CLX.—*The Acetates of Ruthenium.*

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THE ruthenium salts of the acids of the acetic series appear to be unknown. In this paper the preparation of several of the *acetates* is described. They are all of the complex basic type, as is to be expected from the position of the metal in the periodic table (compare chromium and especially iron). Though the great solubility of most of these compounds makes their purification very difficult, the analytical results indicate that definite chemical individuals were obtained.

They were made by the action of the acid on the hydroxide formed by treating ruthenium trichloride, $RuCl_3$, with alkali. This is generally regarded as the hydrated trioxide Ru_2O_3,xH_2O; but Howe (*J. Amer. Chem. Soc.*, 1927, **49**, 2381) maintains that it contains quadrivalent ruthenium, and that its formula should be written RuO_2,xH_2O, whilst Crowell and Yost (*ibid.*, 1928, **50**, 374) and Remy and Lührs (*Ber.*, 1928, **61**, 917; 1929, **62**, 200) consider that in the hydroxide, and in the more or less hydrolysed solutions of the chloride in water, the metal is partly tervalent and partly quadrivalent. This leads to a difficulty in formulating some of the acetates. Most of them are derived from a complex salt which should be written $Ru_2(C_2H_3O_2)_4(OH)_4$ if the metal is quadrivalent, and $Ru_2(C_2H_3O_2)_4(OH)_2(OH_2)_2$ if it is tervalent. The difference in composition for the metal and the carbon lies within the errors of analysis; but the values for the hydrogen, though rather uncertain owing to the difficulty of ensuring complete removal of the water without decomposition, agree best with the assumption that the metal is tervalent. Two of the acetates must contain tervalent ruthenium.

The first product (A) of the action of glacial acetic acid on the trioxide is $Ru_2(C_2H_3O_2)_4(OH)_2(OH_2)_2$. This on hydrolysis yields (B) $Ru_2(C_2H_3O_2)_3(OH)_3(OH_2)_2$ and (C) $Ru_2(C_2H_3O_2)(OH)_5(OH_2)_2$. (It seems simpler to distinguish the compounds by letters, rather than by lengthy systematic names.) These three obviously belong to one type. Two others of a different type were obtained: (D) $Ru_2(C_2H_3O_2)_4(OH)_2$, formed along with (B) in the hydrolysis of (A), and (E) $Ru_2(C_2H_3O_2)_5(OH)$. These differed in properties from the first three, being excessively hygroscopic, and less easily reduced to the metal on ignition.

EXPERIMENTAL.

Pure ruthenium sponge, kindly lent by the Mond Nickel Company, was converted through the tetroxide into the trichloride, and thence by precipitation in aqueous solution with alkali into the hydroxide, which was washed, dried, and used in the subsequent work.

Methods of Analysis.—For the estimation of ruthenium, a weighed quantity of the compound was heated in a porcelain crucible, and then ignited strongly in a stream of hydrogen (introduced by a silica tube passing through the lid) until the weight was constant. For the two compounds (D) and (E) it was necessary, in order to prevent reaction with the crucible in the earlier stages, to wrap the sample in filter paper and heat it at first gently and then more strongly until the paper was burnt away; the subsequent reduction in hydrogen was then carried out as before.

The carbon and hydrogen were determined by combustion.

(A). $Ru_2(C_2H_3O_2)_4(OH)_2(OH_2)_2$.—Freshly prepared hydroxide was boiled for 2 hours with glacial acetic acid. The dark green, almost black, solution was filtered and concentrated on a water-bath. On cooling, a solid separated, which was filtered off and, after removal of as much as possible of the mother-liquor by pressing between filter papers, was dried in a desiccator over sulphuric acid. It formed a black crystalline powder, readily and completely soluble in water or alcohol to a deep green solution (Found: Ru, 40·0; C, 18·71; H, 3·18. $C_8H_{18}O_{12}Ru_2$ requires Ru, 39·93; C, 18·85; H, 3·53%). A further but less pure yield was obtained from the mother-liquor.

(B). $Ru_2(C_2H_3O_2)_3(OH)_3(OH_2)_2$.—A strong solution of the previous compound in water was boiled for about 20 minutes. It became acid, turned brown, and deposited a black precipitate. This was filtered off and dried at 80°. It was insoluble in water (Found: Ru, 43·9; C, 15·45; H, 3·32. $C_6H_{16}O_{11}Ru_2$ requires Ru, 43·51; C, 15·40; H, 3·42%).

(D). $Ru_2(C_2H_3O_2)_4(OH)_2$.—The brownish filtrate from (B) was evaporated on a water-bath. It gave no signs of crystallising, but left a black powder, very hygroscopic and readily soluble in alcohol, from which it was precipitated unchanged by ether. A drop of the concentrated aqueous solution, when evaporated on a warmed microscope slide, formed a network of brownish-black crystals

(Found: Ru, 43·08; C, 19·62; H, 3·34. $C_8H_{14}O_{10}Ru_2$ requires Ru, 42·96; C, 20·28; H, 2·96%).

(C). $Ru_2(C_2H_3O_2)(OH)_5(OH_2)_2$.—On prolonged treatment with water, the tetra-acetate (A) undergoes further hydrolysis; after 24 hours' treatment with dilute acetic acid at 100°, the solution on evaporation left a residue of a black powder, completely soluble in water or alcohol to a brownish-green solution, and approximating in composition to $Ru_2(C_2H_3O_2)_2(OH)_4(OH_2)_2$. When this was boiled with water, nearly all the ruthenium was precipitated as a black powder of the composition of (C) (Found: Ru, 53·30; C, 6·10; H, 3·01. $C_2H_{12}O_9Ru_2$ requires Ru, 53·05; C, 6·26; H, 3·13%).

(E). $Ru_2(C_2H_3O_2)_5OH$.—Freshly prepared ruthenium hydroxide was dissolved in 50% acetic acid, and the deep green solution filtered and evaporated to dryness. A black, very hygroscopic residue remained, which gave a deep green solution in water or alcohol, and was precipitated from the latter as a black powder (Found: Ru, 39·5; C, 23·41; H, 3·5. $C_{10}H_{16}O_{11}Ru_2$ requires Ru, 39·47; C, 23·28; H, 3·10%).

Ruthenium Formates.—Ruthenium hydroxide dissolves readily in 50% formic acid, and the deep green solution on evaporation leaves a black crystalline residue very soluble in water, but, unlike the acetates, insoluble in alcohol. The composition of this approximates to the formula $Ru_3(HCO_2)_7(OH)_2,5H_2O$ (Found: Ru, 41·0; C, 11·2; H, 1·96. $C_7H_{19}O_{21}Ru_3$ requires Ru, 41·00; C, 11·29; H, 2·55%). Belloni (*Arch. Pharm.*, 1909, **247**, 123) obtained in the same way from ferric hydroxide a formate of the similar formula $Fe_3(HCO_2)_7(OH)_2,7H_2O$.

On prolonged heating with water, the *ruthenium formate* is partially hydrolysed, with the production of a series of yellow, brown, and black products, some soluble in water and some in alcohol, which were not further examined.

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