μ_3-Oxo-triruthenium Carboxylate Complexes †

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The green complex formed on treating commercial ruthenium trichloride hydrate with acetic acid and sodium acetate in ethanol is shown to be of the basic acetate oxo-centred triangular type with the formula $[Ru_3O(CO_2Me)_6(H_2O)_3](CO_2Me)$. The complex may be cationic, neutral, or anionic depending on the pH of the solution, owing to ionisation of co-ordinated water. The water molecules may be replaced by pyridine to give $[Ru_3O(CO_2Me)_6py_3]^+$. Both the aquo and pyridine complexes undergo successive one and two electron reductions to give complexes in which the metal atoms are in formal oxidation states $+2\frac{2}{3}$ or (III, III, II) and +2 or (II, II, II) respectively. The reduction to the latter state involves loss of the central oxygen atom from the triangle of metal atoms; this atom may be re-inserted using molecular oxygen, or more specifically by use of a reagent such as pyridine-*N*-oxide. In the presence of triphenylphosphine, $[Ru_3O(CO_2Me)(H_2O)_3]^+$ gives the reduced species $Ru_3O(CO_2Me)_6(PPh_3)_3$. The potentials and reversibility of the redox reactions have been studied electrochemically. Analogous complexes of other carboxylic acids are described. N.m.r., i.r., and electronic absorption spectra of the species are reported.

THE first study of ruthenium carboxylate compounds was by Mond,[1] who obtained a series of complexes, formulated as binuclear species, by refluxing a hydrated ruthenium(III, IV) oxide with the acid. This work has since been questioned,[2] and has not proved reproducible.[3] By reduction, with acetaldehyde, of solutions of ruthenium tetroxide in acetic acid–carbon tetrachloride mixtures, Martin[4] obtained a complex thought to be $[Ru_3(CO_2Me)_6(OH)_2](CO_2Me),7H_2O$ analogous to the basic acetates of chromium(III) and iron(III). The latter two complexes and the so-called manganese(III) acetate have been shown by *X*-ray crystallography to contain the trinuclear oxygen-centred cation, $[M_3O(CO_2Me)_6(H_2O)_3]^+$ ($M = Cr$,[5] Mn,[6] or Fe[7]). It was suggested[3] that Martin's ruthenium acetate had this type of structure and the Raman spectrum of the complex was inter-

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† No reprints available.

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preted on this assumption.[8] It will be shown here, however, that Martin's complex cannot possess the proposed structure but that Mond's acetate contains mainly an oxo-centred species. By the interaction of commercial hydrated ruthenium trichloride with acetic acid, acetic anhydride mixtures, the complex $[Ru_2(CO_2Me)_4]Cl$ was obtained;[3] other similar carboxylates were prepared. An *X*-ray crystallographic study[9] confirmed the proposed tetra-acetato-bridged binuclear structure and showed that $[Ru_2(CO_2Me)_4]^+$ units were linked into chains by Ru–Cl–Ru bridges. The complex has equivalent ruthenium atoms in the mean oxidation state of $+2{\cdot}5$ or, as originally formulated, (II, III).

The above reaction gives not only $[Ru_2(CO_2Me)_4]Cl$, but a green solution and it was later thought[10] that the latter might contain the corresponding neutral dimer. Using somewhat different conditions, namely the interaction of ruthenium chloride, acetic acid, and sodium acetate in ethanol, a green impure material was isolated. This was shown to form adducts with pyridine and triphenylphosphine, which were formulated as adducts of the dimer by analogy with the well known adducts of the dimeric tetra-bridged acetates of Cr^{II}, Cu^{II}, and Rh^{II}.

In further studies of these materials, especially electrochemical studies, it soon became apparent that the green acetate could not be $Ru_2(CO_2Me)_4$ but must be a ruthenium(III) complex of the basic acetate, oxo-centred type. Molecular weight determinations also indicated that the PPh_3 adduct was trinuclear and the oxo-centred structure of the latter was proved by *X*-ray crystallographic study.[11] Hence this complex is $Ru_3O(CO_2Me)_6(PPh_3)_3$ with identical ruthenium atoms in a mean oxidation state of $+2\frac{2}{3}$, or less correctly using the Stock nomenclature with Ru^{II}, Ru^{III}, Ru^{III}.

All the previously known oxo-centred species have the metal atom in the +3 state; the ruthenium acetate system provides the first example of an oxo-acetate of a second or third row element and also of reversible redox reactions.

The μ_3-Oxo-triruthenium(III) *Carboxylates*

Synthesis of Oxo-carboxylates.—The acetate was prepared as before[11] in an impure state; the use of an inert atmosphere is not necessary, and a reflux time of one hour is sufficient. The crude product contains a considerable excess of sodium acetate, from which it can be separated by a number of techniques. A preliminary purification is readily achieved by dialysis in water using a cellophane membrane (Visking tubing) and the pure acetate has been obtained by chromatography on Sephadex (grade G10). It is best purified, however, by recrystallisation from methanol–acetone, from which it separates as a green powder. Analysis supports the stoicheiometry $[Ru_3O(CO_2Me)_6(H_2O)_3]CO_2Me$. The complex is paramagnetic with $\mu_{eff} = 1{\cdot}77$ B.M. at 298 K in the solid state (Gouy method). This is consistent with an $Ru^{III}{}_3O$ unit, in which marked spin–spin interaction would be expected, *via* the central oxygen atom.[12,13]

