in the frequencies of several bands upon chelation to a metal. Such characteristic shifts upon chelation of the catecholate unit have been previously noted for transition metal complexes by us and other workers.³⁷ We find that the bands in the free ligand at

Table V. Positional and Thermal Parameters ($\times 10^4$) for the Nonhydrogen Atoms in $\text{Na}_4[\text{U}(\text{C}_6\text{H}_4\text{O}_2)_4] \cdot 21\text{H}_2\text{O}$

atom	x	y	z	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U ^b	0	0	0	18.03 (9) ^c	18.03 (9)	43.3 (2)	0	0	0
Na	0.18565 (17)	0.04174 (18)	0.7386 (3)	42.7 (11)	42.6 (11)	85 (2)	-4.1 (9)	5.6 (13)	8.4 (13)
O ₁	0.0376 (3)	0.1512 (2)	0.0603 (4)	43.2 (18)	24.9 (15)	52 (3)	-6.5 (12)	2.6 (18)	0.5 (16)
O ₂	0.0287 (3)	0.0941 (2)	0.8092 (4)	38.2 (16)	22.2 (13)	59 (3)	-2.2 (11)	0.4 (17)	0.3 (16)
O ₃ ^d	0.0626 (4)	0.0942 (5)	0.6083 (6)	57 (3)	68 (3)	109 (6)	-2 (2)	0 (3)	25 (3)
O ₄	0.3256 (4)	0.9690 (4)	0.6391 (7)	53 (3)	58 (3)	137 (7)	9 (2)	-3 (3)	-3 (4)
O ₅	0.2218 (4)	0.1322 (5)	0.5446 (6)	44 (2)	79 (4)	124 (7)	-5 (2)	-7 (3)	19 (3)
O ₆	0.2735 (5)	0.1663 (4)	0.8529 (7)	55 (3)	59 (3)	143 (8)	-4 (2)	7 (4)	-14 (4)
O ₇	0.2824 (4)	0.3171 (4)	0.6449 (7)	42 (2)	43 (2)	185 (9)	-3.8 (19)	16 (4)	-9 (3)
O ₈ ^c	0	1/2	1/4	47 (3)	47 (3)	193 (19)	0	0	0
C ₁	0.0449 (3)	0.2148 (3)	0.9629 (5)	25.9 (17)	24.5 (17)	69 (5)	-3.1 (13)	1.9 (18)	0.9 (19)
C ₂	0.0416 (3)	0.1839 (3)	0.8296 (5)	23.4 (16)	22.7 (16)	65 (4)	-0.4 (13)	1 (2)	7 (2)
C ₃	0.0540 (4)	0.2468 (4)	0.7254 (6)	31 (2)	33 (2)	78 (5)	-1.0 (16)	-3 (2)	16 (3)
C ₄	0.0687 (4)	0.3382 (4)	0.7530 (7)	31 (2)	33 (2)	121 (7)	-3.2 (17)	-8 (3)	27 (3)
C ₅	0.0686 (4)	0.3690 (4)	0.8852 (8)	43 (3)	23 (2)	133 (8)	-4.6 (18)	-7 (4)	7 (3)
C ₆	0.0566 (3)	0.3073 (3)	0.9940 (17)	44 (2)	25.1 (15)	111 (7)	-5.8 (14)	9 (7)	-11 (6)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Located on the crystallographic $\bar{4}$ axis at 0, 0, 0. ^c Standard deviations of the least significant figures are given here and elsewhere in parentheses. ^d Atoms O₃-O₈ are water oxygens. ^e Located on the crystallographic $\bar{4}$ axis at 0, 1/2, 1/4.

