The First Hexacarboxylato Diruthenium(III) Complex. Synthesis, *X*-Ray Crystal Structure, and Properties of Tetra-μ-acetato-diacetatodiruthenium(III) Monohydrate

Michael G. B. Drew,*[a] Paula Higgins,[b] and G. Malachy McCann*[b]

[a] *Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.*
[b] *Chemistry Department, St. Patrick's College, Maynooth, Co. Kildare, Ireland*

The reaction of $[Ru_2(\mu\text{-}OAc)_4Cl]$ with AgOAc in AcOH/MeOH gives the red oxidation product $[Ru_2(\mu\text{-}OAc)_4(OAc)_2]\cdot H_2O$ (**1**), the structure of which has been determined by *X*-ray crystallography; this is the first example of a paramagnetic Ru_2^{6+} complex.

The binuclear acetato complexes $[Ru_2(\mu\text{-}OAc)_4]$ (ref. 1) and $[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]BF_4$ (ref. 2) have been structurally characterized and shown to contain metal-to-metal bonded Ru_2^{4+} and Ru_2^{5+} cores, respectively. Their electronic and structural properties were found to be consistent with the metal–metal orbital ordering $\sigma\ 2\pi\ \delta\ \delta^*\ 2\pi^*$, first proposed by Norman and his co-workers.[3] The paramagnetic Ru_2^{4+} (d^{12}) acetato species [$\mu_{eff.}$ 2.1 μ_B per Ru^{2+} (295 K)] has the assigned configuration $\sigma^2\ 2\pi^4\ \delta^2\ \delta^{*1}\ 2\pi^{*3}$, consistent with the presence of two unpaired electrons per dimer unit and a metal–metal bond order of 2. For the Ru_2^{5+} (d^{11}) complex $[Ru_2(\mu\text{-}OAc)_4Cl]$, the magnetic moment[4,5] [$\mu_{eff.}$ 2.88 μ_B per $Ru^{2\cdot5+}$ (298 K)] confirmed that the high-spin $S = 3/2$ ($\delta^{*1}\ 2\pi^{*2}$) configuration was favoured over the $S = \frac{1}{2}$ alternative by close spacing of the π^* and δ^* orbitals. The Ru_2^{5+} species have a metal–metal bond order of 2.5. Although not structurally characterized, the Ru_2^{5+} penta-acetato complex $[Ru_2(OAc)_5]$ has been reported[4,5] [$\mu_{eff.}$ 2.84 μ_B per $Ru^{2\cdot5+}$ (293 K)].[5]

Here we report the synthesis, structure, and physical properties of the hexa-acetato Ru_2^{6+} (d^{10}) complex, $[Ru_2(\mu\text{-}$

Table 1. Bond length data for the complex (**1**) and related complexes.

Complex	Core	d(Ru–Ru) /Å	d(Ru–O) (bridging acetate) (av.)/Å	d(Ru–O) (axial ligand L) (av.)/Å	
$[Ru_2(\mu\text{-}OAc)_4(OAc)_2]\cdot H_2O$ (**1**)	Ru_2^{6+}	2.265(1)	2.018(5)	L = $^{-}$OAc	2.243(6)
$[Ru_2(CH_2Bu^t)_6]$[a]	Ru_2^{6+}	2.311(3)			
$[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]BF_4$[b]	Ru_2^{5+}	2.248(1)	2.00(4)	L = OH_2	2.31(1)
$[Ru_2(\mu\text{-}OAc)_4Cl]\cdot 2H_2O$[b]	Ru_2^{5+}	2.267(1)	2.019(3)	L = Cl^-	2.566(1)
$Cs[Ru_2(\mu\text{-}OAc)_4Cl_2]$[b]	Ru_2^{5+}	2.286(2)	2.02(1)	L = Cl^-	2.521(4)
$[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]$[c]	Ru_2^{4+}	2.262(3)	2.068(4)	L = OH_2	2.335(4)

[a] Ref. 10. [b] Ref. 2. [c] Ref. 1.