The complex as formulated would be a unipositive cation, but in protonic solvents, ionisation of the aquo-ligands may occur. High voltage paper electrophoresis experiments show that in acidic buffers, ($pH < 2$) acetato-oxotriruthenium(III) migrates as a cation, and in alkaline buffers ($pH > 9$) as an anion, the rates of migration in the two cases being equal. In unbuffered dilute potassium chloride solution, cationic, neutral, and anionic species are observed. On titration of an aqueous solution of acetato-oxotriruthenium(III) acetate (pH 6·2) with solutions of sodium hydroxide and hydrochloric acid, a two proton protonation is observed with p*K* 4·35. This is in the region expected for water coordinated to ruthenium(III),[14] and is so assigned. This result, together with the electrophoretic behaviour requires that the cationic and anionic species be univalent. The third aquo-ligand does not deprotonate in the pH range covered by the titration curve (1—12 pH), but the electronic spectrum of the complex undergoes a reversible

TABLE 1

Electronic absorption spectra of ruthenium carboxylates

Complex	Spectrum [λ nm, ε]
$[Ru_3O(O_2CR)_6(H_2O)_3]^+$ [a]	
Acetate	686 (1100); 629 (1000); 391sh (*ca.* 1250)
Acetate (Mond) [b]	*ca.* 720sh; 614; *ca.* 530sh; 366
Acetate (from acetic acid) [b]	*ca.* 720sh; 610; *ca.* 530sh; 366
Propionate	672 (880); 617 (810); 370sh (*ca.* 1180)
n-Butyrate	674; 618; 375sh
Benzoate	686; 633; 386sh
2-Ethylhexanoate	676; 613; 388sh
n-Octanoate	672; 619; 385sh
$[Ru_3O(O_2CR)_6py_3]^+$ [a]	
Acetate	686 (4280); *ca.* 620sh; *ca.* 500sh; 312 (8450)
Propionate	686 (5280); *ca.* 620sh; *ca.* 500sh; 309 (12,900)
n-Butyrate	686 (4690); *ca.* 620sh; *ca.* 500sh; 304 (10,900)
$[Ru_3O(O_2CR)_6(PPh_3)_3]$ [c]	
Acetate	974 (6280); *ca.* 790sh; *ca.* 410sh; 347 (11,900)
Propionate	974 (6630); *ca.* 790sh; *ca.* 410sh; 343 (12,000)
n-Butyrate	974 (5060); *ca.* 790sh; *ca.* 410sh; 338 (12,200)
$[Ru_3O(O_2CMe)_6(H_2O)_3]$ [a]	847 (1620); 409 (1170)
$[Ru_3(O_2CMe)_6(H_2O)_3]$ [a]	850 (2100); 391 (1250)
$[Ru_3O(O_2CMe)_6py_3]$ [a]	890 (7290); 382 (9000)
$[Ru_3(O_2CMe)_6py_3]$ [a]	893 (8630); 382 (9680)

[a] In methanol. [b] Made in glacial acetic acid, measured in methanol. [c] In chloroform.

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[14] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 826.

change in more alkaline solutions, which is probably due to the loss of this proton. Hence we have

$$[Ru_3O(CO_2Me)_6(H_2O)_3]^+ \xrightleftharpoons{-H^+} [Ru_3O(CO_2Me)_6(H_2O)_2(OH)] \xrightleftharpoons{-H^+} [Ru_3O(CO_2Me)_6(H_2O)(OH)_2]^-$$

Treatment of methanolic solutions of the acetate with pyridine produces the blue complex, which may be precipitated from solutions with a number of anions, for example ClO_4^-, BF_4^-, BPh_4^-, or PF_6^-. From chilled solutions containing chloride ions, blue needle crystals are obtained. Analysis of salts indicates the stoicheiometry $[Ru_3O(CO_2Me)_6py_3]X$ ($X = ClO_4^-$ or Cl^-). Paper electrophoresis experiments show this complex to be cationic, migrating at the same rate as the aquo-complex itself; pH titrations show no protonation or deprotonation in the range 1—12 pH, confirming that the behaviour described above is due to dissociation of the aquo-ligands.

The perchlorate salt of the pyridine complex is also paramagnetic, with $\mu_{eff} = 2{\cdot}46$ B.M. (at 298 K). The solubility in organic solvents increases on substitution of the aquo-ligands by pyridine, and, of course, with increasing chain length of the carboxylate group in both cases.

The electronic absorption spectra given in Table 1 serve as a guide for characterisation of the species.

The Mond Reaction.—Hydrated ruthenium oxide dissolves in refluxing acetic acid quite rapidly as stated.[1] The electronic spectrum of the product varies with the mode of preparation of the oxide, probably with the water content. Chromatography of the green products (after removal of acetic acid) in methanol on alumina gave several bands but the main product had the same electronic spectrum as the product obtained on treating $[Ru_3O(CO_2Me)_6(H_2O)_3](CO_2Me)$ with glacial acetic acid. The latter was shown to be anionic in methanol and to be reconverted to the aquo acetate by water. Hence we have

$$[Ru_3O(CO_2Me)_6(H_2O)_3]^+ \xrightleftharpoons[H_2O]{CH_3CO_2^-} [Ru_3O(CO_2Me)_6(CO_2Me)_3]^{2-}$$

Thus it appears that the main product of Mond's reaction is the oxo-acetate with unidentate acetate groups replacing water molecules. The other minor green components probably have both water and acetate co-ordinated, *e.g.*, the neutral $[Ru_3O(CO_2Me)_6(H_2O)_2(CO_2Me)]$.

Attempts to Synthesise the Trifluoroacetate.—The synthetic procedure fails for trifluoroacetate, probably due to the much greater strength of CF_3CO_2H, which possibly prevents the formation of species with Ru-OH-Ru bridges and which, presumably, are intermediates in the formation of the Ru_3O types. Using neutral or almost neutral solutions gives green or yellow solutions whose electronic spectra are quite different from those of the Ru_3O species.