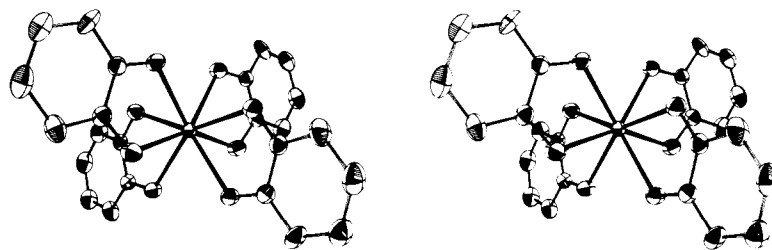


Figure 2. A stereoscopic ORTEP drawing of the $[M(C_6H_4O_2)_4]^{4-}$, $M = Th, U$, unit viewed down the two fold axis. The $\bar{4}$ axis is vertical. The individual atoms are drawn at 50% probability contours of the thermal motion in the Th structure.

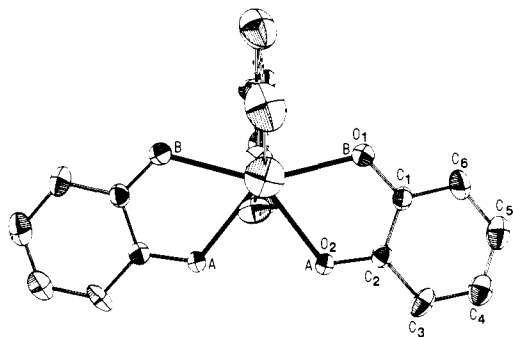


Figure 3. The $[M(C_6H_4O_2)_4]^{4-}$, $M = Th, U$, anion viewed along the mirror plane with the $\bar{4}$ axis vertical. The atom labels used in the text as well as the dodecahedral A and B sites are shown.

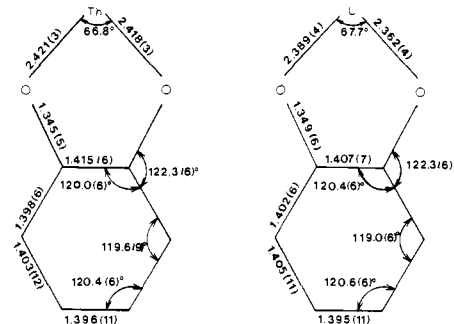


Figure 4. Schematic diagram of the thorium(IV) and uranium(IV) catecholate coordination geometries, showing the average bond distances (Å) and angles.

Table VI. Bond Distances in $Na_4[M(C_6H_4O_2)_4] \cdot 21H_2O$, $M = Th, U$

atoms	distance, Å		atoms	distance, Å	
	Th	U		Th	U
M-O ₁	2.418 (3)	2.362 (4)	Na-O ₃	2.372 (7)	2.353 (6)
M-O ₂	2.421 (3)	2.389 (4)	Na-O ₄	2.515 (7)	2.516 (6)
O ₁ -C ₁	1.349 (6)	1.352 (6)	Na-O ₅	2.410 (6)	2.407 (6)
O ₂ -C ₂	1.340 (5)	1.346 (6)	Na-O ₆	2.501 (7)	2.508 (7)
C ₁ -C ₂	1.415 (6)	1.407 (7)	O ₂ -O ₃	2.048 (7)	2.066 (7)
C ₂ -C ₃	1.401 (6)	1.402 (6)	O ₃ -O ₃	3.170 (12)	3.190 (12)
C ₃ -C ₄	1.385 (8)	1.385 (8)	O ₃ -O ₅	2.520 (8)	2.482 (8)
C ₄ -C ₅	1.396 (11)	1.395 (11)	O ₄ -O ₅	3.014 (9)	2.989 (9)
C ₅ -C ₆	1.421 (16)	1.425 (15)	O ₄ -O ₈	2.814 (6)	2.822 (6)
C ₆ -C ₁	1.396 (7)	1.401 (7)	O ₅ -O ₆	3.202 (10)	3.209 (9)
Na-O ₁	2.376 (5)	2.375 (5)	O ₅ -O ₇	3.015 (10)	3.022 (9)
Na-O ₂	2.546 (5)	2.526 (5)	O ₆ -O ₇	3.036 (10)	3.036 (9)

