Synthesis, Spectroscopic, Magnetic and Electrochemical Properties of Diruthenium-(II,III) and -(III,III) Complexes containing the Mixed-carboxylato Ligand Systems $CH_3CO_2^-$–$CF_3CO_2^-$ and $C_6H_5CO_2^-$–$CF_3CO_2^-$

Paula Higgins and G. Malachy McCann *
Department of Chemistry, St. Patrick's College, Maynooth, Co. Kildare, Ireland

The interaction of the Ru_2^{5+} tetra-μ-carboxylates $[Ru_2(O_2CR)_4Cl]$ (R = CH_3 or C_6H_5) with alcoholic solutions of $Ag(O_2CCF_3)$ yields the Ru_2^{5+} mixed-carboxylato, monotrifluoroacetato derivatives $[Ru_2(O_2CR)_4(O_2CCF_3)L_2]$ (L = H_2O or MeOH). The omission of alcohol and inclusion of trifluoroacetic acid in the reaction medium directs the synthesis to the Ru_2^{5+} mixed-carboxylato, tris(trifluoroacetato) complexes, $[Ru_2(O_2CR)_2(O_2CCF_3)_3(H_2O)_{0.5}]$. Under aerobic conditions the oxidized, paramagnetic Ru_2^{6+} tetrakis(trifluoroacetato) complex $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2]$ is obtained. Conductivity measurements, electronic and i.r. absorption spectra, and magnetic susceptibility data are given. Cyclic voltammetry measurements show that increased numbers of $CF_3CO_2^-$ ligands in the complexes are responsible for an anodic shift in the potential of the $Ru_2^{5+} \rightleftharpoons Ru_2^{4+}$ couple. Structures are proposed for the tris- and tetrakis-(trifluoroacetato) complexes.

Metathesis reactions [equation (1)] are frequently used as a

$$[M_2(O_2CR)_4] + \text{excess of } R'CO_2H \longrightarrow [M_2(O_2CR')_4] + 4RCO_2H \quad (1)$$

convenient synthetic route to new dimetallic carboxylate-bridged complexes.[1] The product and precursor complexes are normally isostructural and the metal–metal bonded core is retained throughout the reaction. It is generally accepted that these carboxylate-exchange reactions proceed in a stepwise manner in which the original four carboxylate ligands are sequentially replaced by four new bridging carboxylates. Using n.m.r. and mass spectrometry, Bear *et al.*[2] followed the reaction of $[Rh_2(O_2CCH_3)_4]$ with excess of CF_3CO_2H, and identified all the intermediate mixed-carboxylato species $[Rh_2(O_2CCH_3)_n(O_2CCF_3)_{4-n}]$ (n = 1—3) that were formed on the way to the fully substituted product $[Rh_2(O_2CCF_3)_4]$. Mass-spectral evidence has been presented for the existence of $[Mo_2(O_2CCH_3)(O_2CCF_3)_3]$, a mixed-carboxylato complex formed as a contaminant during the preparation of $[Mo_2(O_2CCF_3)_4]$ *via* the reaction of $[Mo_2(O_2CCH_3)_4]$ with refluxing CF_3CO_2H.[3] Using mass spectrometry, we have recently identified all five members of an entire family of dimolybdenum(II) mixed-carboxylato complexes $[Mo_2(O_2CC_6H_5)_n(O_2CCH_2OCH_3)_{4-n}]$ (n = 0—4) in a product mixture obtained from the reaction of $[Mo_2(O_2CC_6H_5)_4]$ with excess of $CH_3OCH_2CO_2H$.[4] Recent attempts to prepare $[Ru_2(O_2CR)_4Cl]$ (R = CF_3 or C_6H_5) by prolonged treatment of $[Ru_2(O_2CCH_3)_4Cl]$ with CF_3CO_2H and $C_6H_5CO_2H$, respectively, gave paramagnetic brown solids.[5] Subsequent reactions of these solids with diphosphines indicated that only partial exchange of acetate ligands had occurred and that the brown materials represented the mixed-carboxylato systems $CH_3CO_2^-$–$CF_3CO_2^-$ and $CH_3CO_2^-$–$C_6H_5CO_2^-$, respectively. In the substitution reactions described above the mixed-carboxylato complexes were either not isolated individually, or were not well characterized. The complex $[Mo_2(O_2CCH_3)_4]$ has been found to react with the dicarboxylic acids acetylenedicarboxylic acid (H_2L') and malonic acid (H_2L^2) to give the polymeric mixed-carboxylato complexes $[\{Mo_2(O_2CCH_3)_2L'\cdot 2H_2O\}_n]$ and $[\{Mo_2(O_2CCH_3)_2L^2\}_n]$, respectively.[6] The only mixed-carboxylato species to have been structurally characterized is $[Rh_2(O_2CCH_3)_2(O_2CCPh_3)_2(CH_3CN)_2]\cdot C_6H_5CH_3$ where the two $CH_3CO_2^-$ ligands were shown to be cisoid.[7]

In this paper we present details of the synthesis and properties of some diruthenium(II,III) mixed-carboxylato complexes of the type RCO_2^-–$CF_3CO_2^-$ (R = CH_3 or C_6H_5). In addition, the preparation and physical properties of a novel diruthenium(III,III) $CH_3CO_2^-$–$CF_3CO_2^-$ species are given.

