furan and drying the resulting crystals at room temperature under vacuum (0.1 mm.) for approximately 1 hr.

*Anal.* Calcd. for $C_{19}H_{23}OEu$: C, 54.4; H, 5.33; Eu, 36.2. Found: C, 54.7; H, 5.71; Eu, 36.6.

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CONTRIBUTION FROM THE RESEARCH LABORATORIES
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# The Synthesis and Characterization of Cyclopentadienyl Derivatives of Uranium and Thorium

BY GARY L. TER HAAR AND MICHAEL DUBECK

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The only known cyclopentadienyl derivatives of the actinide elements are the tricyclopentadienyluranium chloride reported by Reynolds and Wilkinson[1] and the tetracyclopentadienyls of uranium and thorium reported by Fischer and co-workers.[2,3] Reynolds and Wilkinson reported that the reaction of uranium trichloride with sodium cyclopentadienide had produced a small amount of air-sensitive, red material which was not completely characterized. Our attempts to prepare tricyclopentadienyluranium from the trichloride in tetrahydrofuran resulted in the isolation of tricyclopentadienyluranium butoxide. The isolation of the butoxide prompted us to prepare, by more efficient methods, the tricyclopentadienyl methoxide and butoxide derivatives of both uranium and thorium. In the course of our study, tricyclopentadienylthorium chloride was also isolated and characterized. Infrared, n.m.r., and X-ray data have been taken and the similarities in structure between the uranium and thorium compounds are discussed.

## Experimental

All experiments were carried out under a nitrogen atmosphere. Solvents were dried and distilled from lithium aluminum hydride and stored under nitrogen. Thorium tetrachloride was purchased from A. D. McKay. Uranium trichloride and tetrachloride were made according to literature preparations.[4] As the uranium compounds were extremely air-sensitive, the apparatus pictured in Fig. 1 was designed and used to purify the samples. The solid to be purified was placed in A, which was a small tube with a coarse frit. Petroleum ether was added and contained in B, and then the apparatus was sealed at D, by coating the 29/26 standard-taper ground-glass joint with molten DeKhotinsky cement. The solvent was cooled to −196°, a vacuum was drawn through stopcock E, and mercury was allowed to flow through H into G, giving a vacuum free from grease. Cold water circulated through the cold finger C, while the solvent was heated gently at 45°. The solvent condensed on the cold finger, flowed through the solid, and down through the hole in the glass plate. After the extraction was complete, the liquid was poured off from the crystals, which were now at the bottom, into F. By cooling the sides of the tube above B, it was possible to distil some of the solvent back and wash the product. These washes were then poured back into F, and F was sealed off with the flame and removed from the system. The product was then dried at $10^{-4}$ torr overnight. After transferring to a nitrogen box, the glass was cracked open at the constriction above B. The sample was removed and stored in a glass vial under high vacuum.

**Preparation of Tricyclopentadienyluranium *n*-Butoxide. (A) From Uranium Tetrachloride.**—In a 500-ml. round-bottom flask, equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet, was placed 250 ml. of dimethoxyethane, 12.0 g. (0.032 mole) of uranium tetrachloride, and 1.45 g. (0.063 mole) of freshly prepared sodium *n*-butoxide. After refluxing 3 hr., the mixture was cooled to 15° and 8.6 g. (0.089 mole) of sodium cyclopentadienide was added. After refluxing an additional 3 hr., the reaction was allowed to proceed at room temperature over the weekend. The solvent was removed under vacuum and the material was sublimed at 120° and $10^{-4}$ torr. A yield of 2.5 g. of a green-brown solid was isolated (15.5%). Purification was accomplished by crystallization from petroleum ether with the aid of the apparatus illustrated in Fig. 1. The purified product was in the form of green flaky crystals, m.p. 148–150°.

*Anal.* Calcd. for $U(C_5H_5)_3OC_4H_9$: C, 45.1; H, 4.78; U, 47.0. Found: C, 45.2; H, 4.84; U, 47.3.

The magnetic susceptibility of tricyclopentadienyluranium butoxide was measured in the solid state by use of the Gouy balance. Measurements were taken at 77, 197, and 298°K. The compound was found to obey the Curie–Weiss law, $M = 2.84\sqrt{(T - \Delta)\chi_M}$, with $\Delta = 82°$ and $M = 2.68$. Using the spin-only formula, a value of 1.86 unpaired electrons is obtained for the metal ion.

