The Synthesis, Magnetic, Electrochemical, and Spectroscopic Properties of Diruthenium(II,II) Tetra-μ-carboxylates and their Adducts. *X*-Ray Structures of $Ru_2(O_2CR)_4L_2$ (R = Me, L = H_2O or tetrahydrofuran; R = Et, L = Me_2CO)†

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The interaction of the reduced 'blue solutions' of ruthenium chloride in methanol with alkali-metal carboxylates yields the air-sensitive paramagnetic complexes, $Ru_2(\mu\text{-}O_2CR)_4$ (R = H, Me, CH_2Cl, Et, or Ph), that form weakly end-co-ordinated bis adducts, $Ru_2(\mu\text{-}O_2CR)_4L_2$ [L = H_2O, MeOH, tetrahydrofuran (thf), Me_2CO, or MeCN]. Electrochemical measurements, electronic and i.r. absorption spectra, and magnetic susceptibility data are given. The structures of $Ru_2(O_2CMe)_4L_2$ (L = H_2O or thf) and $Ru_2(O_2CEt)_4(Me_2CO)_2$ have been determined by *X*-ray crystallography and the well known D_{4h} symmetry of binuclear tetracarboxylates established. The $Ru_2(O_2CR)_4$ core shows a constant geometry with Ru–Ru = 2.261 ± 0.001 Å. The three axial donor ligands show slightly varying Ru ··· O distances of 2.335(4), 2.363(5), and 2.391 (5) Å for water, acetone, and thf respectively.

Whereas numerous representative compounds exist[1,2] for multiply bonded metal–metal (M–M) species in the II,II oxidation state (M = Cr, Mo, W, or Rh) few are known for ruthenium. Unlike the majority of other M^{II}–M^{II} multiply bonded complexes which are bridged by tetracarboxylates, those of ruthenium are the non-bridged species Ru_2L_2 (L = porphyrinate[3] or the dibenzo-tetra-aza macrocycle $[C_{22}H_{22}N_4]^{2-}$[4]) and the tetrabridged complex, $Ru_2(mhp)_4\cdot CH_2Cl_2$ (Hmhp = 2-hydroxy-6-methylpyridine).[5] The difficulty in isolating the hitherto unknown diruthenium(II,II) tetracarboxylates is surprising, first because theoretical calculations by Norman *et al.*[6] suggest no real reason why compounds such as $Ru_2(\mu\text{-}O_2CH)_4$ should be anything other than stable, metal–metal doubly-bonded species possessing two unpaired electrons and a $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$ electronic configuration, and secondly because various electrochemical studies[7–9] have shown that in solution the well known formally II,III species $Ru_2(\mu\text{-}O_2CR)_4Cl$,[10] and more recently the related species $Ru_2\{\mu\text{-}NHC(O)R\}_4Cl$,[11–13] can be reduced in a one-electron reduction.

We now give details of the synthesis and characterisation of the previously elusive ruthenium(II) carboxylates $Ru_2(\mu\text{-}O_2CR)_4$ and $Ru_2(\mu\text{-}O_2CR)_4L_2$. A preliminary report of these studies[14] has been made in which it was noted that $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$ was first isolated, though in low yield, by interaction of Grignard reagents on $Ru_2(\mu\text{-}O_2CMe)_4Cl$ in tetrahydrofuran (thf) where the Grignard reagent may be acting as a one-electron reducing agent competitively with a complicated alkylation reaction. Chemical reactions of the carboxylates will be described subsequently.

Results and Discussion

Tetra-μ-carboxylato-diruthenium(II,II).—The complexes $Ru_2(\mu\text{-}O_2CR)_4$ (R = H, Me, CH_2Cl, Et, or Ph) have been synthesised *via* a common procedure, namely refluxing the reduced 'blue solution' of ruthenium trichloride in methanol[15] in the presence of an excess of the appropriate alkali-metal carboxylate for *ca.* 18 h. In all cases the initial deep blue colour of the solution rapidly changed (*ca.* 2 h) to deep green and after *ca.* 8 h to deep red-brown. At this stage the compounds in solution were presumably the methanol adducts $Ru_2(\mu\text{-}O_2CR)_4(MeOH)_2$. For R = H or Me these adducts can be isolated as air-sensitive, insoluble, orange-brown microcrystalline precipitates which upon drying convert to the brown unsolvated compounds $Ru_2(\mu\text{-}O_2CR)_4$ (R = H or Me). The compounds $Ru_2(\mu\text{-}O_2CR)_4(MeOH)_2$ (R = CH_2Cl, Et, or Ph) have a greater solubility in methanol than those where R = H or Me and consequently the reaction solution is first evaporated to dryness and then extracted into hot solvent (diethyl ether for R = CH_2Cl and acetone for R = Et or Ph) in order to isolate a product free of sodium salts. Upon drying, these compounds are converted to the corresponding unsolvated species.

The yields of the compounds vary considerably from 63% based on ruthenium for the formate to 11% for the monochloroacetate. At present the nature of the residual red-brown solutions remaining after the removal of $Ru_2(O_2CR)_4L_2$ (L = solvent) is uncertain; however it appears likely that the species involved are neutral since no precipitates are formed on addition of large cations $[N(PPh_3)_2]^+$ or anions $[BPh_4]^-$.