Table VII. Bond Angles in $Na_4[M(C_6H_4O_2)_4] \cdot 21H_2O$, $M = Th, U$

atoms	angle, deg		atoms	angle, deg	
	Th	U		Th	U
O ₁ -M-O ₂	66.8 (1)	67.7 (1)	O ₁ -C ₁ -C ₂	117.4 (4)	117.1 (4)
O ₁ -M-O ₂ (90°) ^a	80.7 (1)	80.0 (1)	O ₁ -C ₁ -C ₆	121.2 (9)	121.2 (8)
O ₁ -M-O ₂ (180°)	142.3 (1)	141.8 (1)	O ₂ -C ₂ -C ₁	118.0 (4)	117.6 (4)
O ₁ -M-O ₁ (90°)	93.64 (4)	93.73 (4)	O ₂ -C ₂ -C ₃	123.4 (4)	123.3 (5)
O ₁ -M-O ₁ (180°)	150.8 (2)	150.4 (2)	C ₁ -C ₂ -C ₃	118.6 (4)	119.1 (4)
O ₂ -M-O ₂ (90°)	128.6 (1)	129.5 (1)	C ₂ -C ₃ -C ₄	121.3 (6)	120.6 (5)
O ₂ -M-O ₂ (180°)	75.7 (2)	74.2 (2)	C ₃ -C ₄ -C ₅	119.4 (5)	120.1 (5)
			C ₄ -C ₅ -C ₆	121.3 (6)	121.0 (6)
			C ₅ -C ₆ -C ₁	117.8 (13)	117.4 (12)
			C ₆ -C ₁ -C ₂	121.5 (8)	121.7 (8)

^a The angle between catechols containing the two oxygens is given in parentheses.

1525, 1040, 935, 915, and 845 cm^{-1} are replaced by bands at 1570, 1025, 910, and 864 cm^{-1} in both the uranium and tho-

rium complexes. Since the electronic configuration of the Th(IV) ion is $5f^0$, the visible absorption spectrum is predictably

Table VIII. Weighted Least-Squares Planes^a for the Chelate Rings and Shape Parameters

phenyl ring			chelate ring		
atom	deviation, Å		atom	deviation, Å	
	Th	U		Th	U
C ₁	0.0414 (4)	0.015 (5)	O ₁	0.005 (4)	0.004 (4)
C ₂	-0.007 (4)	-0.009 (4)	O ₂	-0.005 (4)	-0.004 (4)
C ₃	-0.004 (5)	-0.004 (5)	C ₁	-0.012 (4)	-0.010 (5)
C ₄	0.016 (6)	0.014 (5)	C ₂	0.010 (4)	0.009 (4)
C ₅	-0.010 (6)	-0.010 (6)			
C ₆	-0.011 (6)	-0.010 (5)			
	<i>A</i> = 14.529	14.481		<i>A</i> = 14.588	14.530
	<i>B</i> = -2.214	-2.24		<i>B</i> = -1.887	-1.941
	<i>C</i> = 0.413	0.339		<i>C</i> = 0.181	-0.460
	<i>D</i> = 0.151	0.144		<i>D</i> = 0.265	0.247

dihedral angle between phenyl and chelate ring planes Th, 2.6°; U, 2.5°

	Shape Parameters (deg) for [M(C ₆ H ₄ O ₂) ₄] ⁴⁻ , M = Th, U					
	φ ₁	φ ₂	δ ₁	δ ₂	δ ₃	δ ₄
<i>D</i> _{2d} dodecahedron ^b	0.0	0.0	29.5	29.5	29.5	29.5
<i>C</i> _{2v} bicapped trigonal prism ^b	14.1	14.1	0.0	21.8	48.2	48.2
<i>D</i> _{4d} square antiprism ^b	24.5	24.5	0.0	0.0	52.4	52.4
[Th(C ₆ H ₄ O ₂) ₄] ⁴⁻	3.6	3.6	31.3	31.3	31.3	31.3
[U(C ₆ H ₄ O ₂) ₄] ⁴⁻	3.0	3.0	31.1	31.1	31.1	31.1