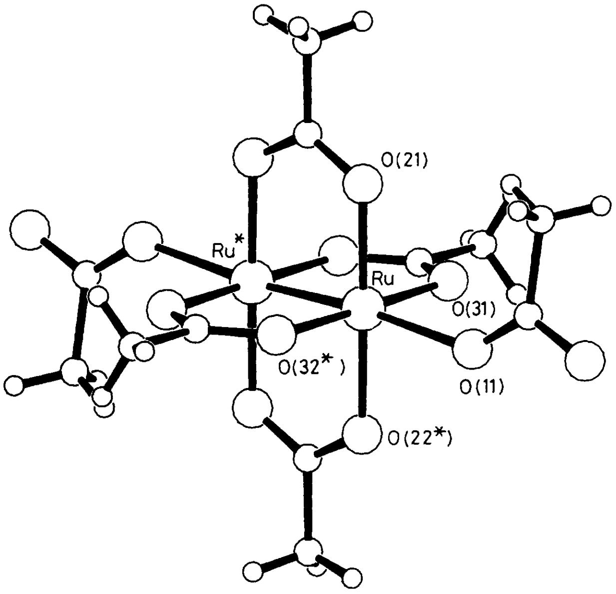

Figure 1. The molecular structure of tetra-μ-acetato-diacetato-diruthenium(III). Selected bond lengths and bond angles: Ru–Ru* 2.265(1), Ru–O(11) 2.243(6), Ru–O(21) 2.021(5), Ru–O(22*) 2.026(5), Ru–O(31) 2.016(5), Ru–O(32*) 2.011(5) Å; O(31)–Ru–O(32*) 178.7(3), O(21)–Ru–O(22*) 179.0(3), O(21)–Ru–O(31) 90.4(2), O(31)–Ru–O(22*) 89.5(2)°.

$OAc)_4(OAc)_2]\cdot H_2O$ (**1**). This complex completes the family of structurally characterized Ru_2^{4+}, Ru_2^{5+} and Ru_2^{6+} acetates. It is formed by the reaction of $[Ru_2(\mu\text{-}OAc)_4Cl]$ with AgOAc (1 : 1 molar ratio) in AcOH/MeOH under anaerobic or aerobic conditions. After removal of the stoicheiometric amount of AgCl the filtrate was concentrated in air to give the red crystalline product (**1**) in 58% yield.† A satisfactory elemental analysis was obtained. The complex behaves as a 1 : 1 electrolyte in MeOH [Λ(1 × 10^{-3} mol dm^{-3}) = 69 S cm^2 mol^{-1}] and gave an electronic spectrum with $\lambda_{max.}$ 422 nm (ε 395 dm^3 mol^{-1} cm^{-1} in MeOH). Two different co-ordination modes for the acetate ligands were evident from the i.r. spectrum (KBr). The medium-intensity band at 1560 cm^{-1} was assigned to $\nu_{asym.}$ (CO_2) of unidentate AcO^-, and the strong detailed band spanning 1365—1450 cm^{-1} contained the $\nu_{asym.}$ (CO_2) and $\nu_{sym.}$ (CO_2) of bridging AcO^- and also, presumably, $\nu_{sym.}$ (CO_2) of unidentate AcO^-. The cyclic voltammogram (1 × 10^{-3} M in 0.07 M Et_4NClO_4–MeOH) showed two reversible one-electron reductions with $E_{\frac{1}{2}}$ +182 and −24 mV, *versus* Ag/AgCl. Magnetic susceptibility measurements at 293 K gave $\mu_{eff.}$ 3.21 μ_B per Ru^{3+} and 4.53 μ_B per Ru_2^{6+} unit. At 93 K values of $\mu_{eff.}$ decreased slightly to 3.10 μ_B per Ru^{3+} and 4.19 μ_B per Ru_2^{6+} unit, suggesting a small degree of temperature-dependent intramolecular antiferromagnetic coupling between the two Ru^{3+} ions in the d^{10} bimetallic core.[7] The magnetic behaviour of the present hexa-acetato species contrasts with that reported for other Ru_2^{6+} complexes: $[Ru_2O(OAc)_4(PPh_3)_2]\cdot MeOH$[8] and $Ru_2L_2^{2+}$ (where L is a dianionic N_4 macrocyclic ligand)[9] are both diamagnetic, and the structurally characterized complexes $[Ru_2(CH_2Bu^t)_6]$[10] and $[Ru_2(C_5NH_4NH)_6(PMe_2Ph)_2]$[6] are reported to have the fully spin-paired configurations $\sigma^2 2\pi^4\delta^2\delta^{*2}$ and $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$, respectively. However, the isoelectronic Os_2^{6+} complexes $[Os_2(\mu\text{-}O_2CR)_4Cl_2]$[11] were reported to have appreciable population of a spin-triplet state at ambient temperature, with a singlet ground-state becoming increasingly favoured at lower temperatures.