Other methods have also failed. On refluxing hydrated ruthenium oxide, according to Mond,[1] with trifluoroacetic acid no reaction occurs in two hours whereas acetic acid has almost completely dissolved the oxide in this time. On prolonged refluxing (several days) or in sealed tubes at 120—160°, green solutions are obtained but the electronic spectra are not those of Ru_3O species.

The interaction of a carboxylic acid and its anhydride on '$RuCl_3,nH_2O$'[3] which produces in addition to $[Ru_2(CO_2R)_4]Cl$, considerable amounts of the green oxo-species, fails for trifluoroacetic acid, and there is no apparent reaction, the trichloride remaining undissolved.

Finally, the exchange of acetate and trifluoroacetate also fails. There is no change for up to 48 h on refluxing the oxo-acetate in trifluoroacetic acid (even pure acid) as judged by the proton resonance spectrum (although the oxo-acetate is paramagnetic a methyl resonance can be observed at τ 7·70) (Table 2). On refluxing the oxo-acetate with sodium trifluoroacetate and trifluoroacetic acid in ethanol (as in the synthesis of the oxo-acetate) only partial exchange occurs. Conversion of the product to the pyridine and triphenylphosphine complexes, which could be isolated, showed that only *ca.* 50% of the CO_2Me groups were replaced by CO_2CF_3 groups and this was confirmed also by ^1H and ^{19}F n.m.r. spectra. No further exchange occurred on refluxing the product with fresh trifluoroacetic mixture.

TABLE 2

Proton resonance spectra of ruthenium carboxylates (τ values at 100 MHz relative to benzene, $\tau = 2{\cdot}80$, as external reference)

Complex	py or PPh_3	Carboxylate
$[Ru_3O(O_2CMe)_6(H_2O)_3]^{+\,a}$		7·70s
$[Ru_3O(O_2CMe)_6py_3]^{+\,b}$	3·57, 4·09, broad	5·55s
$[Ru_3O(O_2CMe)_6(PPh_3)_3]^{c}$	1·59, 1·98, broad	7·97s
$[Ru_3(O_2CEt)_6py_3]^{d}$	−2·12, −0·22, broad	7·01 quartet; 8·60 triplet

[a] D_2O Solution. [b] $CDCl_3$ Solution. [c] C_6D_6 Solution.

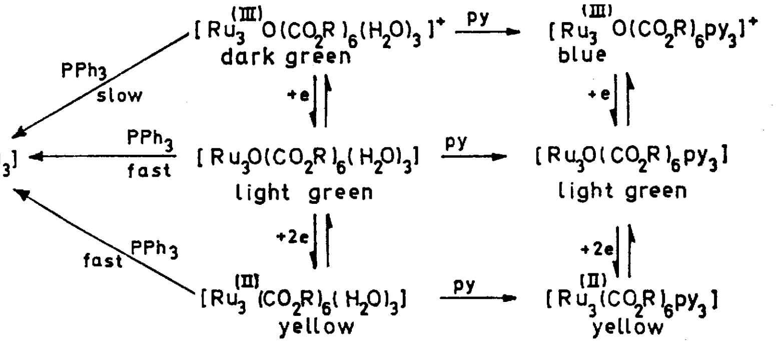
Reduction of μ_3-Oxo-triruthenium Carboxylates

Reduction by Hydrogen.—The acetate, $[Ru_3O(CO_2Me)_6(H_2O)_3](CO_2Me)$, in water or methanol, is readily reduced by hydrogen at 2 atm. pressure at 25° using platinum oxide catalyst, first to a light green and then to a yellow solution. In methanol the first stage takes *ca.* 1 h and the second, *ca.* 3 h. The yellow methanol solution slowly gives a yellow precipitate. In water the first stage takes *ca.* 4 h and the solution throws down a light green complex which is very insoluble in water, so that reduction of the latter to the yellow complex, which is also insoluble, takes *ca.* 24 h.

The light green and yellow complexes are hence readily isolated because of their different solubilities in water and methanol. Analysis of the yellow complex made in water indicates the composition $[Ru_3(CO_2Me)_6(H_2O)_3]$, whereas from methanol it is $[Ru_3(CO_2Me)_6(MeOH)_3]$; the presence of methanol or water is readily shown by appropriate differences in the i.r. spectra [aquo-species, 3500, 3480s, br cm^{-1}; methanolate, 3400w, br, 996 (sharp Me rock) cm^{-1}]. Evidence for the lack of the central oxygen atom is given later. The yellow species in solution react instantly with oxygen to give the light green complex, which is in turn more slowly oxidised to the starting green oxo-acetate on standing. This redox cycle has been repeated three times without evidence of decomposition. The yellow and green solids are also air-sensitive but may be stored in sealed ampoules under nitrogen.

The green complex, which analyses as $[Ru_3O(CO_2Me)_6(H_2O)_3]$ is diamagnetic, but the yellow complex is weakly paramagnetic with μ_{eff} *ca.* 0·4 B.M. per Ru_3 at 298 K.

The blue pyridine complex $[Ru_3O(CO_2Me)_6py_3]^+$ is similarly reduced but more rapidly. The yellow end product in solution is again rapidly oxidised by air first to a light green intermediate and then very slowly (several hours) to the blue starting material. The triphenylphosphine complex $[Ru_3O(CO_2Me)_6(PPh_3)_3]$ is not reduced in methanol. The aquo or pyridine complexes with other carboxylic acids undergo similar redox processes.