All the carboxylato-compounds $Ru_2(\mu\text{-}O_2CR)_4$, which, by analogy with $M_2(\mu\text{-}O_2CR)_4$ (M = Cr or Mo) may be infinite chain structures,[16,17] decompose at temperatures of ⩾200 °C. However, all but the formate and monochloroacetate compounds are sufficiently volatile to show a weak parent-ion peak in their mass spectra. The i.r. spectra (voltalef 3s mull) of the complexes (Table 1) have intense $\nu_{asym.}$ (CO_2) and $\nu_{sym.}$ (CO_2) bands at values close to their free-ion values and are thus consistent with symmetrically co-ordinated bridging carboxylato-groups.[18,19]

Tetra-μ-carboxylato-diruthenium(II,II) *Adducts.*—The unsolvated complexes $Ru_2(\mu\text{-}O_2CR)_4$ are soluble in a range of weakly co-ordinating solvents and from the solutions can be crystallised the weakly co-ordinated adducts $Ru_2(\mu\text{-}O_2CR)_4L_2$ (R = H, L = H_2O or thf; R = Me, L = H_2O, thf, MeOH, Me_2CO, or MeCN; R = CH_2Cl, L = thf; R = Et, L = thf or Me_2CO; R = Ph, L = thf or Me_2CO). Whereas the unsolvated

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† Tetra-μ-acetato-diruthenium(II,II)–water (1/2), tetra-μ-acetato-diruthenium(II,II)–tetrahydrofuran (1/2), and tetra-μ-propionato-diruthenium(II,II)–acetone (1/2) (*Ru–Ru*) respectively.

Supplementary data available (No. SUP 56303, 4 pp.): H-atom co-ordinates, anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Table 1. Selected infrared spectral data (cm^{-1}) for ruthenium(II,II) carboxylates

Complex	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta(\nu_{asym} - \nu_{sym})$	Others
$Ru_2(\mu\text{-}O_2CH)_4$	1 575	1 347	228	
$Ru_2(\mu\text{-}O_2CH)_4(H_2O)_2$	1 580	1 350	230	ν(OH) 3 520, 3 420
$Ru_2(\mu\text{-}O_2CH)_4(thf)_2$	1 580	1 345	235	
$Ru_2(\mu\text{-}O_2CMe)_4$	1 550	1 440	110	
$Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$	1 560	1 448	112	ν(OH) 3 490, 3 370, 3 250
$Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$	1 560	1 440	120	
$Ru_2(\mu\text{-}O_2CMe)_4(MeOH)_2$	1 560	1 437	123	ν(OH) 3 330
$Ru_2(\mu\text{-}O_2CMe)_4(Me_2CO)_2$	1 565	1 435	130	ν(C=O) 1 687
$Ru_2(\mu\text{-}O_2CMe)_4(MeCN)_2$	1 576	1 451	125	ν(C≡N) 2 310, 2 261
$Ru_2(\mu\text{-}O_2CCH_2Cl)_4$	1 580	1 423	157	
$Ru_2(\mu\text{-}O_2CCH_2Cl)_4(thf)_2$	1 595	1 422	173	
$Ru_2(\mu\text{-}O_2CEt)_4$	1 556	1 432	124	
$Ru_2(\mu\text{-}O_2CEt)_4(thf)_2$	1 554	1 430	124	
$Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2$	1 560	1 428	122	ν(C=O) 1 684
$Ru_2(\mu\text{-}O_2CPh)_4$	1 537	1 408	129	
$Ru_2(\mu\text{-}O_2CPh)_4(thf)_2$	1 558	1 418	130	
$Ru_2(\mu\text{-}O_2CPh)_4(Me_2CO)_2$	1 551	1 418	123	ν(C=O) 1 690

Table 2. Analytical and magnetic data for some ruthenium(II,II) carboxylates

	Analysis (%)[a,b]			
Complex	C	H	Other	$\mu_{eff.}$/B.M.[c]
$Ru_2(\mu\text{-}O_2CH)_4$	12.3 (12.6)	1.0 (1.1)		2.1
$Ru_2(\mu\text{-}O_2CH)_4(thf)_2$	— —	— —		(2.1)
$Ru_2(\mu\text{-}O_2CMe)_4$	22.1 (21.9)	2.8 (2.8)	O 29.6 (29.2)	2.1
$Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$	20.7 (20.3)	3.3 (3.4)		2.1
$Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$	31.1 (33.0)	4.5 (4.8)		2.1 (2.2)
$Ru_2(\mu\text{-}O_2CMe)_4(MeOH)_2$	23.9 (23.6)	4.0 (3.9)		2.1
$Ru_2(\mu\text{-}O_2CMe)_4(Me_2CO)_2$	29.2 (30.3)	4.2 (4.3)		2.1
$Ru(\mu\text{-}O_2CMe)_4(MeCN)_2$	27.2 (27.7)	3.3 (3.5)	N 5.0 (5.4)	2.1
$Ru_2(\mu\text{-}O_2CCH_2Cl)_4$	16.7 (17.1)	1.4 (1.4)		2.0
$Ru_2(\mu\text{-}O_2CCH_2Cl)_4(thf)_2$	26.8 (26.7)	3.2 (3.4)		2.0 (2.0)
$Ru_2(\mu\text{-}O_2CEt)_4$	29.1 (29.1)	4.0 (4.1)		2.1
$Ru_2(\mu\text{-}O_2CEt)_4(thf)_2$	— —	— —		(2.1)
$Ru_2(\mu\text{-}O_2CPh)_4$	48.4 (49.0)	3.0 (2.9)		2.1
$Ru_2(\mu\text{-}O_2CPh)_4(thf)_2$	51.7 (52.0)	4.4 (4.4)		2.1 (2.1)
$Ru_2(\mu\text{-}O_2CPh)_4(Me_2CO)_2$	49.7 (50.9)	3.7 (4.0)		2.1