Experimental

Ruthenium trichloride trihydrate was supplied by Johnson Matthey p.l.c., and $[Ru_2(O_2CCH_3)_4Cl]$ (**1**) was prepared by the standard literature procedure.[8] Microanalyses were performed by the Microanalytical Laboratories, University College, Cork, Ireland. Infrared spectra (KBr disc and Nujol mull) were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer 783 grating spectrometer, and electronic spectra were obtained on a Pye Unicam SP8-100 ultraviolet spectrophotometer. The mass spectrum of $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2]$ (**6**) was run on an AEI MS30 double-beam spectrometer (ionization potential 70 eV and probe temperature 250 °C). Conductivity values were recorded using an AGB Scientific Ltd. model 10 conductivity meter. Solid-state magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance and in solution (Evans' method)[9] on a 60-MHz Hitachi Perkin-Elmer R-600 n.m.r. spectrometer. Cyclic voltammograms (*ca.* 20 °C) were recorded using an EG and G model 264A polarographic analyser in combination with an EG and G PARC model 303A electrode assembly. A hanging mercury drop was employed as the working electrode and a platinum wire as the auxiliary electrode. Potentials were recorded with respect to a silver–silver chloride reference electrode.

Preparations.—$[Ru_2(O_2CC_6H_5)_4Cl]$ (**2**). The procedure used was a modification of the literature method.[10] To a solution of benzoic acid (5.0 g, 41 mmol) and benzoic anhydride (5.0 g, 22 mmol) in ethanol (40 cm^3) was added complex (**1**) (0.6 g, 1.27 mmol). The suspension was refluxed (in air) for 4 h, then filtered while hot. The orange-brown microcrystalline product was washed with hot ethanol (4 × 20 cm^3) and dried *in vacuo*. Yield: 0.83 g (91%). The complex is virtually insoluble in all common solvents.

$[Ru_2(O_2CCH_3)_4(O_2CCF_3)(MeOH)_2]$ (**3**). Complex (**1**) (0.22

g, 0.46 mmol), $Ag(O_2CCF_3)$ (0.11 g, 0.49 mmol), and dry MeOH (25 cm^3) were refluxed for 8 h under nitrogen. The precipitated AgCl (0.066 g, 0.46 mmol) was filtered off and the red supernatant evaporated to *ca.* 4 cm^3. On standing in air the red-brown product precipitated. The solid was washed with ice-cold dry MeOH (2 × 1 cm^3) and pentane (2 × 1 cm^3) and dried *in vacuo*. The complex was soluble in methanol, ethanol, acetone, and diethyl ether.

$[Ru_2(O_2CCH_3)_4(O_2CCF_3)(H_2O)_2]$ (**4**). Complex (**1**) (0.70 g, 1.48 mmol), $Ag(O_2CCF_3)$ (0.35 g, 1.58 mmol), trifluoroacetic acid (10 cm^3), trifluoroacetic anhydride (2 cm^3), and EtOH (40 cm^3) were refluxed for 1 h under a nitrogen atmosphere. Silver chloride (0.20 g, 1.4 mmol) was filtered off and the red supernatant evaporated to *ca.* 6 cm^3. On standing in air the red-brown product precipitated. The product was washed with small volumes of ice-cold EtOH and diethyl ether and dried *in vacuo*. Its solubility was similar to that of complex (**3**).

$[Ru_2(O_2CCH_3)_2(O_2CCF_3)_3(H_2O)_{0.5}]$ (**5**). Complex (**1**) (0.40 g, 0.84 mmol), $Ag(O_2CCF_3)$ (0.19 g, 0.86 mmol), and trifluoroacetic acid (30 cm^3) were refluxed for 0.5 h in air. After filtering off the AgCl (0.11 g, 0.77 mmol), the remaining 'red solution' was stirred overnight under an atmosphere of CO (*ca.* 20 °C). The resulting brown solution was evaporated in air to *ca.* 5 cm^3 from which the product eventually precipitated as a brown microcrystalline solid. The solid was washed with a small volume of ice-cold trifluoroacetic acid and allowed to dry in a hood. Yield: 0.13 g (22%). The compound was very soluble in methanol, ethanol, acetone, and dichloromethane, and insoluble in diethyl ether and hexane.

$[Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2]$ (**6**). The procedure used was the same as that for complex (**5**) up to the stage where the 'red solution' was obtained. This solution was then concentrated to low volume (*ca.* 3 cm^3) in air to give the product as a red-brown solid. The solid was washed and dried as described for (**5**). Yield: 0.26 g (35%).