SCHEME Reactions of oxotriruthenium complexes

Electrochemical studies discussed later prove that the first stage is a one-electron and the second stage a further two-electron reduction. The reversibility shows that the trinuclear structure is always retained. I.r. and n.m.r. spectra of the light green and yellow complexes show no evidence for Ru–H bonds and only a single methyl resonance is observed. Solution electrophoresis on the light green aquo and pyridine complexes in aqueous acidic (to suppress ionisation of co-ordinated water) or methanolic media show that both species are neutral. Considering also the electrochemical reversibility of the first stage reduction, this then is evidently

$$[Ru_3O(CO_2R)_6L_3]^+ + e \longrightarrow [Ru_3O(CO_2R)_6L_3] \quad (L = H_2O,\ py)$$

The light green complexes are hence the counterparts of the diamagnetic species $Ru_3O(CO_2Me)_6(PPh_3)_3$ and have the ruthenium atoms in a mean oxidation state $2\frac{2}{3}$.

If the oxo-centred structure were preserved on the further two-electron reduction to the yellow species, the latter would, inescapably, have to be a dianion. Although the yellow form of the acetate is anionic in neutral and alkaline aqueous solution, we have shown by solution electrophoresis, that this is a result of dissociation of co-ordinated water. The species is neutral in acidic media and in neutral methanol but becomes anionic only in alkaline methanol solution. Further, the yellow pyridine complex is neutral irrespective of the solvent or acidity confirming that the behaviour of the aquo-species is due to ionisation of co-ordinated water. The yellow pyridine complex was readily isolated from reduction of strong solutions of $[Ru_3O(CO_2Me)_6py_3]Cl$ in methanol; the precipitate can be recrystallised from petroleum–benzene. Molecular weight determinations on different samples gave a mean value of 860 with a maximum deviation of 8% from the value of 894 calculated for $[Ru_3(CO_3Me)_6py_3]$. Repetition of analyses and molecular weights using the 3-methylpyridine analogue were in agreement with this stoicheiometry.

Hence, to maintain neutrality, the yellow complex can (*a*) gain two protons, (*b*) lose two acetate ligands, or (*c*) lose the central oxygen atom. Electrophoresis rules out (*a*), i.r. and n.m.r. spectra on the propionate (preferred to the acetate because of its higher solubility) are consistent only with the formulation $Ru_3(CO_2C_2H_5)_6py_3$, as is analytical and molecular weight data which shows the trinuclear structure to be retained. Hence we conclude that the two-electron reduction requires removal of the central oxygen atom to give a trinuclear carboxylate bridged complex containing formally three, five-co-ordinate ruthenium(II) atoms. This would account for the extreme sensitivity to oxygen, and, of course, the re-formation of the oxo-centred light green (III, III, II) species on oxidation.

Positive proof for the re-insertion of a single oxygen atom into the yellow complex can be obtained as follows. The butyrate $Ru_3(CO_2C_3H_7)_6py_3$, which is very soluble in methanol, was prepared and treated with a stoicheiometric amount of pyridine-*N*-oxide under rigorously oxygen-free conditions (where the yellow species was unaffected for several hours at least). Re-oxidation to the light green complex occurred within a few minutes and g.l.c. analysis confirmed the presence of pyridine. To eliminate any possibility of the formation of pyridine by dissociation or decomposition of the yellow pyridine complex, the experiment was repeated using pyridine-*N*-oxide to oxidise the 3-methyl pyridine butyrate. G.l.c. analysis showed that the expected amount of pyridine was formed:

$$[Ru_3(CO_2R)_6(Mepy)_3] + C_5H_5NO \longrightarrow [Ru_3O(CO_2R)_6(Mepy)_3] + C_5H_5N$$

On exposure to the air the green solutions were reoxidised to the blue $[Ru_3O(CO_2R)py_3]^+$ complexes. Hence the complete reduction–oxidation sequence is:

$$[Ru_3O(CO_2R)L_3]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} Ru_3O(CO_2R)L_3 \underset{+O}{\overset{+2e}{\rightleftharpoons}} Ru_3(CO_2R)L_3$$

Electrochemical Reductions.—The polarogram of $[Ru_3O(CO_2Me)_6(H_2O)_3]^+$ in water using potassium chloride as base electrolyte shows a cathodic wave at $E\frac{1}{2} = -0{\cdot}19$ V (*vs.* S.C.E.) and the catalysed reduction of hydrogen ions commences at *ca.* —0·9 V. The height of the cathodic wave is linearly proportional to the concentration of the acetate, and to the square root of the height of the mercury reservoir (corrected for back pressure). The cyclic voltammogram of the cathodic wave was obtained in aqueous sodium fluoroborate solution, in which the anodic wave of mercury occurs at a more positive potential, permitting a suitable voltage range to be scanned. The voltammogram and the $E\frac{3}{4}$–$E\frac{1}{4}$ separation observed in the polarogram, both indicate a reversible one-electron reduction. Application of the Heyrovsky–Ilkovick equation gave an *n*-value of 1·08. This value was confirmed by coulometric reduction at the dropping mercury electrode,[15] an *n*-value of 0·81 being obtained. This low value lies outside the experimental error, and is attributed to a slow chemical reduction by the mercury pool accumulating from the electrode, as confirmed separately.

The reversibility of the couple is further confirmed by the polarogram of the partially electrochemically reduced solutions, which shows a composite reduction–oxidation wave. Confirmation of the identity of the electrochemically reduced species with those obtained by chemical reduction is provided by the exact similarity of the polarograms of species undergoing reduction by either method; controlled potential electrolysis at the dropping mercury electrode produces the light green intermediate.