[a] Calculated values in parentheses. [b] Where no entry is indicated consistently good analysis could not be obtained due to facile loss of weakly co-ordinated donor ligands. [c] Solid $\mu_{eff.}$ values were determined at 295 K; solution $\mu_{eff.}$ values, in parentheses, were determined at 305 K in 2% hexamethyldisiloxane–tetrahydrofuran solution; B.M. = 0.927 × 10^{-23} A m^2.

Table 3. Electronic spectra (350—800 nm)[a] and cyclic voltammetry of $Ru_2(\mu\text{-}O_2CR)_4$

		$E^{\frac{1}{2}}$/V[c]		
R	$\lambda_{max.}$/nm[b]	MeCN[d]		thf[e]
H	448 (620)	+*0.25* (−1.23)		+*0.23* (−2.02)
Me	438 (580)	*0.00* (−1.84)	−*0.45*[f]	−*0.05* —
CH_2Cl	446 (280)	+*0.34* (−1.55)		+*0.29* —
Et	441 (750)	−*0.02* (−1.99)		−*0.03* —
Ph	440 (sh)	+*0.13* (−1.41)		+*0.07* (−2.08)

[a] Recorded as ~10^{-3} mol dm^{-3} tetrahydrofuran solutions. [b] Absorption coefficient, $\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}, in parentheses. [c] Values in italic type indicate the reversible redox couple $Ru_2^{II,II}$–$Ru_2^{II,III}$, values in parentheses indicate a irreversible reduction; all $E^{\frac{1}{2}}$ values were measured at 295 K and are referenced with respect to a saturated calomel reference electrode at which ferrocene is oxidised at +0.34 V. [d] Electrolyte solution, 0.2 mol dm^{-3} $NBu^n{}_4PF_6$–MeCN. [e] Electrolyte solution, 0.2 mol dm^{-3} $NBu^n{}_4PF_6$–thf. [f] Electrolyte solution, 0.2 mol dm^{-3} $NBu^n{}_4Cl$–MeCN.

complexes all analysed satisfactorily several of the adducts did not (Table 2); this is due to the facile loss of the weakly co-ordinating axial donor ligands even under mild drying conditions. This ease of loss is also reflected in each adduct having the same decomposition point and mass spectral 'parent ion' as its unsolvated analogue. It also necessitates crystals of those adducts studied crystallographically to be mounted under a solvent atmosphere (see below).

The i.r. spectra of the adducts closely parallel those of the parent unsolvated compounds (Table 1). Some of the adducts, *e.g.*, those containing H_2O, MeOH, Me_2CO, or MeCN axial ligands, show new i.r. bands in the regions expected for these co-ordinated molecules.[18] The ν(C=O) bands of the Me_2CO complexes occur at lower frequency (*ca.* 20—25 cm^{-1}) than that of free acetone while the ν(C≡N) bands of the MeCN adduct occur at 10—20 cm^{-1} higher than that of free acetonitrile. These observations are in accord with the presumed weak Ru–O and Ru–N co-ordination of these donor ligands.[18]

The electronic absorption spectra of $Ru_2(\mu\text{-}O_2CR)_4(thf)_2$ (R = H, Me, CH_2Cl, Et, or Ph) each exhibit a single low-intensity band (438—448 nm) in tetrahydrofuran within the range 350—800 nm (Table 3). These low-intensity bands are qualitatively the same as those of the species, presumably $Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$ ($\lambda_{max.}$ 438 nm, $\varepsilon_{max.}$ 501 dm^3 mol^{-1} cm^{-1} in H_2O), which was generated upon reduction of $Ru_2(\mu\text{-}O_2CMe)_4Cl$ in H_2O.[9] They are also similar to that of the known species $[Ru_2(\mu\text{-}O_2CMe)_4(D_2O)_2]^+$ ($\lambda_{max.}$ 425 nm, $\varepsilon_{max.}$ 699 dm^3 mol^{-1} cm^{-1} in D_2O),[9] where the band has been attributed to an $O(\pi) \longrightarrow MM(\pi^*)$ transition where the '$O(\pi)$' orbital is mainly Ru–O bonding in character, but with an appreciable Ru–Ru π-bonding contribution as well.[1,6] It is reasonable to

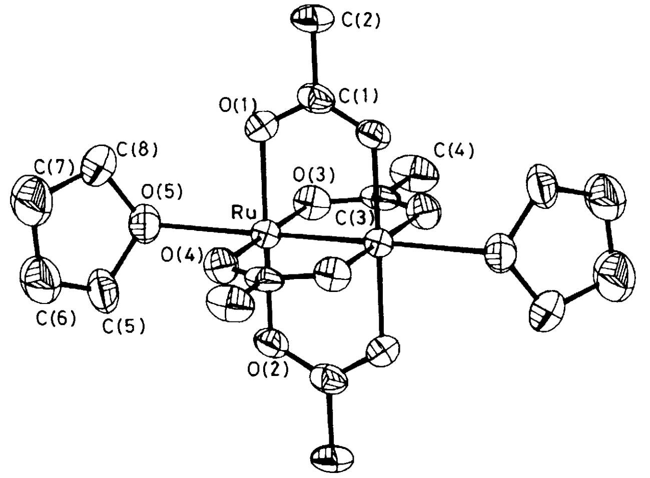

Figure 1. Molecular structure of $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$