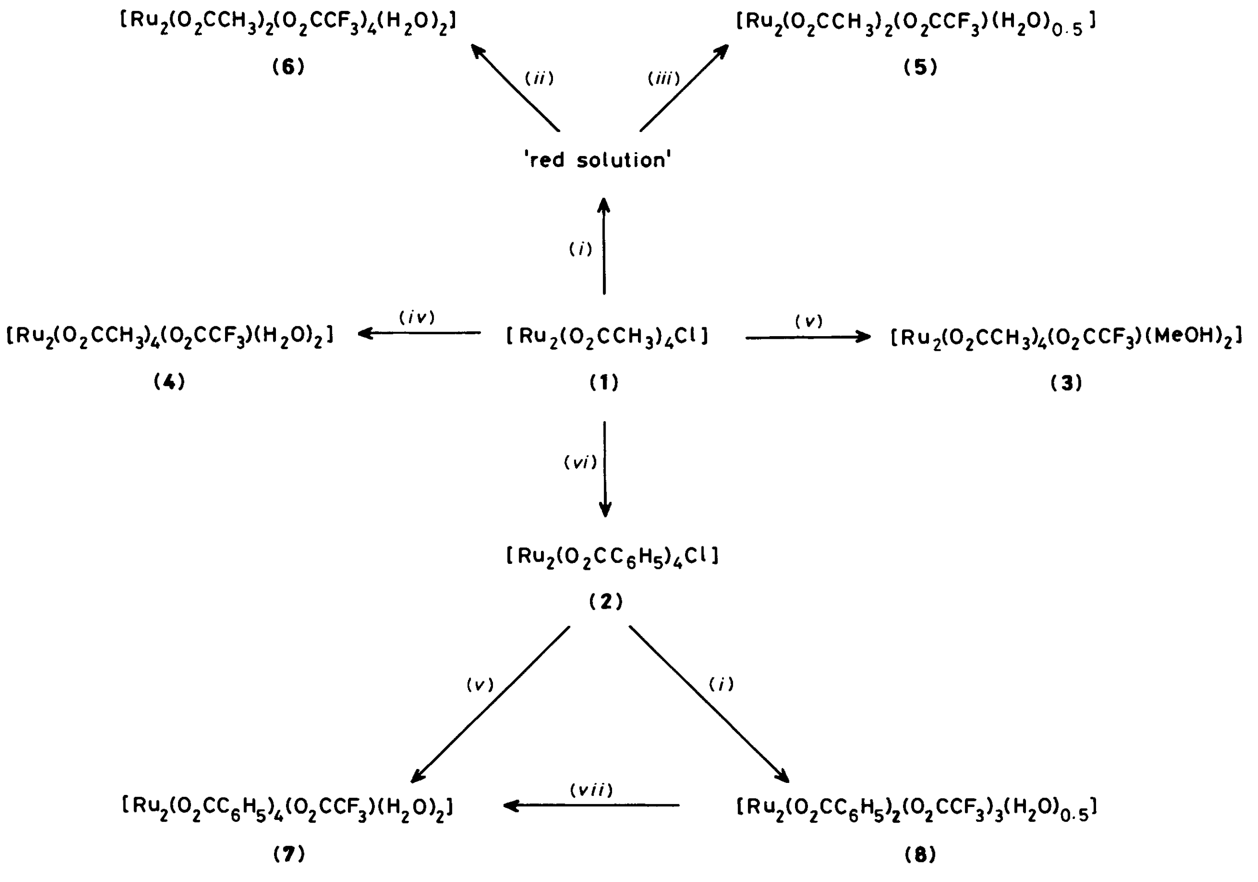
$[Ru_2(O_2CC_6H_5)_4(O_2CCF_3)(H_2O)_2]$ (**7**). Complex (**2**) (0.3 g, 0.42 mmol), $Ag(O_2CCF_3)$ (0.10 g, 0.45 mmol), and MeOH (30 cm^3) were refluxed under nitrogen for 2 h. The precipitated AgCl (0.06 g, 0.42 mmol) was removed by filtration and the red supernatant evaporated in air to *ca.* 4 cm^3 to yield the red-orange product. The solid was washed with a small volume of MeOH and air-dried. It is soluble in methanol, ethanol, and chloroform, and insoluble in water.

$[Ru_2(O_2CC_6H_5)_2(O_2CCF_3)_3(H_2O)_{0.5}]$ (**8**). Complex (**2**) (0.40 g, 0.55 mmol), $Ag(O_2CCF_3)$ (0.13 g, 0.59 mmol), and trifluoroacetic acid (20 cm^3) were refluxed in air for 8 h. The precipitated AgCl (0.076 g, 0.53 mmol) was filtered off and the orange-red filtrate evaporated in air to *ca.* 4 cm^3. The product precipitated as a yellow-orange solid and was then washed with a small volume of ice-cold trifluoroacetic acid and dried *in vacuo*. Yield: 0.16 g (37%). The complex is soluble in methanol, ethanol, acetone, chloroform, and dichloromethane, and insoluble in water and diethyl ether.

Results and Discussion

Synthetic routes to the mixed-carboxylato species (**3**)—(**8**) are summarized in the Scheme.

Tetra(carboxylato)montrifluoroacetatodiruthenium(II,III) *Complexes,* (**3**), (**4**), *and* (**7**).—The reaction of a methanolic solution of complex (**1**) with $Ag(O_2CCF_3)$ (1 : 1 molar ratio) led



Scheme 1. (*i*) CF_3CO_2H, $Ag(O_2CCF_3)$; (*ii*) air; (*iii*) CO; (*iv*) CF_3CO_2H, EtOH, $Ag(O_2CCF_3)$; (*v*) $Ag(O_2CCF_3)$, MeOH; (*vi*) $C_6H_5CO_2H$; (*vii*) MeOH

Table 1. Analytical, conductivity, magnetic, and electronic spectral data for the mixed-carboxylato complexes

Complex	Analysis (%)[a]			Λ_M[b]/S cm^2 mol^{-1}	$\mu_{eff.}$[c]	$\lambda_{max.}$[d]/nm
	C	H	F			
(3) $[Ru_2(O_2CCH_3)_4(O_2CCF_3)(MeOH)_2]$	23.50	2.90	9.05	100	2.92[e]	428
	(24.40)	(3.30)	(9.25)		(4.12)	(490)
(4) $[Ru_2(O_2CCH_3)_4(O_2CCF_3)(H_2O)_2]$	20.80	2.90	8.95	101	2.96[f]	428
	(20.45)	(2.75)	(9.70)		(4.18)	(370)
(5) $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_3(H_2O)_{0.5}]$	18.50	1.05	25.25	70	2.71[e]	424
	(17.95)	(1.05)	(25.60)		(3.83)	(410)
(6) $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2]$	17.80	1.00	27.75	86	1.86[e]	436
	(17.85)	(1.25)	(28.20)		(2.67)	(460)
(7) $[Ru_2(O_2CC_6H_5)_4(O_2CCF_3)(H_2O)_2]$	43.50	2.60	6.30	103	2.92[e]	432 (sh)
	(43.10)	(2.90)	(6.80)		(4.12)	
(8) $[Ru_2(O_2CC_6H_5)_2(O_2CCF_3)_3(H_2O)_{0.5}]$	30.20	1.30	21.55	33	3.12[f]	430 (sh)
	(30.25)	(1.40)	(21.55)		(4.41)	

[a] Theoretical value in parentheses. [b] 1×10^{-3} mol dm^{-3} in MeOH. [c] Values are given both as per Ru and per Ru_2 (in parentheses). [d] Recorded on 1×10^{-3} mol dm^{-3} solutions in MeOH; absorption coefficient, $\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}, in parentheses. [e] Solution $\mu_{eff.}$ (308 K). [f] Solid-state $\mu_{eff.}$ (293 K).

to the precipitation of the stoicheiometric amount of AgCl and subsequent isolation of (3). The diaqua analogue (4) was prepared in a similar manner, although it should be noted that in this case trifluoroacetic acid and trifluoroacetic anhydride were included in the reaction mixture. The most direct route to the red tetrabenzoato monotrifluoroacetato complex (7) involved the reaction of a methanolic suspension of (2) with $Ag(O_2CCF_3)$ (1:1 molar ratio). The Ru_2^{5+} monotrifluoroacetato complexes (3), (4), and (7) showed enhanced solubility properties over their chloro precursors, and their methanol solutions behaved as 1:1 electrolytes (Table 1).