The second stage of the reduction, producing the yellow species cannot be investigated electrochemically for oxotriruthenium(III) acetate, because of the catalytic reduction of the solvent. The pyridine complex, which is soluble in a wider range of solvents than the aquo-form, was therefore studied. The polarograms in methanol, acetone, sulpholane, dimethyl sulphoxide, and dimethylformamide showed a cathodic wave in all cases similar to that of the aquo-form, and occurring at *ca.* —0·1 to —0·2 V. In methanol, the second reduction is again obscured by reduction of the solvent, but this wave may be observed in aprotic solvents; the best results being obtained in acetone, using sodium perchlorate as supporting electrolyte.

The first cathodic wave occurred at $E\frac{1}{2} = -0{\cdot}20$ V (*vs.* S.C.E.) and a second cathodic wave as seen at $E\frac{1}{2} = -1{\cdot}36$ V. Reduction of the solvent begins at *ca.* —1·85 V. Cyclic voltammetry shows that the wave at —0·20 V is reversible, but that the second wave at —1·36 V is irreversible. Use of the Heyrovsky–Ilkovick equation gives an *n*-value of 0·96. Controlled potential electrolysis at —0·4 V (*vs.* aqueous S.C.E.) produces the light green intermediate, and at —1·5 V, the yellow form is obtained. Coulometric reduction on mercury electrodes is not possible owing to reaction of the complex with mercury, but reduction at —0·4 V (*vs.* aqueous S.C.E.) on platinum electrodes, gave *n*-values of 0·91 and 0·99, confirming that the first cathodic wave is again a one-electron process. From the ratio of the heights of the two waves, the second wave arises from a two-electron process.

The polarograms of aquo and pyridine oxotriruthenium(III) propionate and n-butyrate, are analogous to those of the acetate. The potentials of the various reductions are summarised in Table 3.

TABLE 3

Half-wave potentials for reduction of ruthenium carboxylates (relative to external aqueous S.C.E.)

Complex	First wave (V)	Second wave (V)
$[Ru_3O(O_2CR)_6(H_2O)_3]$ [a]		
Acetate	−0·19	
Propionate	−0·24	
n-Butyrate	−0·24	
Benzoate	−0·14	
2-Ethylhexanoate	−0·35	
n-Octanoate	−0·30	
$[Ru_3O(O_2CR)_6py_3]^+$ [b]		
Acetate	−0·20	−1·36
Propionate	−0·24	−1·47
n-Butyrate	−0·21	−1·45
$[Ru_3O(O_2CR)_6(PPh_3)_3]$ [b]		
Acetate		−1·05
Propionate		−1·07
n-Butyrate		−1·10
Thallium(I) [a]	−0·35 v	
Thallium(I) [b]	−0·36 v	

[a] In 0·1M sodium perchlorate in methanol. [b] In 0·1M sodium perchlorate in acetone.

The thermodynamic reversibility of the first reduction wave of these complexes may be expected, as the electrode reaction involves only a simple one-electron transfer. The loss of the central oxygen atom on reduction to the second stage clearly accounts for the lack of thermodynamic reversibility for this process.

The triphenylphosphine complexes of the acetate, propionate, and n-butyrate, which are in the same oxidation state ($2\frac{2}{3}$) as the first reduced species of the corresponding aquo and pyridine adducts, also undergo a two-electron reduction at potentials of *ca.* —1·1 V (*versus* S.C.E.). However, these reductions are not simple and evidently lead to break up of the trinuclear cluster; they will be

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[15] G. A. Gilbert and E. K. Rideal, *Trans. Faraday Soc.*, 1951, **47**, 369.

reported separately. The difference of more than one volt in the two reduction potentials of the acetate accounts for the ready formation of the complex $Ru_3O(CO_2R)(PPh_3)_3$, since the first reduction is well within the reducing power of the phosphine although the reduction is slow and takes several hours. The particular stability of the complex is also due in part to the closed shell electronic configuration, which is readily understood by simple MO theory.[11,13] It is noteworthy that in contrast to the slow reduction of $[Ru_3O(CO_2R)_6(H_2O)_3]^+$ by PPh_3, the interaction of PPh_3 with the light green species $[Ru_3O(CO_2R)_6(H_2O)_3]$ in methanol is rapid (a few minutes) since it merely involves ligand replacement.

The Nature of Martin's Acetate

It is now clear that Martin's acetate [4] cannot have the oxo-centred structure. This complex is difficult to study as it is insoluble in most solvents. It is slightly soluble in water, but the solutions decompose rather quickly and even the solid decomposes on standing. Analysis supports a ratio $Ru : CO_2Me = 1 : 2$ but analysis of the pyridine adduct, isolated as ClO_4^- or BF_4^- salts supports an approximate stoicheiometry $\{[Ru_2(CO_2Me)_2py_4]X\}_n$ ($X = ClO_4^-$ or BF_4^-). Determination of the oxidation state of the ruthenium atoms in Martin's complex by the original method [4] confirms the formulation as ruthenium(III), but the accuracy of the method is too low to exclude the possibility of non-integral oxidation states. The Martin complex is weakly paramagnetic, showing a moment of *ca.* 0·6—0·7 B.M. per ruthenium atom (Gouy method). The pyridine adduct (perchlorate salt) is diamagnetic. Martin's complex is reduced in water by hydrogen at two atmospheres on platinum to a dark green, and then to a yellow species, the latter stage being accompanied by the formation of much ruthenium metal. The reduction is not reversible on exposure to air.

