507. *A Basic Trinuclear Ruthenium Acetate.*

By F. S. Martin.

The reduction of ruthenium tetroxide by acetaldehyde in anhydrous acetic acid–carbon tetrachloride causes precipitation of the trinuclear basic acetate $[Ru_3(OAc)_6(OH)_2](OAc),7H_2O$. This compound dissolves slowly in water to give an intensely blue solution, and rapidly in pyridine to give a solution which becomes green when warmed. $[Ru_3(OAc)_6py_5]Cl,PtCl_6$ (py = pyridine) is precipitated from the aqueous solution of the pyridyl derivative by addition of chloroplatinic acid in dilute hydrochloric acid.

Basic trinuclear complex salts of transitional-group metals are known for chromium, vanadium, iron, and cobalt. The type formula of these compounds is $[M^{III}(X)_6(OH)_2]Y$ where M^{III} represents a tervalent metal, X may be a lower fatty acid radical, *e.g.*, formate or acetate, or half of a dibasic acid radical such as succinate, and Y is any monobasic anion. References to investigations of these compounds are numerous, much of the work being done by Weinland and his collaborators (*e.g.*, *Ber.*, 1916, **49**, 1003; *Z. anorg. Chem.*, 1924, **132**, 209; 1926, **152**, 1). Tervalent iron readily forms this type of trinuclear complex and it might be expected that tervalent ruthenium would behave similarly since other analogous series of compounds of the iron–ruthenium–osmium sub-group are well established, *e.g.*, the trisdipyridyls $[M^{III}(dipy)_3]Cl_3$ and the tris-*o*-phenanthrolines $[M^{III}(phenan)_3]Cl_3$ (Blau, *Monatsh.*, 1898, **19**, 651; Burstall, *J.*, 1936, 173). The general method of preparing the trinuclear basic acetates of iron is to heat ferric hydroxide or chloride with glacial acetic acid. This method has been applied to ruthenium in one case. Mond (*J.*, 1930, 1247) heated hydrated ruthenium oxide with glacial acetic acid and obtained the binuclear complexes $Ru_2(OAc)_4(OH)_2(H_2O)_2$, $Ru_2(OAc)_3(OH)_3(H_2O)_2$, $Ru_2(OAc)(OH)_5(H_2O)_2$, and $Ru_2(OAc)_5(OH)$. On heating the hydrated oxide with formic acid, however, Mond obtained a compound with a formula approximating to $Ru_3(H{\cdot}CO_2)_7(OH)_2,5H_2O$. He based these formulations on the assumption that the hydrated ruthenium oxide used was the tervalent oxide. This assumption is not entirely justified since the method used for the preparation of the oxide (precipitation from ruthenium trichloride by alkali) leads to the simultaneous formation of some ruthenium(IV) hydrated oxide.

The present paper describes how a trinuclear ruthenium(III) compound is obtained by reduction of Ru(VIII) in an anhydrous acetic acid system, the valency of the product being unambiguously determined.

EXPERIMENTAL

Anhydrous solutions of ruthenium tetroxide in carbon tetrachloride were mixed with approx. 50% by volume of glacial acetic acid. Acetaldehyde was added to the mixture until an intensely dark blue precipitate formed and slowly settled. The precipitated *complex* was filtered off on a sintered-glass disc, washed well with carbon tetrachloride, and dried in a vacuum-desiccator over silica gel. Only one product is formed, hence this procedure yields material free from by-products since acetaldehyde is oxidised to acetic acid by ruthenium tetroxide. The valency of the ruthenium in the product was shown to be three by measuring the number of equivalents of ceric iron consumed in oxidation back to Ru(VIII). 2·3 Acetate groups were found per ruthenium atom (Found: Ru, 34·7; OAc, 47·2; H_2O, 14·5. $Ru_3(OAc)_7(OH)_2,7H_2O$ requires Ru, 34·7; OAc, 47·1; H_2O, 14·4%). One acetate group was found to be anionic by adsorption of the blue $[Ru_3(OAc)_6(OH)_2]^+$ cation on a cation-exchange resin (Zeocarb 225), and the compound is therefore formulated $[Ru_3(OAc)_6(OH)_2](OAc),7H_2O$.

