

### Oxotriruthenium Cluster Complexes

By F. A. COTTON, J. G. NORMAN, A. SPENCER, and G. WILKINSON

(Chemistry Departments, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A., and Imperial College of Science and Technology, London S.W.7)

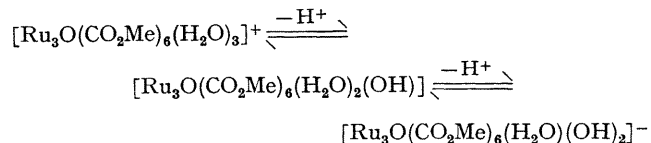
*Summary* X-ray diffraction and other studies have confirmed the existence of a new system of acetato-complexes containing the oxygen-centred triangle  $\text{Ru}_3\text{O}$  which may undergo reversible reduction reactions.

In addition to the tetrabridged binuclear salt<sup>1</sup>  $[\text{Ru}_2(\text{CO}_2\text{Me})_4]\text{Cl}$ , whose structure has been determined by X-ray

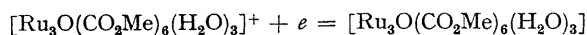
diffraction,<sup>2</sup> the interaction of ruthenium trichloride hydrates with acetic acid also gives a green solution which was believed<sup>3</sup> to contain the dimeric acetate,  $\text{Ru}_2(\text{CO}_2\text{Me})_4$ , as a solvate. The green species gave compounds with triphenylphosphine and pyridine (L) which were regarded as adducts  $\text{Ru}_2(\text{CO}_2\text{Me})_4\text{L}_2$ .

Further studies have shown that these formulations

require revision. We have obtained the pure green complex by chromatography (Sephadex) and crystallisation from methanol and have shown by paper electrophoresis, molecular weight determinations, and pH titrations that it is best formulated as an oxygen-centred triangular species similar to the well known 'basic acetates' of trivalent first-row elements, which contain the ions  $[\text{M}_3\text{O}(\text{CO}_2\text{Me})_6(\text{H}_2\text{O})_3]^+$ , ( $\text{M} = \text{Cr},^4 \text{Mn},^5 \text{Fe}^6$ ). In acid solutions it is a cation and in alkaline solutions an anion.



The dark-green complex is reduced chemically, *e.g.*, by  $\text{H}_2$  on Pt or  $\text{BH}_4^-$ , or electrochemically in a one-electron step at a potential  $+0.13 \text{ V vs. S.C.E.}$ , to a light-green complex (which may also be anionic owing to dissociation of co-ordinated water). The reduction is completely



reversible. Further reduction (by  $\text{H}_2$  on Pt) gives a yellow species which is also re-oxidised by air to the light-green and then to the dark-green species.

The light-green complex is the precursor of the triphenylphosphine complex now shown to be  $[\text{Ru}_3\text{O}(\text{CO}_2\text{Me})_6(\text{PPh}_3)_3]$  formed from it very readily by substitution, whereas the slow formation from the dark-green acetate involves reduction and we find, the formation of  $\text{Ph}_3\text{PO}$ . X-Ray diffraction of this phosphine complex conclusively proves the O-centred triangular structure.

The complex crystallizes in the triclinic space group  $\text{P}\bar{1}$  with unit cell dimensions  $a = 13.372(7)$ ,  $b = 26.21(2)$ ,  $c = 9.375(8) \text{ \AA}$ ;  $\alpha = 99.06(3)$ ,  $\beta = 84.03(2)$ ,  $\gamma = 100.51(1)^\circ$ ;  $V = 3180(30) \text{ \AA}^3$ ;  $D_c = 1.52(1) \text{ g cm}^{-3}$  for  $Z = 2$ ;  $D_m = 1.56(3) \text{ g cm}^{-3}$ . The structure, excluding hydrogen atoms, was determined from the intensities of 3227 unique reflections collected with a counter diffractometer. It was solved by Patterson and difference Fourier syntheses and refined by full-matrix least-squares methods to a conventional  $R = 0.100$  and weighted  $R = 0.091$ . There is no direct metal-metal interaction. The equilateral triangle of ruthenium atoms is bridged by the six acetate groups and the central oxygen atom, which lies essentially in the  $\text{Ru}_3$  plane. One  $\text{PPh}_3$  ligand is co-ordinated to each metal opposite the central oxygen atom. Average values of interatomic distances (and average e.s.d.'s) include:  $\text{Ru-P} = 2.414(7)$ ,  $\text{Ru-O}(\text{central}) = 1.92(2)$ ,  $\text{Ru-O}(\text{acetate}) = 2.06(2)$ ,  $\text{C-O} = 1.26(3)$ ,  $\text{Ru} \cdots \text{Ru} = 3.329(3)$ , and  $\text{O} \cdots \text{O} = 2.26(2) \text{ \AA}$ . The identity of the solid state and solution i.r. spectra indicates that the same structure is maintained in solution.

