(Na_2CrF_4) or 2.01 to 2.18 ($CrClOH \cdot H_3BO_3$). These compounds reacted rapidly with dilute strong acids (H_2SO_4, HCl) to form Cr^{2+} solutions. Also, they reacted with acetate or benzoate buffers to form the insoluble chromium(II) acetate or benzoate, or with formate, glycolate, lactate, or oxalate buffers and NH_3, glycine, or ethylenediamine, to form the characteristic colored Cr^{2+} complexes.

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CONTRIBUTION FROM THE RESEARCH LABORATORIES
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Novel Mercury–Tantalum Carbonyl Derivatives

BY KESTUTIS A. KEBLYS AND MICHAEL DUBECK

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Although tantalum carbonyl is unknown, several tantalum carbonyl derivatives have been reported. For example, sodium bis(diethylene glycol dimethyl ether)hexacarbonyltantalate[1] has been prepared by a reductive carbonylation of tantalum(V) chloride and later converted to tetracarbonylcyclopentadienyltantalum[2] by treatment with cyclopentadienylsodium and mercury(II) chloride. The successful preparation of the above cyclopentadienyl derivative suggested that the method of Werner, *et al.*,[2] might be used to prepare the unknown alkyl and aryl derivatives of tantalum carbonyl according to the equation

$$\mathrm{RLi + HgX_2 + NaTa(CO)_6 \not\longrightarrow RTa(CO)_6 + Hg + NaX + LiX}$$

Our attempts to achieve such transformation, although unsuccessful in the original objective, led to the discovery of a new type of tantalum carbonyl derivative.

When tris(dimethoxyethane)sodium hexacarbonyltantalate was mixed in benzene with an equimolar amount of ethylmercuric chloride the color changed immediately from yellow to red, the hexacarbonyltantalate band at 5.40 μ disappeared, and new bands at lower wave length appeared. No significant gas evolution was noted, and no metallic mercury was deposited. Filtration to remove the precipitated sodium chloride (85% of theory) followed by evaporation of solvent and sublimation gave dark red crystals melting at 65–66° with partial decomposition. The product was insoluble in and unaffected by water; it was soluble in hexane, ether, and chloroform. The infrared spectrum showed principal absorption bands at 4.80, 5.05, and 5.20 μ. The compound contained both mercury and tantalum. Based on the mode of formation, the physical properties, and the chemical composition the new compound was identified as ethylmercurihexacarbonyltantalum, the product of a metathetical reaction according to the equation

$$\mathrm{[Na(C_4H_{10}O_2)_3][Ta(CO)_6] + C_2H_5HgCl \longrightarrow C_2H_5HgTa(CO)_6 + NaCl + 3C_4H_{10}O_2}$$

Solid $C_2H_5HgTa(CO)_6$ showed only limited thermal stability: it decomposed slowly at room temperature, but could be stored at 0° without change for at least 1 month. The decomposition was more rapid in solution, particularly in chlorinated solvents. However, solid $C_2H_5HgTa(CO)_6$ showed remarkable oxidative stability: it could be kept in air at $-20°$ for at least 12 hr. without any sign of decomposition.

The structure of the new compound undoubtedly involves a heptacoordinated tantalum and a mercury–tantalum bond. A possible alternate structure, $C_2H_5HgCOTa(CO)_5$, would involve a hexacoordinated tantalum and a carbonyl bridge between the two metal atoms. Such structure appears unlikely on the basis of infrared spectrum and magnetic susceptibility measurements: there were no bands in the bridging carbonyl region (5.4–5.6 μ), and the new compound was found to be diamagnetic. Physical properties (solubility, volatility) and infrared data argue against an ionic structure, $[C_2H_5Hg]^+[Ta(CO)_6]^-$, for the new compound. Hexacarbonyltantalate anion shows a strong, single band at 5.40 μ. This band is absent in the spectrum of the new compound. The observed shift of the carbonyl absorption to lower wave length is consistent with a decrease of charge on the tantalum atom.[3]

Although first prepared in benzene, $C_2H_5HgTa(CO)_6$ could be prepared most conveniently at 0° using ethyl ether as solvent. Similarly, $CH_3HgTa(CO)_6$ and $C_6H_5HgTa(CO)_6$ were also prepared from $[Na(C_4H_{10}O_2)_3][Ta(CO)_6]$ and the corresponding organomercuric halides. Both compounds were less stable thermally than the ethyl derivative. An attempt to prepare the allyl derivative was unsuccessful. The hexacarbonyltantalate did react with allylmercuric iodide, but failed to give a stable bimetallic derivative. It appeared that a mercury-free organotantalum compound, possibly π-allylpentacarbonyltantalum, was formed, but it was too unstable to be isolated. Similarly, no definite tantalum complexes could be isolated from mixtures obtained by thermal decomposition of $RHgTa(CO)_6$ compounds.

Experimental

Tris(dimethoxyethane)sodium hexacarbonyltantalate was prepared by the method of Werner, *et al.*[2] The mercury compounds were obtained from commercial sources and recrystallized before use. The solvents were purified by distillation from sodium. All manipulations were carried out under nitrogen.

Ethylmercurihexacarbonyltantalum.—Ether (125 ml.) was added in 30 min. to a solid mixture of $[Na(dimethoxyethane)_3][Ta(CO)_6]$ (9.0 g., 14.0 mmoles) and C_2H_5HgCl (3.52 g., 13.3 mmoles) cooled to $-5°$. The resulting mixture was stirred 1 hr. at 0°, then filtered. The solvent was evaporated *in vacuo* leaving a red, crystalline residue which was recrystallized from petroleum ether at $-40°$. There was obtained 6.42 g. (83% yield) of copper-red plates, melting at 65–67° with partial decomposition. The

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[1] R. P. M. Werner and H. E. Podall, *Chem. Ind.* (London), 144 (1961).

[2] R. P. M. Werner, A. H. Filbey, and S. A. Manastyrskyj, *Inorg. Chem.*, **3**, 298 (1964).

[3] W. Beck and R. E. Nitzschmann, *Z. Naturforsch.*, **17b**, 577 (1962); E. W. Abel, *Quat. Rev.* (London), **17**, 143 (1963).

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

Anal. Calcd. for $C_8H_5O_6HgTa$: 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
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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).