^a Equation for the least-squares plane is $A_x + B_y + C_z - D = 0$. ^b Shape parameters for the idealized geometries are from ref 42.

featureless, with only intense $\pi \rightarrow \pi^*$ bands in the ultraviolet region at 287 and 239 nm. In contrast, the uranium complex has many visible bands in addition to the UV peaks found in the thorium complex. In aqueous solution peaks are observed at 425, 450, 475, 510, 542, 592, 655, 675, and 875 nm. Measurements of the absorption spectrum on large oriented single crystals of the uranium complex doped into the thorium complex are currently in progress.

Analyses of preferred geometries for eight-coordinate compounds have been carried out by several workers.³⁸⁻⁴² The general conclusion is that the trigonal-faced dodecahedron and the square antiprism lie very close in energy. However, in the tetrakis(catecholato) complexes of thorium and uranium the structures preferred in the solid state are clearly dodecahedral as defined by Hoard and Silverton.³⁸ In describing a dodecahedron, these authors use the ratio of metal-ligand bond lengths ($M-A/M-B$) as well as two angles, θ_A and θ_B , defined as the angle between the principal symmetry axis ($\bar{4}$) and each metal-ligand vector. In their "most favorable" geometry the bond length ratio is 1.03, $\theta_A = 35.2^\circ$, and $\theta_B = 73.5^\circ$. For the thorium complex these parameters are respectively 1.00, 37.9° , and 75.4° where θ_A applies to the angle between the $\bar{4}$ axis and the M-O2 vector. For uranium, the corresponding numbers are 1.01, 37.1° , and 75.2° . For comparison, the single angle between the principal axis and the metal ligand vector needed in describing a square antiprism is 57.3° for the hard-sphere case. An alternative set of shape parameters have been proposed where δ is the dihedral angle between faces of the polyhedron defined by the ligand atoms and ϕ measures the non-planarity of the trapezoidal-type atoms BAAB.⁴¹ For thorium, $\phi = 3.6 (1)^\circ$ and all four dihedral angles are $31.3 (2)^\circ$. For uranium, $\phi = 3.0 (2)^\circ$ and the dihedral angles are all $31.1 (1)^\circ$. For the ideal dodecahedron, $\phi = 0^\circ$ and all four δ are 29.5° . In the bicapped trigonal prism $\phi = 14.1^\circ$ and δ has values of 0.0, 21.8, 48.2, and 48.2° . In the square antiprism $\phi = 24.5^\circ$ and $\delta = 0.0, 0.0, 52.4$, and 52.4° . Clearly, in the solid state, both [U(C₆H₄O₂)₄]⁴⁻ and [Th(C₆H₄O₂)₄]⁴⁻ are best characterized as having dodecahedral coordination geometries.

In the thorium complex both metal-oxygen bond lengths are very nearly identical; however, in the uranium complex they differ by 0.027 (5) Å. This is a significant difference, especially in light of the nearly identical thorium catecholato structure,

and is undoubtedly due to the 5f² electronic configuration of the uranium. The difference in average M-O distances in the two complexes (0.044 Å) is close to that of the difference in their ionic radii.⁴³

One explanation might be that interligand repulsion between oxygens at the A sites causes the change in M-O bond lengths upon going from the thorium to the smaller uranium metal center. In the uranium complex these oxygens are separated by 2.883 (7) Å compared to 2.972 (6) Å in the thorium complex. The former is near the van der Waals contact distance for oxygen atoms.⁴⁴ It might be suggested that some of the observed change in bond lengths serves to minimize intermolecular oxygen repulsion; however, the observed effect is much greater than expected from the change in ionic radii alone and there is no increase in the O-U-O bond angle [$75.6 (2)^\circ$ and $74.2 (2)^\circ$ for the Th and U complexes, respectively].