The above formulations on conventional oxidation state

concepts indicate that in the dark-green acetate the three Ru atoms are  $+3$ ; in agreement with an odd-electron group, the complex is paramagnetic with a moment (1.77 B.M.) corresponding to one unpaired electron per  $\text{Ru}_3\text{O}$  group. The first reduced species and the phosphine adduct are even-electron systems, formally  $2 \times \text{Ru}^{\text{III}}$  and  $1 \times \text{Ru}^{\text{II}}$  with a mean oxidation state of  $2\frac{2}{3}$ , and have very low moments. The yellow species is again paramagnetic and is anionic. These facts and the structure are most conveniently explained by simple MO theory.

Considering the  $\text{Ru}_3\text{O}$  group as a unit in the point group  $D_{3h}$ , with the  $C_3$  axis coincident with  $z$ , we may set aside one  $\sigma$ -orbital on each metal, of the proper symmetry for combining with an  $sp^2$  oxygen orbital to form the normal  $\sigma$ -bond framework. Five orbitals on each metal are also used in  $\sigma$ -bonding to the carboxylate oxygen atoms and the phosphorus or other ligand atom. There are then three  $d$ -type orbitals remaining on each metal. One of these is capable of forming a linear combination with the same type of  $d$ -orbital on each of the other two metal atoms which will have the proper symmetry for interaction with the  $p_z$  orbital on the oxygen atom, leading to one bonding and one anti-bonding MO. The other eight combinations of the  $d$ -type metal orbitals are non-bonding with respect to the metal-oxygen interaction. The resulting correlation diagram for the  $\text{Ru}_3\text{O}$   $\pi$  system thus has one strongly bonding, one strongly anti-bonding, and eight essentially non-bonding MO's. The 16 electrons from the three metal atoms and the two electrons available from the central oxygen atom just fill all the bonding and non-bonding orbitals, accounting for both the diamagnetism of  $\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{PPh}_3)_3$  and its particular stability as a  $16d$ -electron system.

The blue pyridine complex<sup>3</sup> has been shown to be  $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3]^+$ ; it gives crystalline salts with  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$  etc., is paramagnetic, and undergoes the same reduction sequence as  $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]^+$ .

Both the light-green and yellow acetates react with many ligands such as CO, NO,  $\text{SO}_2$  etc., to give crystalline compounds and further, the protonated solutions<sup>3</sup> of the dark-green acetate or the triphenylphosphine complex (which are hydrogenation catalysts) evidently still contain the  $\text{Ru}_3\text{O}$  group and addition to them of a variety of ligands such as sulphate or dithiocarbamates gives crystalline complexes. There is evidently an extensive chemistry of the  $\text{Ru}_3\text{O}$  group in different oxidation states and there is some resemblance to the chemistry of the N-centred triangles in complexes<sup>7</sup> such as  $[\text{Ir}_3\text{N}(\text{SO}_4)_6]^{4-}$ . The chemistry of these and of other  $\text{M}_3\text{O}$  complexes of second- and third-row elements will be described separately.

Finally, the cation  $[\text{Ru}_2(\text{OAc})_4]^+$  undergoes a 1-electron reduction in aqueous solution with  $E_{\frac{1}{2}} = +0.36 \text{ V vs. S.C.E.}$ , and on reduction in methanol followed by addition of triphenylphosphine a phosphine adduct is obtained.

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