TABLE 4

Analytical data for ruthenium carboxylato complexes

Complex	Found					Required				
	C	H	N	Cl or P	Ru	C	H	N	Cl or P	Ru
$[Ru_3O(CO_2Me)_6(H_2O)_3]CO_2Me$	21·7	3·4			39·4	21·4	3·4			38·8
$[Ru_3O(CO_2Me)_6py_3]ClO_4$	32·0	3·4	4·0	3·4		32·0	3·3	4·1	3·5	
$[Ru_3O(CO_2Me)_6(PPh_3)_3]$ [a]	54·4	4·5		6·0	20·1	54·2	4·5		6·5	20·6
$[Ru_3O(CO_2Me)_6(H_2O)_3]$	19·4	3·2			41·6	19·7	3·3			41·8
$[Ru_3(CO_2Me)_6(H_2O)_3]$	19·9	3·4				20·2	3·4			
$[Ru_3(CO_2Me)_6(MeOH)_3]$	24·3	3·5				24·0	3·6			
$[Ru_3(CO_2Me)_6py_3]$ [b]	35·7	3·8	4·5			36·2	3·7	4·7		
$[Ru_3(CO_2Me)_6(Mepy)_3]$ [c]	38·6	4·3	4·2			38·5	4·2	4·5		
$[Ru_3O(CO_2Et)_6(H_2O)_3]CO_2Et$	28·5	4·5				28·7	4·7			
$[Ru_3O(CO_2Et)_6py_3]ClO_4$	36·0	4·0	3·8	3·3		36·1	4·1	3·8	3·2	
$[Ru_3O(CO_2Et)_6(PPh_3)_3]$	57·2	5·3		6·0		57·7	5·0		6·2	
$[Ru_3O(CO_2Pr)_6py_3]ClO_4$	39·6	4·9	3·3	3·1		39·6	4·9	3·5	3·0	
$[Ru_3O(CO_2Pr)_6(PPh_3)_3]$	57·1	5·4		6·1		57·3	5·4		5·7	

[a] $M = 1420$ (benzene); M required 1459. [b] M (methanol), (*i*) 870, 855; (*ii*) 825, 875, M required 894. [c] M (methanol) 975, 910; M required 936.

The above behaviour suggests that Martin's complex may be polymeric containing mainly ruthenium(III), which is reduced *via* mixed oxidation state complexes. If this is so, the pyridine adduct probably arises *via* bridge-splitting, but on the available evidence, no satisfactory formulation can be given.

EXPERIMENTAL

Ruthenium trichloride trihydrate was from Johnson Matthey Limited. Other reagents were AnalaR grade. I.r. spectra were recorded on Perkin-Elmer 257 and 457 instruments, and electronic spectra on a Cary 14 recording spectrophotometer. Proton resonance spectra (100 MHz) were obtained with a Perkin-Elmer R14 spectrometer. pH Measurements utilised an E.I.L. Vibron pH meter; a Miles ' Hivolt ' apparatus was used for the electrophoretic studies. Polarography and microcoulometry were carried out using either a Radelkis type OH 142 or a Beckmann Electroscan ™30 polarograph. Macrocoulometry was performed with the Electroscan, or with a Chemical Electronics TA 70/2A Potentiostat. Elemental analyses (Table 4) were by the Microanalytical Laboratory, Imperial College. Ruthenium was determined by reduction to the metal under hydrogen; molecular weights were obtained using a Hitachi–Perkin-Elmer model 115 instrument. A Perkin-Elmer model F11 Gas Chromatograph with Kent Chromalog integrator was used for g.l.c. analyses.

Tris(aquo)hexa-μ-acetato-μ_3-oxo-triruthenium(III,III,III) *Acetate*.—The green complex was prepared according to the original method.[10] After 4 h reflux, the dark green reaction mixture was cooled at (−40°) for 2 h, and the precipitate of sodium chloride and sodium acetate was removed. The filtrate was evaporated on a rotary evaporator, dissolved in methanol, filtered, and again evaporated. The resulting solid was dried (12 h) *in vacuo* over sodium hydroxide pellets, to give the crude acetate in almost quantitative yield based on ruthenium content but containing *ca.* 15% of sodium acetate. This product may be used directly for preparative purposes. The pure acetate was obtained by two recrystallisations from methanol–acetone, the complex separating as a green powder on cooling to −40°.

Tris(pyridine)hexa-μ-acetato-μ_3-oxo-triruthenium(III) *Perchlorate*.—To crude oxotriruthenium(III) acetate (0·5 g) in methanol (5 ml) was added pyridine (2 ml). The solution was heated for 5 min on steam, the colour changing from dark green to dark blue. After cooling to room temperature, sodium perchlorate monohydrate (0·125 g) in methanol (2 ml) was added, the blue precipitated complex collected, washed with methanol, and dried *in vacuo* over silica gel, yield 0·32 g (55%, based on Ru content of crude acetate). Addition of lithium chloride in methanol produces the chloride salt in similar yield.

Tris(triphenylphosphine)hexa-μ-acetato-μ_3-oxo-triruthenium(II,III,III).—Triphenylphosphine (1·1 g) in warm methanol (25 ml) was added under nitrogen to crude oxotriruthenium(III) acetate (0·5 g) in methanol (5 ml), and the mixture was stirred overnight. After removal of the methanol, the residue was dissolved in benzene, and the solution was filtered. Ethanol (*ca.* 5 vols.) was added to the filtrate, which was then stored at 7° to yield light green crystals of the *complex* which were collected, washed with ethanol and then ether, and dried *in vacuo* over silica gel, yield 0·45 g (55%, based on Ru content of crude acetate).