Di(carboxylato)tris(trifluoroacetato)diruthenium(II,III) *Complexes,* (5) *and* (8).—Under non-alcoholic conditions, complex (1) was treated (aerobically or under N_2) with a mixture of $Ag(O_2CCF_3)$ and CF_3CO_2H. After removal of the AgCl and subsequent work-up of the 'red solution' under an atmosphere of CO the Ru_2^{5+} diacetatotris(trifluoroacetato) complex (5) was recovered. The yellow-brown dibenzoato analogue (8) was prepared in such a way that after removal of the AgCl the work-up was carried out in air. On refluxing a methanolic solution of (8) in air the solid disproportionated to give the tetrabenzoatomonotrifluoroacetate species (7). Although a second product was not isolated from this reaction it was noted that the remaining red supernatant, on standing in air, slowly turned green. A comparison of the conductivity values of (5) and (8) reveals that the former is the stronger electrolyte. All of the mixed-carboxylato Ru_2^{5+} complexes mentioned so far have five carboxylate ions in their molecular formula and, as such, are comparable to the known complexes $[Ru_2(O_2CCH_3)_5]$[10,11] and $[Ru_2(O_2CC_6H_5)_5]\cdot C_6H_5CO_2H$[12] which contain five acetato and five benzoato anionic ligands, respectively.

Di(acetato)tetrakis(trifluoroacetato)diruthenium(III,III), (6).—This Ru_2^{6+} complex is obtained when the 'red solution', formed from the reaction of (1) with $Ag(O_2CCF_3)$ and CF_3CO_2H, is worked-up in air. We believe this to be the first example of a mixed-carboxylato Ru_2^{6+} complex, and the second example of a carboxylato Ru_2^{6+} species.[*] Under the instrumental conditions used (see earlier) no parent ion was detected in the mass spectrum of (6). However, peaks were evident at m/e = 601 and 542 corresponding to the fragments $[Ru_2(O_2CCH_3)(O_2CCF_3)_3]^+$ and $[Ru_2(O_2CCF_3)_3]^+$, respectively. The complex behaves as a 1:1 electrolyte in MeOH.

Table 2 shows that in the i.r. region 1 500—1 350 cm^{-1} the spectra of the monotrifluoroacetato complexes (3) and (4) resemble that of the parent acetato complex (1). Complexes (3) and (4) have an additional band at 1 685 cm^{-1} plus three or four weak bands between 700 and 850 cm^{-1}. These new bands are assigned to the $CF_3CO_2^-$ group, and they are seen to occur in similar positions to those reported for the ionic compound $NH_4(O_2CCF_3)$ (Table 2, refs. 14—16). A similar set of $CF_3CO_2^-$ bands was found for (7), and the $C_6H_5CO_2^-$ bands were unchanged with respect to their positions in the spectrum of the parent complex (2). We thus conclude that in the monotrifluoroacetato complexes (3), (4), and (7) the single $CF_3CO_2^-$ group is probably ionic in nature and the four acetato and benzoato ligands are bridging bidentate as in the parent complexes (1) and (2).

The tris(trifluoroacetato) complexes (5) and (8) each had two new bands in the $\nu_{asym}(CO_2)$ region of the spectra which were not present in the spectra of the parent complexes (1) and (2). For (5) the bands appeared at 1 645 and 1 575 cm^{-1} and for (8) at 1 635 and 1 580 cm^{-1}. In addition, both (5) and (8) had seven or eight weak bands in the region 870—530 cm^{-1} all of which are attributable to $CF_3CO_2^-$ groups. Therefore, it would appear that there are two different types of $CF_3CO_2^-$ groups present in both (5) and (8). Furthermore, on the basis of the positions of the asymmetric CO_2 stretching bands, it would seem that neither of these two $CF_3CO_2^-$ groups is ionic in nature. These observations, when taken in conjunction with the assignments made for a number of Mo_2^{4+} trifluoroacetate complexes,[17–19] lead us to conclude that the bands at *ca.* 1 630 cm^{-1} are due to $\nu_{asym}(CO_2)$ of bridging $CF_3CO_2^-$ and those at *ca.* 1 580 cm^{-1} are attributable to $\nu_{asym}(CO_2)$ of unidentate $CF_3CO_2^-$. The symmetric CO_2 stretching bands are buried in the broad band spanning *ca.* 1 500—1 320 cm^{-1}. The absence of any observable changes in the band positions for the bridging $CH_3CO_2^-$ and $C_6H_5CO_2^-$ ligands of the parent complexes (1) and (2) suggests that these ligands are also bridging bidentate in the substituted species (5) and (8). Assuming that the Ru_2^{5+} cores are ligated by four bridging carboxylato ions, the molecular formula $[Ru_2(O_2CR)_2(O_2CCF_3)_3(H_2O)_{0.5}]$ [R = CH_3 (5) or C_6H_5 (8)] then tells us that the complex must comprise two bridging RCO_2^- groups, two bridging $CF_3CO_2^-$ groups, and a unidentate $CF_3CO_2^-$ group. The proposed structures of (5) and (8) are shown in Figure 1(*a*).