An alternative explanation lies in a ligand field effect. A simple one-electron qualitative crystal field picture of the *D*_{2d} uranium complex predicts a nondegenerate ground state arising from either the f_{xy^2} metal orbital (a_1 symmetry) or from the f_{z^2} orbital (b_2 symmetry). In the lanthanide and actinide series Russell-Saunders coupling is a reasonable first approximation. In this coupling scheme the ground term for U⁴⁺ (5f² configuration) is ³H₄. A ligand field of *D*_{2d} symmetry will decompose a $J = 4$ state into five nondegenerate (singlet) states and two twofold degenerate (doublet) states. If one of the nondegenerate states is lowest in energy and the next ligand field state is $\Delta E \text{ cm}^{-1}$ higher (where $\Delta E > kT$) no first-order temperature-dependent paramagnetic susceptibility will be observed. However, the magnetic field will induce a second-order temperature-independent susceptibility as observed here for the uranium catechol complex.⁴⁵ A more quantitative description must await further information about the ordering of the ligand field levels. Thus from electron-repulsion arguments one expects the ligand oxygen that is closer to the z axis to interact more with the filled metal orbital, thereby lengthening this metal-oxygen bond relative to the other. In accordance with this picture, the U-O2 distance is longer than the U-O1 distance.

To summarize, the tetrakis(catecholato) complexes of tetravalent uranium and thorium readily form in aqueous solutions to give isomorphous crystals with dodecahedral coordi-

nation about the metal. Optimized macrochelates employing catecholates for specific uptake of tetravalent actinide ions should allow the appended catecholates to dispose themselves about the metal in such a dodecahedral geometry. While the overall geometries of $[U(C_6H_4O_2)_4]^{4-}$ and $[Th(C_6H_4O_2)_4]^{4-}$ are nearly identical, the significant difference in the U-O bonds (A and B sites) compared with the difference in the Th complex is ascribed to a ligand field effect of the U(IV) $5f^2$ electronic configuration.

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Supplementary Material Available: Structure factor amplitudes and root mean square amplitudes of vibration along principal axes (61 pages). Ordering information is given on any current masthead page.

