passed through a bed of pulverized sodium thiocyanate at room temperature the solid became brick-red in color. The product was extracted with water, leaving a red insoluble material having the properties of parathiocyanogen, $(CNS)_x$.

Reaction with Alkenes. Tetrafluoroethylene, oxygen difluoride, and nitrogen were introduced separately in the molar amounts, 0.0019, 0.0038, and 0.015, respectively, into a glass vessel cooled by liquid nitrogen. The vessel was then allowed to warm slowly to room temperature. As it did so, hexafluoroethane and carbonyl fluoride were formed. No pentafluoroethyl hypofluorite was found in the product.

A mixture of equal volumes of **ethylene** and oxygen difluoride at a total pressure of 100 mm. exploded after standing at room temperature for about 10 min. Other such mixtures at a total pressure of 60 mm. did not explode but instead reacted slowly giving fluoroethane and 1,2-difluoroethane. In two cases the product, when condensed, exploded after removal of unreacted oxygen difluoride.

1,2-Difluoroethane had strong absorption bands in the infrared at 3.40, 9.18, 9.40, 9.65, 9.70, and 11.16 (center of a triplet) μ. Medium bands occurred at 6.85, 7.20, 8.05, and 11.70 μ. In the mass spectrum "peaks" were found for the following ions in the order of decreasing abundance: CH_2F^+, $C_2H_3^+$, $C_2H_4^+$, $C_2H_3F^+$, $C_2H_2F^+$, $C_2H_2^+$, C_2H^+, CHF^+, CF^+, CH_2^+, $C_2H_4F_2^+$, $C_2H_4F^+$, $C_2H_3F_2^+$, C_2HF^+, $C_2H_2F_2^+$, C_2F^+, $C_2HF_2^+$, C_2^+, F^+, and CH^+.

Attempted Reaction with Dioxane in Water.—Since oxygen difluoride is somewhat soluble in water, it may very well behave as a fluorinating agent for various substances in aqueous solution. An unsuccessful attempt was made to replace the hydrogen atoms in dioxane by shaking a dilute aqueous solution of this substance in contact with gaseous oxygen difluoride at room temperature. No evidence was found for replacement of hydrogen atoms bound to carbon.

Other Reactions.—Oxygen difluoride reacted vigorously with ammonia, trimethylamine, or pyridine to give the acid fluoride of the base and a gas containing nitrous oxide. Hydrazine burst into flame upon contact with OF_2. With an aqueous solution of $N_2H_4\cdot H_2SO_4$ or $NH_2OH\cdot H_2SO_4$ the reaction of OF_2 was slow, the gaseous product containing N_2 or N_2O, respectively. From tetrafluorohydrazine the product contained NO_2 and NF_3. Exploratory studies were made of the reaction of oxygen difluoride with C_2N_2, SO_2, or SOF_2.

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CONTRIBUTION FROM THE RESEARCH DIVISION,
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New Air-Stable Chromium(II) Compounds

BY A. J. DEYRUP

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New chromium(II) compounds were prepared for use as convenient, air-stable materials for making chromium(II) electroplating baths.[1,2] These are Na_2CrF_4 and $CrXOH\cdot H_3BO_3$ ($X = Cl, Br, I$). Attempts to precipitate sodium analogs of $KCrF_3$ and $NH_4CrF_3\cdot 2H_2O$[3] yielded no evidence for $NaCrF_3$, but resulted in the compound Na_2CrF_4. Attempts to prepare a "chromous borate"[4] by the reaction of a chromium(II) salt with an alkali borate resulted in a pyrophoric product. Modification of the pH to the range 2.9–4.0 before allowing chromium(II) chloride to react with boric acid led to $CrClOH\cdot H_3BO_3$. Bromine and iodine analogs of the last compound were made similarly.