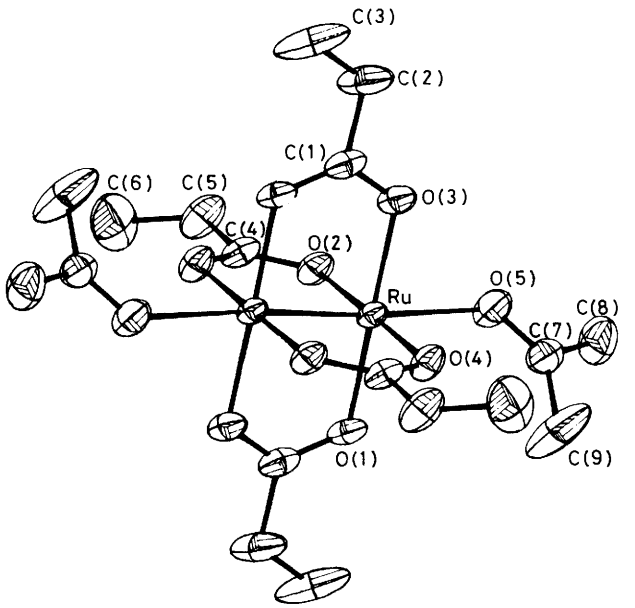

Figure 2. Molecular structure of $Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2$

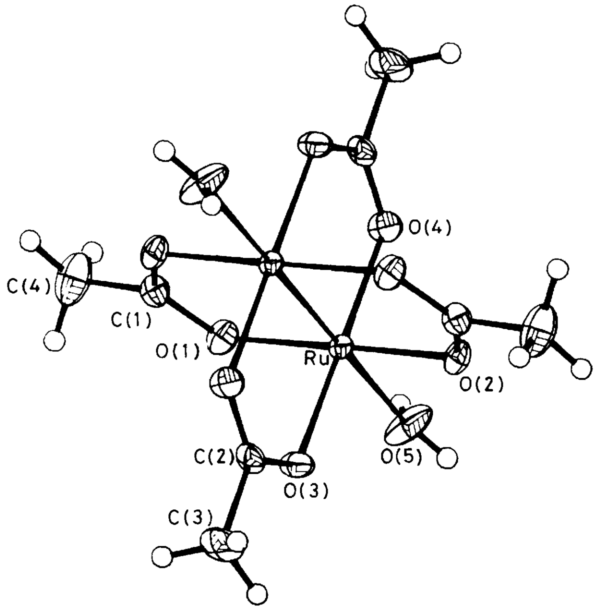

Figure 3. Molecular structure of $Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$

attribute the single low-intensity band of the corresponding $Ru^{II,II}$ compounds to a similar source. However, further experimental and theoretical work is required before a more definitive assignment of this band and the remainder of the absorption spectrum is possible.

Solid and solution[20] magnetic susceptibility measurements at ambient temperature for the carboxylato-compounds $Ru_2(\mu\text{-}O_2CR)_4L_2$ (Table 2) indicate that $\mu_{eff.}$ is consistently 2.0—2.2 B.M. per Ru. This implies two unpaired electrons per binuclear unit which is in excellent agreement with the theoretical predictions of Norman *et al.*[6] for $Ru_2(\mu\text{-}O_2CH)_4$ (electronic configuration $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$) and with the experimental observations of Garner and co-workers[5] for $Ru_2(mhp)_4{\cdot}CH_2Cl_2$ (electronic configuration $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*3}$). However, despite the obvious paramagnetism of these compounds none of them gave an e.s.r. spectrum when observed as 2-methyltetrahydrofuran glasses at 77 K. This may be due to a large zero-state splitting arising from strong magnetic dipole–dipole interaction between the two unpaired electrons in the assumed triplet ground state.