**(B) From Uranium Trichloride.**—To a mixture of 150 ml. of tetrahydrofuran and 2.2 g. (0.025 mole) of sodium cyclopentadienide was added 3.0 g. (0.0087 mole) of uranium trichroride. After refluxing for 3 days, the solvent was removed under vacuum and the residue was sublimed at 120° and $10^{-4}$ torr. The subremate was further purified with the recrystallization procedure outlined above. A product was isolated that had an infrared spectrum and melting point identical with those of the product prepared from uranium tetrachloride.

*Anal.* Calcd. for $U(C_5H_5)_3OC_4H_9$: C, 45.1; H, 4.78. Found: C, 45.0; H, 4.83.

**The Preparation of Tricyclopentadienyluranium Methoxide.**—The procedure was identical with that used for the butoxide.

*Anal.* Calcd. for $U(C_5H_5)_3OCH_3$: C, 41.4; H, 3.91; U, 51.3. Found: C, 42.1; H, 4.20; U, 50.7. The product was also green and of similar volatility and stability, however it did not melt but darkened over a long temperature range. The visible spectra of the butoxide and methoxide were taken in cyclohexane. For $U(C_5H_5)_3OC_4H_9$, absorbance was noted at 672 and 587 mμ with $\epsilon_m$ of 1570 and 690, respectively; for $U(C_5H_5)_3OCH_3$, at 672 and 587 mμ with $\epsilon_m$ of 1580 and 724, respectively.

**The Preparation of Tricyclopentadienytlhorium Chloride.**—To a mixture of 800 ml. of ethyl ether and 65 g. (0.63 mole) of potassium cyclopentadienide was added 18.0 g. (0.047 mole) of anhydrous thorium tetrachloride. This reaction mixture was stirred for 3 days at room temperature and then filtered. The collected solids were sublimed at 220° and $10^{-4}$ torr and 9.5 g. (44%) of white solid was collected. Further purification by re-sublimation at 200° and $10^{-4}$ torr gave 6.0 g. of product.

*Anal.* Calcd. for $Th(C_5H_5)_3Cl$: C, 38.9; H, 3.27; Cl, 7.66; Th, 50.1; mol. wt., 463. Found: C, 39.3; H, 3.36; Cl, 7.8; Th, 49.6; mol. wt. (ebullioscopically in methylene chloride), 455. The solid had a molar susceptibility at 299°K. of $-122 \times 10^{-6}$ c.g.s.u. The material is somewhat soluble in tetrahydrofuran, chloroform, and dichloromethane, but only slightly soluble in petroleum ether. Solutions in water break down rapidlp by cleavage of the cyclopentadienyl groups from the matal. While

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[1] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

[2] E. O. Fischer and Y. Hristidu, *Z. Naturforsch.*, **17**, 275 (1962).

[3] E. O. Fischer and A. Treiber, *ibid.*, **17**, 276 (1962).

[4] J. F. Suttle, *Inorg. Syn.*, **5**, 145 (1957); J. A. Hermann and J. F. Suttle, *ibid.*, **5**, 143 (1957).

the solid was moderately air-sensitive, solutions were extremely labile.

**The Preparation of Tricyclopentadienylthorium *n*-Butoxide.**—A mixture of 200 ml. of dimethoxyethane, 18.8 g. (0.05 mole) of thorium tetrachloride, and 4.8 g. (0.05 mole) of sodium *n*-butoxide was refluxed for 3 hr. After cooling to room temperature, 13.0 g. (0.15 mole) of sodium cyclopentadienide was added and refluxing was resumed for 15 hr. The solvent was removed under vacuum and the yellow residue was sublimed at 135° and $10^{-3}$ torr to yield 9.5 g. (38%) of a white sublimate. The volatile product was washed with petroleum ether and resublimed, m.p. 148–150°.

*Anal.* Calcd. for $Th(C_5H_5)_3OC_4H_9$: C, 45.6; H, 4.83; Th, 46.4. Found: C, 45.6; H, 4.89; Th, 45.8. The air-sensitive compound was soluble in tetrahydrofuran, chloroform, and methylene chloride, and somewhat soluble in petroleum ether.

**The Preparation of Tricyclopentadienylthorium Methoxide.**—The procedure for the preparation of the methoxide was identical with that for the butoxide homolog. The white methoxide was of similar volatility and stability. It was somewhat less soluble in organic solvents and did not melt but turned brown over a long temperature range.

*Anal.* Calcd. for $Th(C_5H_5)_3OCH_3$: C, 41.9; H, 3.96. Found: C, 42.2; H, 4.07.