Experimental

Sodium Fluorochromate(II), Na_2CrF_4.—A chromium(II) sulfamate solution was made by allowing 0.4 g.-atom of chromium powder to react with 0.4 mole of NH_2SO_3H in 200 ml. of water. The temperature was slowly raised to 90°. The bright blue solution was filtered to remove excess chromium and transferred to a flask containing 0.8 mole of NaF and 200 ml. of water. The mixture was stirred and heated to 80–100°, then allowed to cool. The precipitate was washed with 1:1 methanol–water, then with methanol, then dried. Deoxygenated water and nitrogen atmosphere were used throughout until the product was dry. The compound formed a mat of pale blue needles about 0.4 mm. long. The yield was about 75–78% based on Cr^{2+} and F^-. In other experiments a pure chromium(II) chloride solution formed the same product. Completeness of precipitation appeared to depend on a molal solubility product of the order of $[Na^+]^2[Cr^{2+}][F^-]^4 = 10^{-3}$ to 10^{-4}.

Anal. Calcd. for Na_2CrF_4: Na, 26.4; F, 43.7; Cr, 29.9. Found: Na, 27.8; F, 43.1; Cr (total), 29.5; Cr (divalent), 28.6.

Specific Properties.—The X-ray powder diffraction pattern was complex, with d = 4.86, 2.81, and 2.76 Å. as the strongest lines. The magnetic moment of Cr from magnetic susceptibility was about 5.2 B.M. Heating in air at 180° for 1 hr. caused less than 0.2% change in weight or titratable Cr^{2+} content.

$CrXOH\cdot H_3BO_3$ (X = Cl, Br, I).—$CrClOH\cdot H_3BO_3$ was made by pouring 1 l. of 1 M pure $CrCl_2$ soution into 500 ml. of water containing 1.5 moles of H_3BO_3, 0.57 mole of $CaCl_2\cdot 2H_2O$, and 0.25 mole of $CaCO_3$. The mixture was held at 50° and stirred until gas evolution stopped, then was allowed to cool while stirring for 16 hr. The pale blue precipitate was filtered and washed by complete redispersion to a dilution ratio of (5:1)[8] with a 4.8% H_3BO_3 solution to prevent hydrolysis. It was dried under a high vacuum. The small amount of free boric acid left in it was calculated from the concentration in the wash solution and the weight of water trapped during drying. Air-free water and a nitrogen atmosphere were used throughout until after drying.

In other experiments, it was found necessary to hold the pH in the range 2.9–4.0 (as by the $CaCO_3$–Ca^{2+} buffer system) to avoid formation of air-oxidizable impurities. Similar Br and I compounds were formed, but of lower purity.

Anal. Calcd. for $CrClOH\cdot H_3BO_3$: H, 2.4; Cr, 31.3, Cl, 21.3; B, 6.5; Ca, 0. Found: H, 2.7; Cr, 31.2; Cl, 20.9; B, 7.1; Ca, 0.

Specific Properties.—$CrClOH\cdot H_3BO_3$ was a pale blue tetragonal crystalline powder. It showed a sharp X-ray powder diffraction pattern, indexed as tetragonal, $a_0 = 6.31$, $c_0 = 5.675$ Å. Density measurements in toluene showed 2.43 ± 0.03 g./cm.^{3}. From density and unit cell dimensions, the molecular weight of the unit cell was 331 ± 3 (double the formula weight is 332.6). The magnetic moment of Cr was found to be about 4.5 B.M.

General Properties.—All the compounds described were light or pale blue and remained so for over 2 years in unsealed laboratory containers. They could, however, be discolored toward green by access of very small amounts of air during any stage of preparation. Formation conditions indicate appreciable solubility in pure water, and this appeared to be so under the anaerobic conditions of preparation. However, after drying, they did not dissolve in pure water. It is possible that they may superficially oxidize in moist air. However, the chromium valence analysis increased on 2-year air exposure only from 2.03 to 2.18

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[1] A. J. Deyrup, U. S. Patent 2,996,353 (Aug. 15, 1961).

[2] A. J. Deyrup, U. S. Patent 3,088,801 (May 7, 1963).

[3] W. Traube, E. Burmeister. and R. Stahn, *Z. anorg. allgem. Chem.*, **147**, 50 (1925).

[4] A. Moberg, *J. prakt. Chem.*, (1) **44**, 332 (1848).

(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
OF THE ETHYL CORPORATION, DETROIT, MICHIGAN

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

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

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

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

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 $[Na(\text{dimethoxyethane})_3][Ta(CO)_6]$ (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. Nitzchmann, *Z. Naturforsch.*, **17b**, 577 (1962); E. W. Abel, *Quat. Rev.* (London), **17**, 143 (1963).