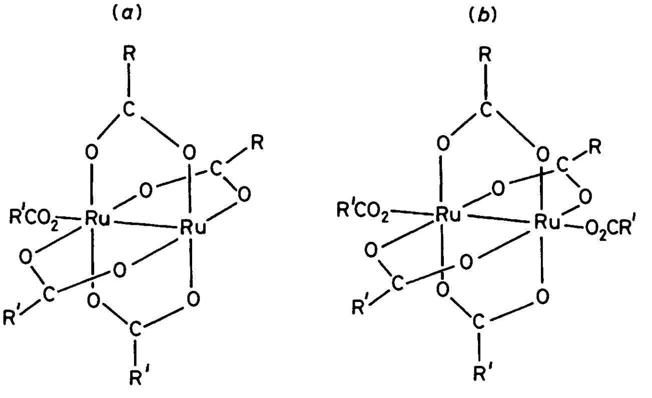
---

[*] We have recently synthesized and characterized the Ru_2^{6+} complex $[Ru_2(O_2CCH_3)_6(H_2O)]$.[13]

Table 2. Selected i.r. data (cm^{-1}) for the complexes[14–16]

	$CH_3CO_2^-$			$C_6H_5CO_2^-$			$CF_3CO_2^-$	
Compound	$\nu_{asym}(CO_2)^a$	$\nu_{asym}(CO_2)$	Others^b	$\nu_{asym}(CO_2)^c$	$\nu_{asym}(CO_2)$	Others^d	$\nu_{asym}(CO_2)^e$	Others^f
(**1**) $[Ru_2(O_2CCH_3)_4Cl]$	(1 500—1 350)		690, 625, 605					
(**3**) $[Ru_2(O_2CCH_3)_4(O_2CCF_3)(MeOH)_2]^g$	(1 500—1 350)		695, 630, 608				1 685	840, 805, 795, 725
(**4**) $[Ru_2(O_2CCH_3)_4(O_2CCF_3)(H_2O)_2]$	(1 500—1 350)		695, 630, 608				1 685	840, 805, 795, 725
(**5**) $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_3(H_2O)_{0.5}]$	(1 500—1 350)		690, 625, 605				1 645, 1 575	870, 840, 790, 780, 740, 730, 700, 530
(**6**) $[Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2]$	(1 480—1 358)		700, 620, 605				1 630, 1 560	865, 850, 780, 738, 720, 530
(**2**) $[Ru_2(O_2CC_6H_5)_4Cl]$				(1 500—1 320)		850, 810, 720, 690, 535		
(**7**) $[Ru_2(O_2CC_6H_5)_4(O_2CCF_3)(H_2O)_2]$				(1 500—1 320)		850, 810, 720, 690, 535	1 680	840, 800, 725
(**8**) $[Ru_2(O_2CC_6H_5)_2(O_2CCF_3)_3(H_2O)_{0.5}]$				(1 500—1 320)		850, 810, 720, 695, 535	1 635, 1 580	870, 855, 790, 785, 740, 730, 550
$NH_4(O_2CCF_3)^h$							1 667	823, 803, 719

^{a} $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ are indistinguishable in the broad band covering the region 1 500—1 350 cm^{-1}. This broad band also includes CH_3 deformation bands (ref. 16). ^{b} CO_2 rock, CO_2 sym def., and CO_2 out-of-plane, respectively. ^{c} $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ are indistinguishable in the broad band covering the region 1 500—1 320 cm^{-1}. ^{d} No attempt has been made to correlate these bands to specific vibrations of the benzoate ion. ^{e} For the mixed-carboxylate species the $CF_3CO_2^-$ $\nu_{sym}(CO_2)$ band is buried in the broad $\nu_{asym,\ sym}(CO_2)$ band associated with the other carboxylate ion present. ^{f} These bands are associated with C–C stretches, CO_2 deformations, and CF_3 bends of the $CF_3CO_2^-$ ion. ^{g} Bands due to MeOH were present at 3 360, 2 940, and 1 005 cm^{-1}. ^{h} $\nu_{sym}(CO_2)$ at 1 465 cm^{-1}. See ref. 17.



$Ru_2(O_2CR)_2(O_2CR')_3$
(**5**) R = CH_3, R' = CF_3
(**8**) R = C_6H_5, R' = CF_3

$Ru_2(O_2CR)_2(O_2CR')_4$
(**6**) R = CH_3 R' = CF_3

Figure 1. Proposed structures for (*a*) the Ru_2^{5+} tris(trifluoroacetato) complexes (**5**) and (**8**), and (*b*) the Ru_2^{6+} tetrakis(trifluoroacetato) complex (**6**). Solvent molecules have been omitted. Isomeric forms are possible for (*a*) and (*b*). Structure (*b*) is similar to that recently found for the complex $[Ru_2(O_2CCH_3)_6(H_2O)]$[13]

The i.r. spectrum of the Ru_2^{6+} tetrakis(trifluoroacetato) complex (**6**) was very similar to that of the Ru_2^{5+} tris(trifluoroacetato) species (**5**). As the two $CH_3CO_2^-$ ligands in (**6**) are bridging bidentate we believe that two of the four $CF_3CO_2^-$ groups are also bridging bidentate, and that the remaining two $CF_3CO_2^-$ groups are unidentate. The proposed structure of (**6**) is illustrated in Figure 1(*b*).

It is noteworthy that complexes (**3**)—(**8**) are isolated with solvent molecules (H_2O or MeOH) in their molecular formula and that O–H stretch bands are evident (*ca.* 3 450 cm^{-1}) in their i.r. spectra. The relative intensities of these bands diminish significantly when the samples are heated (*ca.* 60 °C) under high vacuum for 24 h. Upon re-exposure to the atmosphere the samples take in water as judged from the enhancement of the O–H stretching bands. It is not known whether these solvent molecules are co-ordinated to the metal ions, hydrogen bonded to the oxygens of the carboxylate ligands, or simply located in holes in the crystal lattice.