Cyclic voltammetric studies in 0.2 mol dm^{-3} $NBu^n{}_4PF_6$–thf or acetonitrile solutions of $Ru_2(\mu\text{-}O_2CR)_4$ (R = H, Me, CH_2Cl, Et or Ph), *i.e.*, $Ru_2(\mu\text{-}O_2CR)_4(thf)_2$ or $Ru_2(\mu\text{-}O_2CR)_4(MeCN)_2$ respectively, show a single facile reversible one-electron oxidation (Table 3) to generate the $[Ru_2(\mu\text{-}O_2CR)_4L_2]^+$ cations, which have a close analogue in the complex $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]BF_4$.[1] The thf adducts are consistently slightly more easily oxidised ($\leqslant$0.06 V) than their MeCN analogues, which is in accord with Gutmann's view of solvent donicity.[21] A more profound change in the ease of oxidation is effected however by using 0.2 mol dm^{-3} $NBu^n{}_4Cl$–MeCN as the electrolyte solution. Under these conditions $Ru_2(\mu\text{-}O_2CMe)_4(MeCN)_2$ is almost certainly converted to $[Ru_2(\mu\text{-}O_2CMe)_4Cl_2]^{2-}$ {*cf.* $Cs[Ru_2(\mu\text{-}O_2CMe)_4Cl_2]$ (ref. 1)} which, as expected, undergoes a single reversible one-electron oxidation at a potential considerably more negative (0.45 V) than its neutral precursor. Under similar high Cl^- : compound ratios $Ru_2\{\mu\text{-}NHC(O)Me\}_4Cl$ in 0.1 mol dm^{-3} LiCl–dimethyl sulphoxide (which probably generates the $[Ru_2\{\mu\text{-}NHC(O)Me\}_4Cl_2]^-$ anion) undergoes both a reversible one-electron oxidation and a reversible one-electron reduction (+0.47 and −0.96 V respectively *vs.* s.c.e.);[13] a further reversible one-electron reduction in this and related amido-complexes may be ligand based.[12,13] These observations are consistent with those of Bear and co-workers,[22] on $Rh_2(\mu\text{-}O_2CMe)_n(MeCN)_2$ (n = 0—4) in 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$–MeCN which also show that the amido ligand is more capable of stabilising higher oxidation states.

Varying the R group on the carboxylate bridging ligand also has a sizeable effect on the observed oxidation potential in both the thf and MeCN solvate series (Table 3). In general, there is a shift in both the reversible oxidation and irreversible reduction potentials such that electron-withdrawing groups, such as CH_2Cl, produce more difficult oxidations and easier reductions than electron-donating groups such as Me or Et which have the opposite effect. However, the present data set of five compounds is deemed insufficient upon which to base a linear free-energy relationship of the type used by Bear and co-workers[23] in their study of rhodium(II) carboxylates.

Table 4. Selected bond lengths (Å) and angles (°)

(*a*) $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$

O(1)–Ru(1)	2.060(5)	O(2)–Ru(1)	2.063(5)
O(3)–Ru(1)	2.061(5)	O(4)–Ru(1)	2.057(5)
O(5)–Ru(1)	2.391(5)	Ru(1)–Ru(1′)	2.261(3)
C(1)–O(1)	1.255(8)	C(3)–O(3)	1.264(7)
O(2)–Ru(1)–O(1)	179.4(1)	O(3)–Ru(1)–O(1)	89.2(2)
O(3)–Ru(1)–O(2)	90.9(2)	O(4)–Ru(1)–O(1)	91.0(3)
O(4)–Ru(1)–O(2)	88.9(2)	O(4)–Ru(1)–O(3)	179.5(1)
O(5)–Ru(1)–O(1)	89.2(2)	O(5)–Ru(1)–O(2)	91.4(2)
C(1)–O(1)–Ru(1)	118.4(4)	C(3)–O(3)–Ru(1)	118.6(5)
C(5)–O(5)–Ru(1)	117.0(4)	C(8)–O(5)–Ru(1)	119.0(5)
C(2)–C(1)–O(1)	117.7(7)	C(4)–C(3)–O(3)	118.3(7)

(*b*) $Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2$

O(1)–Ru(1)	2.075(4)	O(2)–Ru(1)	2.056(4)
O(3)–Ru(1)	2.062(4)	O(4)–Ru(1)	2.077(4)
O(5)–Ru(1)	2.363(5)	Ru(1)–Ru(1′)	2.260(3)
C(4)–O(2)	1.271(5)	C(1)–O(3)	1.267(5)
C(7)–O(5)	1.214(5)	C(2)–C(1)	1.499(6)
C(3)–C(2)	1.485(7)	C(5)–C(4)	1.503(7)
C(6)–C(5)	1.464(7)	C(8)–C(7)	1.478(7)
C(9)–C(7)	1.487(7)		
O(2)–Ru(1)–O(1)	89.9(2)	O(3)–Ru(1)–O(1)	179.4(1)
O(3)–Ru(1)–O(2)	90.6(2)	O(4)–Ru(1)–O(1)	89.7(2)
O(4)–Ru(1)–O(2)	179.3(1)	O(4)–Ru(1)–O(3)	89.8(2)
O(5)–Ru(1)–O(1)	92.5(2)	O(5)–Ru(1)–O(2)	85.5(2)
O(5)–Ru(1)–O(3)	87.9(2)	O(5)–Ru(1)–O(4)	95.1(2)
C(4)–O(2)–Ru(1)	118.8(3)	C(1)–O(3)–Ru(1)	119.0(3)
C(3)–C(2)–C(1)	117.5(5)	C(5)–C(4)–O(2)	116.7(4)
C(6)–C(5)–C(4)	117.0(5)	C(8)–C(7)–O(5)	120.7(5)
C(9)–C(7)–O(5)	120.2(5)	C(9)–C(7)–C(8)	119.1(5)