## Results and Discussion

Tricyclopentadienyluranium butoxide was first prepared by us during our attempts to prepare tricyclopentadienyluranium. Degradation studies coupled with elemental analysis support the proposed molecular formula, $U(C_5H_5)_3OC_4H_9$. Its decomposition with methanolic hydrogen chloride liberated 1 equiv. of 1-butanol, identified qualitatively and quantitatively by vapor phase chromatography. Mass spectrometric examination of the complex revealed that the alkoxide is a normal butoxide group rather than a branch chain or unsaturated derivative. In addition, magnetic susceptibility measurements are consistent with uranium possessing two unshared electrons and formally in a +4 oxidation state. From the data it can only be deduced that the new complex is tricyclopentadienyluranium butoxide.

The use of solvents other than tetrahydrofuran in carrying out the reaction between sodium cyclopentadienide and uranium trichloride failed to produce any characterizable products. It thus appears that in the presence of tetrahydrofuran, at some stage in the reaction, an oxidation–reduction reaction takes place in which the ether is cleaved and reduced to the butoxide anion and uranium is oxidized to the +4 state.

Although tricyclopentadienyluranium butoxide was initially prepared in the manner described above, the best procedure for its preparation is to start with uranium tetrachloride.

$$UCl_4 + NaOR \longrightarrow NaCl + [UCl_3OR]$$

$$[UCl_3OR] + 3NaC_5H_5 \longrightarrow U(C_5H_5)_3OR + 3NaCl$$

Several grams of the complex can readily be prepared in this manner and it was with this material that most of the chemical and physical studies were carried out. This complex of uranium is extremely air-sensitive and rapidly loses its characteristic bright green color. It is soluble to some extent in practically all organic solvents and is extremely soluble in tetrahydrofuran. Tricyclopentadienyluranium methoxide was also prpared by the latter procedure. Its physical and chemical properties are quite similar to those of the butoxide derivative. It possesses the bright green color characteristic of this class of compounds, is soluble in organic solvents, and also exhibits remarkable volatility.

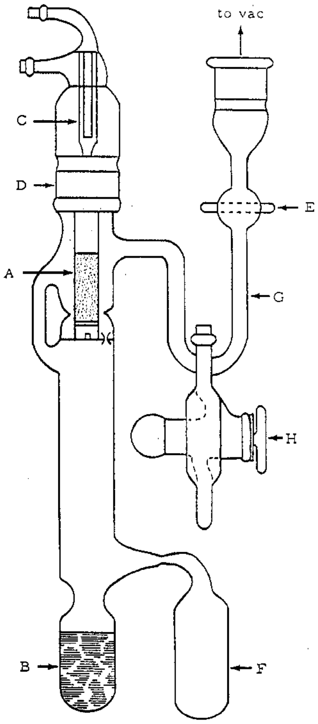

Fig. 1.—High vacuum liquid–solid extractor.

Both of the thorium alkoxide derivatives, $(C_5H_5)_3ThOCH_3$ and $(C_5H_5)_3ThOC_4H_9$, are white as opposed to the green of the analogous uranium compounds. The tricyclopentadienylthorium alkoxides exhibit similar properties to those of the uranium analogs. They are readily oxidized in air and hydrolyzed in water. Magnetic measurements show that these compounds are diamagnetic, which is in keeping with a +4 valence state.

During the course of our studies with thorium, we were able to synthesize and isolate the new compound tricyclopentadienylthorium chloride, $(C_5H_5)_3ThCl$. The complex is quite similar in chemical and physical properties to the tricyclopentadienylthorium alkoxides. It is white, soluble to some extent in organic solvents, can be readily sublimed, and is also diamagnetic.

The bonding in the uranium and thorium complexes appears to be similar and probably involves interactions between the central atom and the cyclopentadienyl rings that are more polar in character than those between the metal and the rings in ferrocene. That interactions of this nature exist with the cyclopentadienyl-actinide derivatives is indicated by the fact that some ferrocene is produced when these derivatives are treated with ferrous chloride. In addition, the n.m.r. spectra (Table I) reveal rather low-field cyclopentadienyl hydrogens in the region of $\tau$ 3.80. Such low-field ring hydrogen shifts are consistent with the suggested polar interactions between the ring and the central actinide atom. Polar bonds would not tend to deplete the electron density from the rings to the extent that occurs when strongly covalent, high molecular orbital overlap bonding is present. Induced ring currents in the relatively electron-rich rings would tend to deshield the ring hydrogens to an extent comparable to benzene and this is consistent with the observed shifts of $\tau$ 3.8.