References and Notes

- Previous paper in this series: F. L. Weiti, K. N. Raymond, W. L. Smith, and T. R. Howard, *J. Am. Chem. Soc.*, **100**, 1170 (1978). Part of this work was presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, Abstract No. 67.
- A. Catsch, "Radioactive Metal Mobilization in Medicine", Charles C. Thomas, Springfield, Ill., 1964.
- B. J. Stores, B. R. Atherton, and D. S. Buster, *Health Phys.*, **20**, 369 (1971).
- H. Foreman, W. Moss, and W. Langham, *Health Phys.*, **2**, 326 (1960).
- P. W. Durbin in "Handbook of Experimental Pharmacology", Vol. 36, Springer-Verlag, New York, N.Y., 1973.
- J. B. Neilands, Ed., "Microbial Iron Metabolism", Academic Press, New York, N.Y., 1974.
- S. Isied, G. Kuo, and K. N. Raymond, *J. Am. Chem. Soc.*, **98**, 1762 (1976).
- A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Allg. Chem.*, **196**, 160 (1931).
- R. P. Agarwal and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, **24**, 160 (1931).
- K. Andr , *Z. Anorg. Allg. Chem.*, **361**, 254 (1968).
- While this work was in progress we obtained a copy of the Ph.D. Dissertation of B. Menes (Friedrich-Wilhelms-Universit t, Berlin, 1929) wherein the synthesis of $Na_4[U(C_6H_4O_2)_4] \cdot 21H_2O$ is reported.
- A. Rosenheim and B. Keimly, *Z. Anorg. Allg. Chem.*, **206**, 31 (1932).
- R. L. Gustafson and A. E. Martell, *Ann. N.Y. Acad. Sci.*, **88**, 322 (1960).
- A. Avdeef, T. L. Bregante, and K. N. Raymond, Abstracts, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, No. 7.
- S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1974).
- D. Grdenic and B. Matkovic, *Nature (London)*, **182**, 465 (1958).
- R. J. Hill and C. E. F. Rickard, *J. Inorg. Nucl. Chem.*, **39**, 1593 (1977).
- A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis", 3rd ed., Longmans, London, 1961, p 442.
- H. St. R de, *J. Phys. Chem.*, **77**, 424 (1973).
- F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes", Chapman and Hall, London, 1973.
- The programs used for the PDP 8/E computer were those written by Enraf-Nonius Corp. In addition to local programs for the Lawrence Berkeley Laboratory CDC 7600 computer, the following programs or modifications were used: Zalkin's FORDP Fourier program; Ibers' NUCLS, a group least-squares version of the Busing-Levy ORFLS program; ORFFE, a function and error program by Busing and Levy; and Johnson's ORTEP, a thermal ellipsoid plot program.
- The θ - 2θ scan technique was used to collect intensity data for the unique form $h, k, \pm l$ to a 2θ angle of 70° for the thorium salt and to 64° for the uranium salt. For the latter a duplicate form $-h, k, \pm l$ was also collected to 2θ of 10° and these data were averaged after correcting for absorption (R factor for averaging, 3.1% of F^2). For each reflection the scan angle was extended 25% on each side to estimate the background count. The scan time was variable with a maximum of 120 s. During data collection on the thorium compound the intensities of the 523, 541, and 222 reflections were measured as standards every 5400 s of X-ray exposure and showed no significant fluctuations. For the uranium compound, the 600, 060, and 004 reflections were monitored and showed a linear isotropic reduction in intensity of 8%. The data were corrected accordingly. For each crystal three high-angle orientation reflections were monitored every 100 reflections and a new orientation matrix calculated if the setting angles had changed by more than 0.1° in any axis.
- An attenuator decreasing the intensity of the diffracted beam by a factor of 18.17 was automatically inserted into the beam when the prescan indicated an intensity too high for accurate counting. The θ scan angle was calculated as $(0.60 + 0.35 \tan \theta)$, and an aperture with a height of 4 mm and a variable width ($\text{width} = 2.50 + 0.50 \tan \theta$) was located 173 mm from the crystal.
- K. I. Abu-Dari, J. D. Ekstrand, D. P. Freyberg, and K. N. Raymond, submitted for publication.
- L. K. Templeton and D. K. Templeton, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p. 143.
- In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w , is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for the nonhydrogen atoms were taken from the tabulations of Cromer and Mann (ref 27). Hydrogen scattering factors were those calculated by Stewart, Davidson, and Simpson (ref 28). Corrections for anomalous dispersion effects for the metal were made using $\Delta f'$ and $\Delta f''$ values of Cromer (ref 29).
- D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
- $R = \sum (|F_o| - |F_c|)^2 / \sum |F_o|^2$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The error in an observation of unit weight is defined as $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{var}})]^{1/2}$.
- See paragraph at end of paper regarding supplementary material.
- V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3626 (1970).
- G. F. Wessels, J. G. Leopoldt, and L. D. C. Bok, *Z. Anorg. Allg. Chem.*, **393**, 284 (1972).
- H. Titze, *Acta Chem. Scand.*, **24**, 405 (1970).
- I. Jelenic, D. Grdenic, and A. Bezjak, *Acta Crystallogr.*, **17**, 758 (1964).
- F. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).
- Y. Itoh, M. Nakahara, and Y. Kondo, *Nippon Kagaku Zasshi*, **92**, 227 (1971).
- J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
- D. G. Blight and D. L. Kepert, *Inorg. Chem.*, **11**, 1556 (1972).
- E. L. Muettterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
- M. A. Porai-Koshits and L. A. Aslanov, *Zh. Strukt. Khim.*, **13**, 266 (1972).
- E. L. Muettterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
- R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).
- L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 260.
- B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1966.