(*c*) $Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$

O(1)–Ru(1)	2.079(4)	O(2)–Ru(1)	2.072(4)
O(3)–Ru(1)	2.054(4)	O(4)–Ru(1)	2.068(4)
O(5)–Ru(1)	2.335(4)	Ru(1)–Ru(1″)	2.262(3)
C(1)–O(1)	1.264(5)	C(2)–O(3)	1.268(5)
C(4)–C(1)	1.486(5)	C(3)–C(2)	1.488(6)
O(2)–Ru(1)–O(1)	178.6(1)	O(3)–Ru(1)–O(1)	91.9(2)
O(3)–Ru(1)–O(2)	87.0(2)	O(4)–Ru(1)–O(1)	88.5(2)
O(4)–Ru(1)–O(2)	92.6(2)	O(4)–Ru(1)–O(3)	179.1(1)
O(5)–Ru(1)–O(1)	87.8(2)	O(5)–Ru(1)–O(2)	93.2(2)
O(5)–Ru(1)–O(3)	92.9(2)	O(5)–Ru(1)–O(4)	87.9(2)
C(1)–O(1)–Ru(1)	119.2(3)	C(2)–O(3)–Ru(1)	118.3(3)
C(4)–C(1)–O(1)	118.2(4)	C(3)–C(2)–O(3)	118.1(4)

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (′) $1-x$, $1-y$, $-z$; (″) $1-x$, $1-y$, $2-z$.

X-Ray Structural Data.—Three complexes were subjected to *X*-ray analysis, their choice resting mainly on the good quality of crystals obtained. These are $Ru_2(O_2CMe)_4(thf)_2$, $Ru_2(O_2CEt)_4(Me_2CO)_2$ and $Ru_2(O_2CMe)_4(H_2O)_2$. The three complexes are shown in Figures 1—3, and selected bond lengths and angles are given in Table 4. The most notable features of the structures is the particularly constant geometry of the $Ru_2(O_2CR)_4$ unit, and the slight variation in Ru–O distances to the donor ligands, in the order H_2O < Me_2CO < thf. As discussed previously,[14] the Ru–Ru distance, which we correlate with an electronic configuration $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$, is slightly longer than the distance found in the closely analogous Ru_2^{5+} complex $[Ru_2(O_2CMe)_4(H_2O)_2]BF_4$,[1] which has one antibonding electron less, but is somewhat longer than the metal–metal distance in the essentially unsolvated Ru_2^{4+} complex $Ru_2(mhp)_4{\cdot}CH_2Cl_2$.[5] This strongly suggests that the weakly co-ordinating oxygen donors may, nevertheless, have some effect on the Ru–Ru bond length, as do stronger ligands (*e.g.*, Cl) on the Ru_2^{5+} core (see for example, ref. 1, p. 196).

Experimental

Microanalyses were by Imperial College and Pascher Laboratories. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 683 grating spectrometer in voltalef 3s mulls. Mass spectra were obtained on a VG 7070 spectrometer. Magnetic measurements were made on an Evans' balance (solid) and in solution by Evans' method on a Perkin-Elmer R32 (90 MHz) n.m.r. spectrometer. Electronic spectra were obtained on a Perkin-Elmer 551 spectrophotometer and e.s.r. spectra on a Varian E12 (*X*-band) spectrometer employing 100 kHz magnetic field modulation. Electrochemical studies employed an E.G. and G PAR model 174A polarographic analyser and 0.2 mol dm^{-3} $NBu^n{}_4PF_6$ or $NBu^n{}_4Cl$ solutions in tetrahydrofuran or acetonitrile at ambient temperature, with platinum working and auxiliary electrodes and a saturated calomel electrode (s.c.e.) reference electrode (against which ferrocene is oxidised at $E_{\frac{1}{2}} = +0.34$ V). Scan rates of 20—500 mV s^{-1} were employed on all cyclic voltammetric studies.

All operations were carried out under an atmosphere of purified argon. Solvents were dried conventionally then distilled and degassed before use. Analytical data are given in Table 2.

Preparations.—For each reaction involving the use of methanolic 'ruthenium blue solution', a methanol solution (50 cm^3) containing Johnson Matthey 'ruthenium trichloride trihydrate' (4.00 g) was reduced by hydrogen as previously described.[15]

Tetra-μ-formato-diruthenium(II,II). The blue solution was filtered into degassed methanol (50 cm^3) containing sodium formate (3.20 g). After heating under reflux for *ca.* 2 h, the initial intense blue colour of the solution was replaced by deep green. Heating under reflux for a further 16 h gave rise to a deep red-brown solution and an orange-brown microcrystalline product. The solution was filtered hot and the solid washed with water (3 × 20 cm^3) and dried *in vacuo* at 80 °C as a brown powder. Yield: 1.84 g (63%); m.p. 200 °C (decomp.).

Tetra-μ-formato-diruthenium(II,II)-*bis*(*water*). The complex $Ru_2(\mu\text{-}O_2CH)_4$ was recrystallised from hot water as deep red crystals which rapidly lose H_2O upon drying in a slow stream of argon at 10 °C.

Tetra-μ-formato-diruthenium(II,II)-*bis*(*tetrahydrofuran*). The complex $Ru_2(\mu\text{-}O_2CH)_4$ was dissolved in hot tetrahydrofuran and then cooled to −20 °C overnight to yield red-orange crystals which rapidly lose thf upon drying in a slow stream of argon at 10 °C.

Tetra-μ-acetato-diruthenium(II,II). This complex was prepared as for $Ru_2(\mu\text{-}O_2CH)_4$ using the blue solution and lithium acetate (4.70 g). The orange-brown microcrystalline product was washed with methanol (3 × 20 cm^3) and dried *in vacuo* at 80 °C as a brown powder. Yield: 1.56 g (47%); m.p. 276 °C (decomp.). Mass spectrum: *m*/*e* 438, $[Ru_2(O_2CMe)_4]^+$.

