product could be sublimed at 30–45° (0.2 mm.), giving dark red crystals melting at 65–66°.

Anal. Calcd. for $C_8H_6O_6HgTa$: C, 16.6; H, 0.87; Ta, 31.3. Found: C, 16.4; H, 1.14; Ta, 31.2. The presence of Hg was established by emission spectroscopy.

The infrared spectrum of the compound (in ethyl ether) showed principal bands at 4.85, 5.05, and 5.20 μ. The spectra of recrystallized and sublimed samples were identical. Measurement of the magnetic susceptibility showed that the compound was diamagnetic.[4]

Methylmercurihexacarbonyltantalum.—A suspension of CH_3HgBr (2.10 g., 7.1 mmoles) in 60 ml. of ether was added in 50 min. at −5° to a stirred suspension of $[Na(dimethoxyethane)_3][Ta(CO)_6]$ (4.55 g., 7.1 mmoles) in 10 ml. of ether. The resulting mixture was stirred 15 min. at 0°, 30 min. at 25°, then filtered into a receiver cooled to −40°. The filtrate was evaporated to dryness *in vacuo*, and the residue was recrystallized from petroleum ether. This gave 1.93 g. (48%) of fine, dark red crystals.

Anal. Calcd. for $C_7H_3O_6HgTa$: C, 14.9; H, 0.53; Ta, 31.2. Found: C, 15.2; H, 0.74; Ta, 35.0.

The compound decomposed without melting at 50–60°; it could be sublimed at 35–55° (0.2 mm.), giving dark red crystals (17% recovery); in ethyl ether it showed principal infrared bands at 4.85, 5.05, and 5.20 μ.

Phenylmercurihexacarbonyltantalum.—This compound was obtained in a similar way in 30% yield. The purified product (copper-red plates) showed principal infrared bands at 4.80, 4.85, 5.05, and 5.20 μ. Attempts to sublime this compound resulted in rapid and complete decomposition. Owing to pronounced thermal instability at room temperature, no microanalysis or other physical measurements were attempted.

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[4] We wish to thank Prof. S. Kirschner of Wayne State University, Detroit, Mich., for carrying out the magnetic susceptibility measurement.

CONTRIBUTION FROM THE RESEARCH LABORATORIES
OF THE ETHYL CORPORATION, DETROIT, MICHIGAN

The Tetrahydrofuranate of Europium(III) Cyclopentadienide

BY SWITLANA MANASTYRSKYJ AND MICHAEL DUBECK

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During the course of our studies with the lanthanide cyclopentadienides,[1,2] we developed a method for the synthesis of the hitherto unreported europium tricyclopentadienide. Although the tricyclopentadienides of essentially all the lanthanides were prepared and characterized by Birmingham and Wilkinson,[3] the europium complex has not yet been reported. One reason for this is that the methods employed for the syntheses of the known lanthanide tricyclopentadienides are not applicable to europium. We have found, however, that if europium trichloride is treated with three equivalents of sodium cyclopentadienide in tetrahydrofuran and the reaction solution is carefully concentrated and cooled to induce crystallization, europium(III) cyclopentadienide can be isolated in the form of a monotetrahydrofuranate. In addition to the elemental analysis, the new compound was adequately identified as $(C_5H_5)_3Eu \cdot C_4H_8O$ by determining its molar magnetic susceptibility, which was found to be 5589 × 10^{-6} (c.g.s.u.) at 300°K. This value for the susceptibility indicates that europium is formally in a +3 oxidation state, a requirement for bonding to three cyclopentadienide anions.

Generally, this new mahogany-brown complex of europium possesses properties similar to other lanthanide cyclopentadienides. It is very prone to oxidation and hydrolytic cleavage, which necessitates handling under vacuum or nitrogen with the complete exclusion of protolytic solvents. It is soluble in tetrahydrofuran, carbon disulfide, and acetone, but it is essentially insoluble in nonpolar media such as petroleum ether. Tetrahydrofuran cannot be pumped from the complex under vacuum at room temperature. The ether is slowly lost at temperatures in the region of 100°. However, a characterizable product cannot be isolated at this stage nor by the attempted sublimation of the complex at 240° and 10^{-4} mm. The extent to which tetrahydrofuran is retained by the complex indicates that tetrahydrofuran is bound to europium with a fairly strong coordinate bond.

The unique property of europium in possessing a tricyclopentadienide that is different from the neighboring elements of the lanthanide series is noteworthy. A novel dicyclopentadienide of europium was recently isolated by Fischer,[4] which further attests the unusual chemistry of europium. In connection with this anomalous behavior of europium, we have also observed that, although dichloroeuropium cyclopentadienide can be prepared,[2] the chloroeuropium dicyclopentadienide cannot be made with methods applicable to samarium and gadolinium,[1] and the complex is presently unknown. Treatment of europium trichloride with two equivalents of sodium cyclopentadienide in tetrahydrofuran yields only the monotetrahydrofuranate of europium(III) cyclopentadienide in somewhat lower yields than are obtained with three equivalents of the alkali cyclopentadienide.

Experimental

The Preparation of Europium(III) Cyclopentadienide Monotetrahydrofuranate, $(C_5H_5)_3Eu \cdot C_4H_8O$.—In a typical preparation, 0.077 mole of sodium cyclopentadienide dissolved in 68 ml. of tetrahydrofuran was added to a rapidly stirred dispersion of 6.65 g. (0.026 mole) of anhydrous europium trichloride[5] in 175 ml. of tetrahydrofuran. Following the cyclopentadienide addition, which was carried out over a period of 2.5 hr. at room temperature, the brown-red reaction mixture was stirred overnight at room temperature under a blanket of prepurified nitrogen and then filtered. Concentration of the filtrate coupled with cooling in ice-water promoted the crystallization of 7.1 g. (65.7%) of shiny mahogany-brown plate-like crystals. An analytical sample was prepared by recrystallizing the initial product from tetrahydro-

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[1] R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963).

[2] S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

[3] J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

[4] E. O. Fischer and H. Fischer, *Angew. Chem.*, **76**, 52 (1964).

[5] Anhydrous $EuCl_3$ was prepared from a hydrate purchased from American Potash. The procedure employed is outlined in *Inorg. Syn.*, **5**, 153 (1957).

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 subre mate 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 ϵ_m of 1570 and 690, respectively; for $U(C_5H_5)_3OCH_3$, at 672 and 587 mμ with ϵ_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 resublimation 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 -122×10^{-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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