The *X*-ray crystal structure of (**1**) is shown in Figure 1.‡ Relevant interatomic distances for this and related species are summarised in Table 1. For (**1**) the Ru–Ru distance of 2.265(1) Å is almost identical with that reported for $[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]$, and slightly longer than that reported for $[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]BF_4$. However, for the latter example of a Ru_2^{5+} species it is more appropriate to compare the Ru–Ru distance in (**1**) with that in $[Ru_2(\mu\text{-}OAc)_4Cl]\cdot 2H_2O$ and $Cs[Ru_2(\mu\text{-}O)_4Cl_2]$ where the axial ligands are anionic. The Ru–Ru distances in these Ru_2^{5+} complexes are slightly longer than in the present Ru_2^{6+} species. In the non-bridged Ru_2^{6+}

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† Although the conditions of the synthesis were essentially non-oxidizing, the oxidation of Ru_2^{5+} to Ru_2^{6+} was evident. Since the yield was >50%, and no second product was found, we believe that the reaction did not go *via* the disproportionation $2Ru_2^{5+} \rightarrow Ru_2^{4+} + Ru_2^{6+}$. A similar Ru_2^{5+} to Ru_2^{6+} oxidation was found by Cotton and his co-workers[6] in a reaction in which the conditions were reducing in nature rather than oxidizing.

‡ The molecule contains a crystallographic centre of symmetry. *Crystal data:* $[Ru_2O_{12}C_{18}H_{18}]\cdot 1.4H_2O$, triclinic, space group $P\bar{1}$, a = 9.368(8), b = 8.376(8), c = 7.965(7) Å, α = 92.2(1), β = 83.7(1), γ = 51.8(1)°, U = 483.8 Å^3, M = 581.62, D_c = 1.90 g cm^{-3}, μ(Mo-K_α) = 15.93 cm^{-1}, F(000) = 288, λ(Mo-K_α) = 0.7107 Å. Of 1607 unique intensity data measured, 1467 had $I > 3\sigma(I)$, and were refined to R = 0.048 (R_w = 0.052). Non-hydrogen atoms were anisotropic; hydrogen atoms were refined as parts of rigid methyl groups. The water molecule was given occupancy of 0.70. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

complex $[Ru_2(C_2Bu^t)_6]$[10] the Ru–Ru bond distance is the longest of all. It is noteworthy that the average Ru–O (bridging acetate) distances in $[Ru_2(\mu\text{-}OAc)_4(H_2O)_2]$ are consistently greater than those in (**1**), and that the latter distances are very similar to those in $[Ru_2(\mu\text{-}OAc)_4Cl]\cdot 2H_2O$ and $Cs[Ru_2(\mu\text{-}OAc)_4Cl_2]$. This indicates that the Ru–O (bridging acetate) interaction is stronger in the Ru_2^{6+} and Ru_2^{5+} cases than in the Ru_2^{4+}, a trend consistent with the increased positive charge on the Ru_2 core. Also, the Ru–O (axial acetate) distance in (**1**) is much shorter than the Ru–Cl distances in $[Ru_2(\mu\text{-}OAc)_4Cl]\cdot 2H_2O$ and $Cs[Ru_2(\mu\text{-}OAc)_4Cl_2]$, indicating the stronger attraction of the Ru_2^{6+} core for axial anionic ligands.

Finally, the structure found for (**1**) is identical with that proposed for the V_2^{6+} complex $[V_2(OAc)_6]$,[12] a compound which also exhibits unexpected magnetic properties.

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