Tetra-μ-acetato-diruthenium(II,II)-*bis*(*water*). The complex $Ru_2(\mu\text{-}O_2CMe)_4$ was recrystallised from hot water as deep red crystals which were dried *in vacuo* at 20 °C. Yield: 58%.

Tetra-μ-acetato-diruthenium(II,II)-*bis*(*tetrahydrofuran*). The complex $Ru_2(\mu\text{-}O_2CMe)_4$ was dissolved in hot tetrahydrofuran and then cooled to −20 °C overnight to yield brown crystals which were dried in a slow stream of argon at 20 °C. Yield: 73%.

Tetra-μ-acetato-diruthenium(II,II)-*bis*(*methanol*). The complex $Ru_2(\mu\text{-}O_2CMe)_4$ was recrystallised from hot methanol as an orange-brown microcrystalline precipitate which was dried *in vacuo* at 20 °C. Yield: 95%.

Tetra-μ-acetato-diruthenium(II,II)-*bis*(*acetone*). The complex $Ru_2(\mu\text{-}O_2CMe)_4$ was dissolved in hot acetone and then cooled to −20 °C overnight to yield red-brown crystals which were dried in a slow stream of argon at 20 °C. Yield: 84%.

Tetra-μ-acetato-diruthenium(II,II)-*bis*(*acetonitrile*). The

Table 5. Crystal data, intensity data, collection parameters and details of refinement

Complex	$Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$	$Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2$	$Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$
Formula	$C_{16}H_{28}O_3Ru_2$	$C_{15}H_{26}O_3Ru_2$	$C_8H_{16}O_4Ru_2$
M	582.53	610.636	474.408
a/Å	9.598(2)	9.628(1)	13.235(1)
b/Å	15.803(3)	8.576(3)	8.638(2)
c/Å	14.606(3)	8.157(2)	14.038(2)
α/°	90.00	97.17(2)	90.00
β/°	90.00	65.09(1)	116.88(1)
γ/°	90.00	94.75(2)	90.00
U/Å^3	2 215.4	605.72	1 431.45
System	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcn*	$P\bar{1}$	*C*2/*c*
D_c/g cm^{-3}	1.746	1.67	2.20
Z	4	1	8
F(000)	1 168	308	918
μ/cm^{-1}	12.67	11.6	19.48
Crystal size/mm	0.3 × 0.2 × 0.2	0.2 × 0.125 × 0.2	0.1 × 0.225 × 0.275
θ min., max.	1.5, 25	1.5, 25	1.5, 25
Temperature	r.t.	r.t.	r.t.
Total data measured	2 245	2 296	1 403
Total data unique	1 948	2 138	1 264
Total data observed	1 261	1 794	1 162
Significant test	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
No. of parameters	184	200	123
Absorption correction	ψ-scan	ψ-scan	ψ-scan, DIFABS *
Transmission factor	0.915—0.998	0.878—0.998	0.857—0.998
Weighting scheme	$1/[\sigma^2(F_o) + 0.0008F_o^2]$	$1/[\sigma^2(F_o) + 0.0001F_o^2]$	$1/[\sigma^2(F_o) + 0.0001F_o^2]$
$R = \Sigma(\Delta F)/\Sigma(F_o)$	0.0279	0.0239	0.0201
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o]$	0.0302	0.0243	0.0208

* N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A.*, 1983, **39**, 158.

Table 6. Fractional atomic co-ordinates (× 10^4) for $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$

Atom	*x*	*y*	*z*
Ru(1)	4 145(0.5)	5 485(0.5)	89(0.5)
O(1)	3 201(4)	4 708(3)	1 037(2)
O(2)	5 105(4)	6 253(2)	−863(2)
O(3)	5 273(4)	6 034(3)	1 132(2)
O(4)	3 035(4)	4 931(3)	−956(2)
O(5)	2 265(4)	6 466(3)	257(2)
C(1)	3 771(6)	4 014(4)	1 225(3)
C(2)	3 106(8)	3 474(5)	1 949(5)
C(3)	6 432(6)	5 712(4)	1 350(3)
C(4)	7 226(7)	6 099(5)	2 112(4)
C(5)	1 984(7)	7 019(5)	−508(5)
C(6)	562(9)	6 766(7)	−852(6)
C(7)	−92(9)	6 421(8)	−43(8)
C(8)	956(7)	6 169(6)	602(5)

Table 7. Fractional atomic co-ordinates (× 10^4) for $Ru_2(\mu\text{-}O_2CEt)_4(Me_2CO)_2$

Atom	*x*	*y*	*z*
Ru(1)	3 824(0.5)	4 616(0.5)	989(0.5)
O(1)	3 384(3)	3 472(3)	−1 146(3)
O(2)	4 723(3)	2 601(3)	1 211(3)
O(3)	4 268(3)	5 777(3)	3 099(3)
O(4)	2 938(3)	6 654(3)	733(3)
O(5)	1 485(3)	3 684(4)	3 187(4)
C(1)	5 557(4)	6 479(4)	2 748(5)
C(2)	5 826(5)	7 278(6)	4 336(6)
C(3)	7 236(7)	8 289(7)	3 941(7)
C(4)	6 150(4)	2 395(4)	319(5)
C(5)	6 757(5)	926(5)	573(6)
C(6)	8 235(6)	406(7)	−836(7)
C(7)	194(4)	3 437(5)	3 285(5)
C(8)	−893(5)	2 374(6)	4 574(7)
C(9)	−314(6)	4 198(8)	2 097(9)

complex $Ru_2(\mu\text{-}O_2CMe)_4$ was dissolved in hot MeCN and then cooled to −20 °C overnight to yield bright red crystals which were dried in a slow stream of argon at 20 °C. Yield: 81%.