Oxotriruthenium(III) *Propionate and its Pyridine and Triphenylphosphine Derivatives.*—Sodium hydroxide (0·59 g) was dissolved by warming in a mixture of ethanol (25 ml) and propionic acid (26 ml). To the resulting solution was added (at room temperature), ruthenium trichloride trihydrate (1 g), and the mixture was refluxed under nitrogen for 4 h. The solution was cooled at −40° for 2 h, filtered, and evaporated on a rotary evaporator. The residue was dried *in vacuo* over sodium hydroxide overnight. The resulting crude aquo-oxotriruthenium(III) propionate was dissolved in methanol (15 ml) and the solution was filtered and divided in three parts.

(*a*) *Tris(aquo)hexa-μ-propionato-μ_3-oxo-triruthenium*(III) *Propionate.*—To the methanolic solution (5 ml) was added a large excess of diethyl ether, and the solution was stored at −40°. After one week, dark green, almost black crystals of the *complex* had formed. These were collected, washed with ether, and dried *in vacuo* over silica gel, yield 0·06 g.

(*b*) *Tris(pyridine)hexa-μ-propionate-μ_3-oxo-triruthenium*(III) *Perchlorate.*—To the methanolic solution (5 ml) was added pyridine (2 ml), and the solution was stirred for 1 h. Sodium perchlorate monohydrate (0·1 g) in methanol (1 ml) was added and the solution was left for 1 h at −40°. The blue crystalline *complex* was collected, washed with diethyl ether, and dried *in vacuo* over silica gel, yield 0·22 g.

(*c*) *Tris(triphenylphosphine)hexa-μ-propionato-μ_3-oxo-triruthenium*(II,III,III).—To the methanolic solution (5 ml) was added triphenylphosphine (0·5 g) and the solution was stirred overnight under nitrogen. The resulting solution was cooled at −40° for 4 h, and filtered. The precipitate was washed with ether, then dissolved in benzene and again filtered. Ethanol (*ca.* 5 vols.) was added to the filtrate, which was left at −40° overnight. The light green *crystals* were collected, washed with ethanol, and dried *in vacuo* over silica gel, yield 0·2 g.

Oxotriruthenium(III) *n-Butyrate and its Pyridine and Triphenylphosphine Derivatives.*—The n-butyrate was prepared as for the propionate. The crude product, after drying, was dissolved in methanol as before. Tris(aquo)hexa-μ-n-butyrato-μ_3-oxo-triruthenium(III) n-butyrate could not be isolated in solid form, but the crystalline derivatives were readily obtained.

Tris(pyridine)hexa-μ-n-butyrato-μ_3-oxo-triruthenium(III) *Perchlorate.*—This complex was prepared as for the propionate, except that ethanol was used as solvent. After the reaction mixture had been stirred for 1 h, sodium perchlorate monohydrate (0·2 g) was dissolved in the solution. Petroleum (60—80°) was added, and the solution was stored at −40°. After *ca.* 3 h, the blue crystals of the *complex* which formed were collected, washed with petroleum, and dried *in vacuo* over silica gel, yield 0·21 g.

Tris(triphenylphosphine)hexa-μ-n-butyrato-μ_3-oxo-triruthenium(II,III,III).—This *complex* was prepared and purified as for the propionate analogue, yield 0·11 g.

Reduction of Oxotriruthenium(III) *Acetate.*—Reductions were carried out in glass pressure bottles (Fisher and Porter 8 oz Compatibility Bottles) at two atm. pressure, using Adams catalyst (PtO_2). Water or methanol was used as solvent. Where used, commercial 'White Spot' nitrogen was purified by passage through chromium(II) solutions.

(*a*) *Tris(aquo)-hexa-μ-acetato-μ_3-oxo-triruthenium*(II,III,III).—Crude oxotriruthenium(III) acetate (1·5 g) in water (10 ml) was stirred under hydrogen (2 atm.) in the presence of catalyst (*ca.* 3—5 mg). The dark green solution became light green. The precipitate, formed after *ca.* 4 h, was transferred under nitrogen to a centrifuge tube, centrifuged, and the supernatant liquid discarded. The product was then stirred with deoxygenated water, centrifuged, and the supernatant liquid was again discarded. The product was dried on a vacuum line, to yield the *complex* as a light green powder. The dry solid was stored in sealed ampoules under nitrogen. It is slowly re-oxidised to the starting material by air. The complex is insoluble in most solvents.

(*b*) *Tris(aquo)hexa-μ-acetato-triruthenium*(II).—Crude oxotriruthenium(III) acetate (0·5 g) in water (5 ml) was stirred under hydrogen (2 atm.) in presence of Adams catalyst (3—5 mg) for 2 days. The yellow precipitate which formed was collected, washed, dried and stored as for the light green reduced complex. The dry solid is oxidised fairly quickly in air. The complex is insoluble in most solvents.

(*c*) *Tris(methanol)hexa-μ-acetato-triruthenium*(II).— This complex was prepared as for the aquo-form, using methanol as solvent and for washing.

(d) *Tris(pyridine)hexa-μ-acetato-triruthenium*(II).— The complex $[Ru_3O(CO_2Me)_6py_3]Cl$ was reduced in methanol as described above for the aquo-form. The yellow precipitate which formed was recrystallised (under deoxygenated nitrogen) from benzene–petroleum (60—80°). The resulting *complex* was washed with petroleum and dried *in vacuo*. It is soluble in alcohol and in benzene.

The yellow 3-*methylpyridine complex* $[Ru_3(CO_3Me)_6(MeC_5H_4N)_3]$ was prepared and recrystallised (twice) by the above methods.

Mond's Reaction.—Hydrated ruthenium oxide was prepared by addition of strong aqueous solutions of sodium hydroxide to ruthenium trichloride trihydrate in 4M hydrochloric acid. The resulting black precipitate was washed with water until free of alkali.