TABLE I

N.M.R. SPECTRA OF THORIUM DERIVATIVES

| Compd. | Solvent | Peak position ($\tau$)[a] | Assignment |
|---|---|---|---|
| $Th(C_5H_5)_3OC_4H_9$ | Benzene | 3.90 (singlet) | $-C_5H_5$ |
| | | 6.25 (triplet) | $-OCH_2-$ |
| | | 8.52 (multiplet) | $-CH_2-CH_2-$ |
| | | 8.94 (triplet) | $-CH_3$ |
| $Th(C_5H_5)_3OCH_3$ | Benzene | 3.70 (singlet) | $-C_5H_5$ |
| | | 6.11 (singlet) | $-OCH_3$ |
| $Th(C_5H_5)_3Cl$ | Benzene | 3.80 (singlet) | $-C_5H_5$ |
| $Th(C_5H_5)_3Cl$ | $CDCl_3$ | 3.70 (singlet) | $-C_5H_5$ |

[a] Measured relative to $(CH_3)_4Si$ on a Varian 4300 spectrometer at 60 Mc.

TABLE II

INFRARED SPECTRA (CM.$^{-1}$) OF ACTINIDE DERIVATIVES[a]

| $Th(C_5H_5)_3Cl$ | $Th(C_5H_5)_3$-$OCH_3$ | $Th(C_5H_5)_3$-$OC_4H_9$ | $U(C_5H_5)_3$-$OC_4H_9$ | $U(C_5H_5)_3$-$OCH_3$ |
|---|---|---|---|---|
| ... | ... | ... | 4000 s | 3970 s |
| 3060 w | 3060 w | 3060 w | 3060 w | 3050 w |
| 2930 m | 2920 m | 2900 s | 2900 s | 2910 s |
| 2880 m | 2870 s | ... | ... | 2870 s |
| 2820 m | 2800 s | 2830 s | 2775 s | ... |
| 1785 w | 1730 s | 1760 w | 1735 m | 1768 w |
| 1680 m | 1650 m | 1645 w | 1655 m | 1650 w |
| ... | ... | 1450 m | 1462 m | ... |
| 1439 m | 1440 s | 1440 m | 1443 m | 1439 s |
| 1379 w | 1372 s | 1372 s | 1372 m | 1360 w |
| 1118 m | 1125 s | 1123 s | 1121 s | 1106 s |
| ... | 1092 s | 1092 s | 1078 s | ... |
| 1070 w | 1072 m | ... | ... | 1066 w |
| ... | 1034 m | 1032 m | 1033 m | 1042 w |
| 1013 s | 1012 s | 1010 s | 1012 s | 1010 s |

[a] s, strong; m, medium; w, weak. Spectra were taken with carbon tetrachloride as solvent.

The tricyclopentadienylthorium and uranium butoxides appear to be isostructural according to X-ray powder patterns.[5] The great similarity in *d*-values and their relative intensities indicate the two compounds have the same type of unit cell and molecular symmetry. In addition, molecular similarity is indicated by infrared spectra (Table II). Although structural similarity is proposed for the thorium and uranium complexes, an absolute structure determination is lacking without additional information. However, it is most probable that the cyclopentadienyl rings and the alkoxide or chloride are arranged symmetrically about the central atom at the corners of a distorted tetrahedron in the manner proposed for tricyclopentadienyluranium chloride.

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[5] The X-ray powder diffraction data which include intensities and *d*-values for tricyclopentadienylthorium and uranium butoxide have been deposited as Document Number 8047 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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## Solvent Effects on the Phosphorus-31 Chemical Shift in Triphenylphosphine Oxide[1]

BY GARY E. MACIEL AND RONALD V. JAMES

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Some recent work on the effect of solvents on the $C^{13}$ chemical shift of the carbonyl group of acetone[2] and other carbonyl-containing compounds[3] indicates that the shift is quite sensitive to an environment consisting of proton donors and relatively insensitive to the environment if proton donors are not present. The effect of major importance appears to be associated with the ability of the molecules of moderately acidic solvents to donate a proton in a hydrogen-bonded complex, or the ability of highly acidic solvents to produce a cationic protonated carbonyl group. The relatively larger range of chemical shifts observed in $P^{31}$ magnetic resonance studies[4-11] and the higher natural abundance of $P^{31}$ than $C^{13}$ (100% *vs.* 1.1%), as well as the generally smaller line widths of $P^{31}$ resonance lines,[4] usually result in greater precision and sensitivity in $P^{31}$ n.m.r. studies compared with similar $C^{13}$ work. These considerations have prompted us to undertake a solvent-shift study of the $P^{31}$ resonance of triphenylphosphine oxide to see if a behavior similar to that found in the $>C^{13}{=}O$ case,[2,3] but more sensitive to solvent and more precisely defined, would obtain. Some previous data on the effect of solvents on $P^{31}$ chemical shifts have been reported, and hydrogen bonding was mentioned as a likely influence.[4,12,13]

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[1] This investigation was supported by a PHS research grant (GM-11439-01) from the National Institute of General Medical Science, Public Health Service.

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