The electronic spectra (range 360—800 nm) of methanol solutions of the mixed-carboxylato Ru_2^{6+} and Ru_2^{5+} complexes show a single, well defined absorption band in the region $\lambda_{max.}$ 424—436 nm, $\varepsilon_{max.}$ 370—490 dm^3 mol^{-1} cm^{-1} (Table 1). For the mixed acetato–trifluoroacetato complexes (**3**)—(**6**) the position and intensities are within the ranges reported for other Ru_2^{5+}[10,11] and Ru_2^{4+}[20] carboxylato complexes. This band has been assigned to an O(π) $\longrightarrow$ Ru–Ru(π*) transition in diruthenium tetracarboxylato species.[21] It is noteworthy that for the mixed benzoato–trifluoroacetato complexes (**7**) and (**8**) the band at *ca.* 430 nm is essentially only a weak shoulder on an intense change-transfer band ($\lambda_{max.}$ *ca.* 300 nm). This compares favourably with the spectral data reported for the Ru_2^{4+} tetrabenzoato complex $[Ru_2(O_2CC_6H_5)_4]$ [$\lambda_{max.}$ 440 (sh) nm].[20]

Room-temperature magnetic moments (Table 1) for the mixed-carboxylato Ru_2^{5+} complexes are in the range $\mu_{eff.}$ 3.83—4.41 per dimer. The values are consistent with species

Table 3. Electrochemical measurements for the mixed-carboxylato complexes*

Complex	Scan rate, ν/mV s^{-1}	E_{p_c}	E_{p_a}	ΔE_p	$E_{\frac{1}{2}}$	i_{p_c}/i_{p_a}	Comments
(3)	50	−142	−77	65	−109	*ca.* 1	Reversible
(5)	100	(i) 174	238	64	206	*ca.* 1	Reversible
		(ii) −666	No anodic peak				Irreversible
	50	(i) 172	233	61	203	*ca.* 1	Reversible
		(ii) −638	No anodic peak				Irreversible
(6)	200	−884	No anodic peak				Irreversible
(7)	100	−68	−10	58	−39	*ca.* 1	Reversible
	50	−68	−10	58	−39	*ca.* 1	Reversible
(8)	200	(i) 71	224	153	147	*ca.* 2	Quasi-reversible
		(ii) −667	No anodic peak				Irreversible
		(iii) −1 080	No anodic peak				Irreversible
	100	(i) 139	260	121	200	*ca.* 1.6	Quasi-reversible
		(ii) −677	No anodic peak				Irreversible
		(iii) −1 097	No anodic peak				Irreversible

* The measurements were carried out on dilute solutions (1×10^{-3} mol dm^{-3}) of the complexes in MeOH using tetraethylammonium perchlorate (7×10^{-2} mol dm^{-3}) as the supporting electrolyte. All potentials, mV (±5), were recorded with respect to the Ag–AgCl reference electrode.

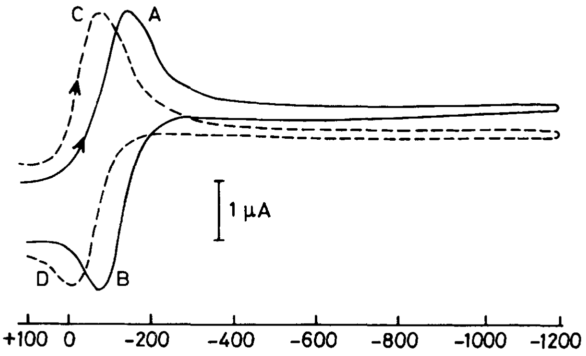


Figure 2. Cyclic voltammograms of the Ru_2^{5+} monotrifluoroacetato complexes (3) (——) and (7) (– – – –)

containing three unpaired electrons per binuclear unit[10,11,22] and conforming to an orbital distribution of the eleven metal electrons of $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$.[21] For the Ru_2^{6+} complex (6) the value of $\mu_{eff.}$ 2.67 per dimer unit (or $\mu_{eff.}$ 1.86 per Ru^{3+})† infers two unpaired electrons per binuclear molecule. This paramagnetism translates to an orbital population of either $\sigma^2\pi^4\delta^2\pi^{*1}\delta^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*2}$, giving a resultant metal-to-metal bond order of three. The same two possible electronic configurations were forwarded by Wilkinson and co-workers[23] to account for the paramagnetism observed for the isoelectronic, triply bonded Os_2^{6+} complexes $[Os_2(O_2CR)_4Cl_2]$ [for R = Me, $\mu_{eff.}$ (288 K) 1.17 per Os^{3+}]. However, the paramagnetism that is evident for complex (6) contrasts with the diamagnetism reported for the purple Ru_2^{6+} complex $[Ru_2O(O_2CCH_3)_4(PPh_3)_2]{\cdot}MeOH$.[8] The latter complex is believed to contain a bridging oxo and two bridging acetato ligands, and the six-co-ordinate geometry around each Ru^{3+} ion is completed by a chelating acetato anion and an unidentate phosphine molecule. The trifluoroacetato analogue was also isolated. The metal–metal bonded Ru_2^{6+} macrocyclic complex $[Ru_2(N_4C_{22}H_{22})_2]$ was also reported to be diamagnetic.[24] Although no magnetic data were reported for the complex $[Ru_2(CH_2Bu^t)_6]$ the ten electrons associated with the Ru_2^{6+} core were presumed to be fully spin-paired and distributed amongst the M_2^{6+} orbitals as $\sigma^2\pi^4\delta^2\delta^{*2}$.[25]

Electrochemical data for the mixed-carboxylato complexes are given in Table 3. The Ru_2^{5+} monotrifluoroacetato complexes (3) and (7) each showed a single, reversible one-electron reduction peak (Figure 2) with $E_{\frac{1}{2}}$ values of −109(AB) and −39 mV(CD), respectively. Assuming that each complex, upon dissolution in the supporting electrolyte solution, first ionizes to $[Ru_2(O_2CR)_4]^+$ and $CF_3CO_2^-$ (R = CH_3 or C_6H_5) and then solvates to $[Ru_2(O_2CR)_4(MeOH)_2]^+$ then the reversible process can be expressed as in equation (2). The difference in the

$$\underset{(Ru_2^{5+})}{[Ru_2(O_2CR)_4(MeOH)_2]^+} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{(Ru_2^{4+})}{[Ru_2(O_2CR)_4(MeOH)_2]} \quad (2)$$