Tetra-μ-monochloroacetato-diruthenium(II,II). As for the complex $Ru_2(\mu\text{-}O_2CH)_4$ using sodium monochloroacetate (5.40 g). The deep red-brown solution was evaporated to dryness and the residue extracted with diethyl ether until no further colour was generated in solution. This solution was evaporated to dryness and the residue recrystallised from hot water as golden brown plates which were dried *in vacuo* at 80 °C. Yield: 0.48 g (11%); m.p. 280 °C (decomp.).

Tetra-μ-monochloroacetato-diruthenium(II,II)-*bis*(*tetrahydrofuran*). The complex $Ru_2(\mu\text{-}O_2CCH_2Cl)_4$ was dissolved in hot thf and then cooled to −20 °C overnight to yield a yellow-orange microcrystalline precipitate which was dried in a slow stream of argon at 10 °C. Yield: 93%.

Tetra-μ-propionato-diruthenium(II,II). As for the complex $Ru_2(\mu\text{-}O_2CH)_4$ using sodium propionate (4.40 g). The deep brown solution was filtered and the filtrate evaporated to dryness. The residue was extracted into hot acetone until no further colour was generated in solution. Cooling this solution to −20 °C overnight produced deep red-brown crystals which were dried *in vacuo* at 20 °C as a dark brown powder. Yield: 1.05 g (28%); m.p. 280 °C (decomp.). Mass spectrum: *m*/*e* 494, $[Ru_2(O_2CEt)_4]^+$.

Tetra-μ-propionato-diruthenium(II,II)-*bis*(*tetrahydrofuran*). The complex $Ru_2(\mu\text{-}O_2CEt)_4$ was dissolved in hot thf, the solution cooled to −78 °C overnight to yield orange-brown crystals which rapidly lose thf upon drying in a slow stream of argon at 10 °C.

Tetra-μ-propionato-diruthenium(II,II)-*bis*(*acetone*). The complex $Ru_2(\mu\text{-}O_2CEt)_4$ was dissolved in hot acetone; cooling

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for $Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2$

Atom	*x*	*y*	*z*
Ru(1)	5 428(0.5)	4 292(0.5)	9 608(0.5)
O(1)	3 961(2)	4 451(2)	8 169(2)
O(2)	6 865(2)	4 113(2)	11 061(2)
O(3)	4 877(2)	2 290(2)	10 013(2)
O(4)	5 981(2)	6 324(2)	9 219(2)
O(5)	6 254(2)	2 959(3)	8 691(2)
C(1)	3 137(2)	5 240(4)	8 125(2)
C(2)	4 305(2)	2 400(4)	10 530(2)
C(3)	3 940(4)	945(5)	10 853(4)
C(4)	2 133(4)	5 438(6)	7 070(3)

to −20 °C overnight yielded deep red-brown crystals which rapidly lost bound acetone upon drying in a slow stream of argon at 10 °C.

Tetra-μ-benzoato-diruthenium(II,II). As for the complex $Ru_2(\mu\text{-}O_2CH)_4$ using sodium benzoate (6.60 g). The deep red-brown solution was evaporated to dryness and the residue extracted into hot acetone until no further brown colour was produced in solution. Cooling this solution to −20 °C overnight produced deep red crystals which upon drying *in vacuo* at 80 °C became a brown powder. Yield: 2.17 g (41%); m.p. 320 °C (decomp.). Mass spectrum: *m*/*e* 686, $[Ru_2(O_2CPh)_4]^+$.

Tetra-μ-benzoato-diruthenium(II,II)*-bis*(*tetrahydrofuran*). A solution of $Ru_2(\mu\text{-}O_2CPh)_4$ in hot tetrahydrofuran was cooled to −20 °C overnight to yield orange-brown needles which were dried *in vacuo* at 20 °C. Yield: 88%.

Tetra-μ-benzoato-diruthenium(II,II)*-bis*(*acetone*). As for $Ru_2(\mu\text{-}O_2CPh)_4(thf)_2$ to yield deep red crystals which were dried in a slow stream of argon at 10 °C. Yield: 90%.

Crystallography.—Crystals were sealed under solvent saturated argon in glass capillaries. All crystallographic measurements were made using a CAD4 diffractometer, operating in the ω/2θ scan mode (ω scan width = 0.8 + 0.35 tanθ) with graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner described previously in detail.[24]

The structures were each solved *via* the heavy-atom method, and refined routinely by least-squares methods using SHELX.[25] In each case, hydrogen atoms were located experimentally and successfully refined freely, with isotropic thermal parameters; heavy atoms were refined anisotropically. Crystal data and details of intensity measurements and structure refinements are given in Table 5. Final atomic co-ordinates are given in Tables 6—8.

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