On refluxing the resulting wet oxide with glacial acetic acid for 2 h, most of the oxide dissolved to give a green solution. After removal of acid and immediate chromatography on alumina, using methanol, the electronic spectrum of the main band indicated that it was $[Ru_3O(O_2CMe)_9]^{2-}$.

When the wet oxide was washed with methanol and ether, and dried *in vacuo* before refluxing with acetic acid, chromatography of the resulting green solutions produced diffuse bands, showing absorption maxima in the region 620—700 nm. No species similar to $[Ru_3O(O_2CMe)_9]^{2-}$ were obtained.

Oxidations of the Yellow Complexes with Pyridine-N-*oxide.*—All operations (except reductions) were carried out under argon, which was purified by passage through two Dreschel bottles of chromium(II) solution, two of concentrated sulphuric acid, and two of methanol. Hydrogen (at one atmosphere) was passed through one Dreschel bottle of chromium(II) and one of methanol.

Pyridine-*N*-oxide (B.D.H.) was purified as follows. The solid (5 g) was placed in a cold-finger type sublimation apparatus, which was connected to a vacuum line. With continuous pumping, the lower portion of the apparatus was heated in an oil-bath to 160°. When the melt ceased to boil, the apparatus was removed from the vacuum line and allowed to cool. The condensing surface of the cold-finger was cleaned, and the apparatus was then returned to the vacuum line. Dry ice–acetone mixture was placed in the cold-finger, and the apparatus was again heated in an oil-bath, with continuous pumping to *ca.* 160°. Pure pyridine-*N*-oxide collected on the condensing surface as a white crystalline deposit. When sufficient had collected, the apparatus was allowed to cool, and air was then admitted. The pure product is quite hygroscopic, and was stored in a desiccator, over silica-gel.

All flasks were sealed with rubber bungs forced into the necks of 'Quickfit' flasks to provide adequate seals. Passage of gases and transfer of solutions was effected *via* steel tubes, inserted through the bungs.

Tris(3-methylpyridine)hexa-μ-n-butyrate-μ_3-oxo-tri-ruthenium(III) perchlorate (0·3 g) in methanol (4 ml) was placed in a 25 ml conical flask containing PtO_2 (*ca.* 10 mg). The flask was swept with argon and then hydrogen was passed until the complex was reduced to the yellow species (24 h). Argon was passed through a solution of pyridine-*N*-oxide (0·025 g) in methanol (2 ml) contained in a 10 ml 'Quickfit' flask. After 1 h, the exit tube from the flask containing pyridine-*N*-oxide was inserted into the flask containing the ruthenium solution. The hydrogen inlet tube was then removed from the latter flask. Argon was thus passed first through the pyridine-*N*-oxide solution and then through the ruthenium solution. No oxidation of the latter solution had occurred after 30 min, indicating that no oxygen was present in the system. The exit tube from the 10 ml flask was then inserted into the pyridine-*N*-oxide solution, which was forced over into the ruthenium solution. The latter solution was greenish yellow within 1 min, and green in *ca.* 5 min. After 1 h, g.l.c. analysis of the reaction mixture showed the presence of pyridine, the amount of pyridine being within 10% of that expected. On exposure to air, the green solution was oxidised back to the blue starting material which was recovered. G.l.c. analysis on the pyridine-*N*-oxide, on both the initial ruthenium complex, and an air-oxidised solution of the yellow species, showed that pyridine was not arising from these sources. The entire experiment was repeated, with identical results.

Electrophoresis and pH *Titrations.*—High-voltage paper electrophoresis was carried out at 2 or 4 kV (50 or 100 V cm^{-1}). Solution electrophoresis was at 120 V (10 V cm^{-1}). Formic acid–acetic acid buffer (25 and 75 ml per litre respectively, pH 1·8) and sodium borate buffer (0·05M, pH 9·2) were used for acidic and alkaline experiments. On experiments with the reduced forms, solution electrophoresis was carried out under nitrogen, purified by chromium(II) solutions.

For pH titrations, solutions of concentration 2×10^{-3}M were titrated with standardised 1M sodium hydroxide or hydrochloric acid solutions. A micropipette was used, the internal volume of which had been determined by calibration with mercury.

Titrations were performed at 25° under nitrogen, which was purified by passage through Dreschel bottles of chromium(II) (oxygen removal) and potassium hydroxide (carbon dioxide removal) solutions, and then through water.

Electrochemistry.—Nitrogen or argon used was passed through Dreschel bottles of chromium(II) solution, and of the supporting electrolyte.

Acetone was purified by refluxing with $KMnO_4$, drying ($CaCl_2$), and redistilling. Sodium perchlorate was dried at 80° *in vacuo* for 24 h. Polarographic studies in acetone, or methanol were carried out using a three-electrode controlled potential polarograph (Electroscan ^{TM}30) to eliminate the *ir* drop. All potentials in methanol or acetone are relative to the aqueous S.C.E. separated from the ruthenium solutions by a 0·1M aqueous sodium perchlorate bridge, an agar plug being used to minimise contamination with water. All half-wave potentials quoted were measured with the controlled-potential polarograph (Electroscan). Pilot ion potentials for the Tl(I)/Tl(Hg) couple are given in Table 3. Micro-coulometry at the D.M.E. was carried out using a miniature H-cell. Cyclic voltammetry at a hanging mercury drop electrode was carried out with an instrument designed by Dr. R. D. Gee of this department.[16] Coulometry at the mercury pool or platinum foil electrodes utilised a conventional H-cell. The auxiliary electrode was of platinum foil in 0·5M aqueous lithium chloride or sodium perchlorate solution, separated from the working electrode by an agar bridge.

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[16] R. D. Gee, Ph.D. Thesis, University of London, 1971.