$E_{\frac{1}{2}}$ values for the two complexes highlights the ability of the phenyl rings of the benzoate ligands in (7) to stabilize the reduced Ru_2^{4+} core. This contrasts with the electron-donating properties of the methyl groups on the acetate ligands which would tend to have a relatively destabilizing effect on the Ru_2^{4+} core. The Ru_2^{5+} complex $[Ru_2(O_2CC_3H_7)Cl]$ was reported to undergo a single, quasi-reversible one-electron reduction [$E_{\frac{1}{2}}$ 0 mV *versus* saturated calomel electrode (s.c.e.)] in ethanol–tetrabutylammonium perchlorate.[22]

The voltammograms of the tris(trifluoroacetato) complexes (5) and (8) are shown in Figure 3. The diacetato complex (5) undergoes a reversible, diffusion-controlled one-electron reduction at $E_{\frac{1}{2}}$ 206 mV (EF). The voltammogram also shows an irreversible reduction peak (G) at E_{p_c} −666 mV. For this latter reduction, measurement of the peak geometry gave a separation between the peak and half-peak potentials ($E_{p_c} - E_{p/2}$) of 105 mV compared to a theoretical value of $56.5/n$ mV expected for a reversible, diffusion-controlled peak shape; $E_{p_c} - E_{p/2}$ values greater than 60 mV are diagnostic of electrode reactions in which the rate of electron transfer is the rate-determining step.[26] The absence of a reverse oxidation peak for G confirms this irreversibility. For an irreversible reaction the current–voltage curve is predicted to be broader than for a reversible reaction and is given by the equation $E_{p_c} - E_{p/2} = 48/\alpha n$, where n is the number of electrons transferred in the rate-determining step and α is the transfer coefficient.[26–28] From our value of $E_{p_c} - E_{p/2}$ = 105 mV a value of αn = 0.46 was obtained, inferring that α = 0.46 and n = 1. We thus conclude that the irreversible peak G corresponds to a rate-determining, one-electron reduction process. In the voltammogram of the analogous dibenzoato complex (8) the first

---

† The value of the room-temperature magnetic moment for $[Ru_2(O_2CCH_3)_6(H_2O)]$ was $\mu_{eff.}$ 3.21 per Ru^{3+}, 4.53 per Ru_2^{6+} unit.[13]

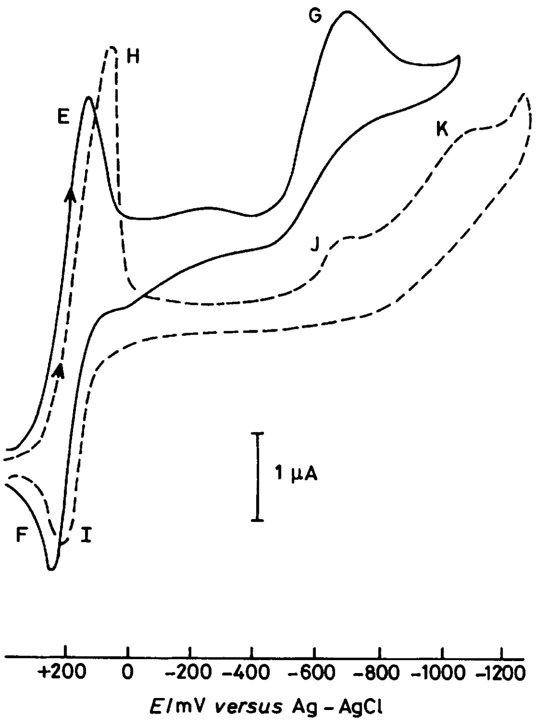


Figure 3. Cyclic voltammograms of the Ru_2^{5+} tris(trifluoroacetato) complexes (**5**) (——) and (**8**) (– – – –)

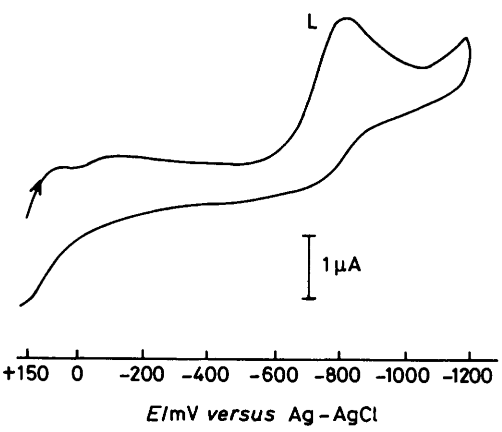


Figure 4. Cyclic voltammogram of the Ru_2^{6+} tetrakis(trifluoroacetato) complex (**6**)

reduction (HI) occurred at E_{p_c} 139 mV for ν 100 mV s^{-1}. The fact that ΔE_p for this process is >60 mV indicates sluggish (quasi-reversible) electron-transfer kinetics, and in the absence of controlled-potential coulometry data it is difficult to assess positively the number of electrons involved in this step. However, from the fact that ΔE_p approaches a value of $60/n$ mV with decreasing scan rate and the ratio i_{p_c}/i_{p_a} approaches unity at lower ν one can cautiously infer that this first reduction represents the transfer of a single electron. For this process we have estimated a value of $E_{\frac{1}{2}}$ 200 mV at ν 100 mV s^{-1}. This is similar to the value found for the first reversible reduction of (**5**). Complex (**8**) also exhibited two irreversible reduction peaks at E_{p_c} −677 (J) and −1 097 mV (K), the latter being associated with the larger peak current. The potential for peak J is close to that of the irreversible reduction peak G of the diacetato analogue (**5**). The voltammograms of these tris(trifluoroacetato) complexes can be summarized as in equation (3). On comparing