The complex dissolves in pyridine to give a blue solution, becoming intensely green when warmed. When the excess of pyridine is removed by evaporation a sticky green residue, highly soluble in water, is obtained. The green aqueous solution, on addition of chloroplatinic acid dissolved in dilute hydrochloric acid, yields a blue-green precipitate. This *salt* was washed with cold water and dried *in vacuo* over silica gel {Found: Ru, 18·5; C_5H_5N, 25·3; Cl, 15·3; H_2O, 7·8. $[Ru_3(OAc)_6(C_5H_5N)_5]Cl,PtCl_6,7H_2O$ requires Ru, 18·7; C_5H_5N, 24·4; Cl, 15·3; H_2O, 7·8%}.

Preparation of Ruthenium Tetroxide.—This oxide was distilled from ruthenium(IV) sulphate solutions in the presence of periodic acid. The distillate was collected in ice-cold carbon tetrachloride, and the solution was freed from water by shaking it with anhydrone.

Analysis.—(*a*) Ruthenium was analysed by the absorptiometric method of Marshall and Richard (U.S.A.E.C. unclassified document no. AECU 224). In this method the sample is fused with potassium hydroxide and potassium nitrate in a silver dish. The melt is dissolved in 2N-potassium hydroxide, and the orange ruthenate colour is determined in a Spekker absorptiometer with a combination of Wratten 50 and O.B.2 filters.

(*b*) Acetate groups were determined by distillation from phosphoric acid solution. The distillate was boiled under reflux to remove carbon dioxidc, and the acetic acid titrated with standard alkali.

(*c*) Pyridine was determined by distillation from strongly alkaline solution, the distillate being titrated with standard hydrochloric acid to screened methyl-orange.

(*d*) Chlorine was determined by precipitation with silver nitrate after fusion of the sample with sodium carbonate and dissolution in water.

(*e*) Water was determined by the loss of weight on heating in an electric air-oven at 115°.

Confirmation of Valency.—A sample of the complex was heated at 90° with a known excess of ceric ammonium sulphate in 2N-sulphuric acid for about 1 hour, the ruthenium being all converted into the volatile ruthenium(VIII) oxide. This was removed by air-sparging the hot solution, and the excess of ceric ion was titrated with ferrous ammonium sulphate. The consumption of ceric ion was five equivs. per ruthenium atom, and the oxidation state of the ruthenium is therefore $8 - 5 = +3$.

DISCUSSION

The hexa-acetatodihydroxytriruthenium univalent cation described here is exactly analogous to the chromium and iron complexes described, *e.g.*, by Weinland *et al.* (*locc. cit.*). The univalent trinuclear cation never contains less than six acetato- (or other monobasic acido-) groups or less than three dibasic acido-groups. The hydroxy-groups, however, may be replaced, either singly or both together, resulting in an increase in valency of the cation from one to two to three. Thus the compounds $[Cr_3(OAc)_6OH](OAc)_2,5H_2O$ and $[Fe_3(OAc)_6](OAc)Cr_2O_7,H_2O$ have been described by Weinland (*Ber.*, 1908, **41**, 3236). The trinuclear ruthenium chloroplatinate described above is an example of a pyridyl derivative of the tervalent cation type. Weinland has described both pyridyl and ammino-derivatives of the triferric and trichromium hexa-acetato-bases.

The complex $[Ru_3(OAc)_6(OH)_2]OAc,7H_2O$ dissolves in alkali hydroxides, giving an immediate green solution, but the colour changes from blue to brown slowly in dilute acids and rapidly in concentrated acids. The substance is apparently stable to ammonia, whereas under the same conditions the triferric compound yields a precipitate of ferric hydroxide.

Since osmium tetroxide is similar to ruthenium tetroxide in many of its reactions, it seems possible that the analogous triosmium complex could be prepared by reduction of the tetroxide in acetic acid and thus complete the series for the Fe–Ru–Os sub-group.

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