$$\underset{(Ru_2^{5+})}{[Ru_2(O_2CR)_2(O_2CCF_3)_2(MeOH)_2]^+} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{(Ru_2^{4+})}{[Ru_2(O_2CR)_2(O_2CCF_3)_2(MeOH)_2]} \xrightarrow{+ne} \text{decomposition products} \quad (3)$$
$$(R = CH_3 \text{ or } C_6H_5)$$

the $E_{\frac{1}{2}}$ values for the reversible $(Ru_2^{5+}) \rightleftharpoons (Ru_2^{4+})$ couples of the two monotrifluoroacetato complexes to those of the two corresponding tris(trifluoroacetato) species a definite anodic potential shift is evident for the species containing the largest numbers of $CF_3CO_2^-$ ligands. This indeed is the trend predicted for increasing numbers of electron-withdrawing CF_3 substituents in the complexes.[20,28,29]

Within the potential range +150 to −1 200 mV* only a single, irreversible reduction peak L (E_{p_c} − 884 mV) was observed in the voltammogram of the Ru_2^{6+} tetrakis(trifluoroacetato) complex (**6**), Figure 4. Using the relationship $E_{p_c} - E_{p/2} = 48/\alpha n$ mV, values of $\alpha = 0.35$ and $n = 1$ were obtained. It thus appears that at the starting potential of + 150 mV, two one-electron reductions have occurred: $Ru_2^{6+} \underset{-e}{\overset{+e}{\rightleftharpoons}} Ru_2^{5+} \underset{-e}{\overset{+e}{\rightleftharpoons}} Ru_2^{4+}$. The single reduction peak in the voltammogram of (**6**) represents the one-electron irreversible reduction of the Ru_2^{4+} species to decomposition products. This interpretation of the voltammogram is substantiated by the fact that we have already seen that in progressing from the Ru_2^{5+} monotrifluoroacetato complex (**3**) to the Ru_2^{5+} tris(trifluoroacetato) species (**5**) there is an anodic shift in potential for the $Ru_2^{5+} \rightleftharpoons Ru_2^{4+}$ couple. Thus, on adding a further $CF_3CO_2^-$ ligand to give the tetrakis(trifluoroacetato) species (**6**) one would expect a further anodic shift in potential for this couple. Indeed, using similar electronegativity arguments, Bear and co-workers[29] have forecast that an Ru_2^{5+} complex of formulation $[Ru_2(O_2CCF_3)_4Cl]$ would be initially reduced at *ca.* + 600 mV to generate an extremely stable Ru_2^{4+} dimer.†

Acknowledgements

We thank the Department of Education, Ireland for a post-graduate grant (to P. H.) and Johnson Matthey p.l.c. for the loan of ruthenium trichloride.

References

1 F. A. Cotton and R. A. Walton, 'Multiple Bonds between Metal Atoms,' Wiley, New York, 1982.
2 J. L. Bear, J. Kitchens, and M. R. Willcott III, *J. Inorg. Nucl. Chem.*, 1971, **33**, 3479.
3 D. J. Santure and A. P. Sattelberger, *Inorg. Chem.*, 1985, **24**, 3477.
4 G. M. McCann and H. Ryan, *Inorg. Chim. Acta*, 1987, **133**, 11.
5 E. B. Boyar, P. A. Harding, S. D. Robinson, and C. Brock, *J. Chem. Soc., Dalton Trans.*, 1986, 1771.
6 R. J. Murenik, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1275.
7 F. A. Cotton and J. L. Thompson, *Inorg. Chim. Acta*, 1984, **81**, 193.
8 R. W. Mitchell, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 846.

---

* The magnitude of the switching potential in the positive direction was dictated by the use of Hg as the working electrode.

† In order to verify the presence and reversibility of the couples, $Ru_2^{6+} \rightleftharpoons Ru_2^{5+} \rightleftharpoons Ru_2^{4+}$, it would be necessary to use a working electrode which itself would not undergo oxidation at the higher positive potentials required.

9 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
10 M. Mukaida, T. Nomura, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2143.
11 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2285.
12 M. Spohn, J. Strähle, and W. Hiller, *Z. Naturforsch.*, 1986, **41**, 541.
13 G. M. McCann, P. Higgins, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1987, 1385.
14 C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.
15 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
16 R. C. Mehrotra and R. Bohra, 'Metal Carboxylates,' Academic Press, London, 1983, pp. 48—60.
17 C. D. Garner and R. G. Senior, *J. Chem. Soc., Dalton Trans.*, 1976, 1041.
18 G. S. Girolami and R. A. Andersen, *Inorg. Chem.*, 1982, **21**, 1318.
19 F. A. Cotton and D. G. Lay, *Inorg. Chem.*, 1981, **20**, 935.
20 A. J. Lindsay, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 2321.
21 J. G. Norman, jun., G. E. Renzoni, and D. A. Case, *J. Am. Chem. Soc.*, 1979, **101**, 5256.
22 F. A. Cotton and E. Pedersen, *Inorg. Chem.*, 1975, **14**, 388.
23 T. Behling, G. Wilkinson, T. A. Stephenson, D. A. Tocher, and M. D. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2109.
24 L. F. Warren and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 1978, 909.
25 R. P. Tooze, M. Motevalli, M. B. Hursthouse, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1984, 799.
26 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, 706.
27 R. S. Nicholson, *Anal. Chem.*, 1965, 1351.
28 K. Das, K. M. Kadish, and J. L. Bear, *Inorg. Chem.*, 1978, **17**, 930.
29 T. Malinski, D. Chang, F. N. Feldmann, J. L. Bear, and K. M. Kadish, *Inorg. Chem.*, 1983, **22**, 3225.

Received 16*th March* 1987; *Paper* 7/477