Non-polymeric Diruthenium(II,III) Carboxylates. Crystal Structures of $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ (thf = tetrahydrofuran)†

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The reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with trimethylacetic acid and isobutyric acid in methanol–water gave $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(H_2O)]$ **2** respectively. Recrystallization of these compounds from tetrahydrofuran (thf) led to $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(thf)]$ **3** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4**, which lose thf giving $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4]$ **5** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4]$ **6**. The complexes were characterized by elemental analysis, IR spectroscopy, conductivity and magnetic measurements; the crystal structures of **1** and **4** were determined by X-ray diffraction methods. Complex **1** has two ruthenium atoms bridged by four trimethylacetato ligands, one axial position being occupied by a chlorine atom and the other by a water molecule. Complex **4** has a similar structure with one chlorine atom and one thf molecule occupying the axial positions. Thus, in both cases the crystal structure determination shows the non-polymeric nature, the first examples for compounds of this type with alkanecarboxylate ligands.

It is widely accepted that all chlorotetra(alkanecarboxylato)- and tetra(arenecarboxylato)-diruthenium(II,III) compounds are polymers.[1] Several crystal structure determinations have shown that the $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units are linked by bridging chlorine atoms giving infinite chains.[2–6] Similarly, the chlorotetraamidatodiruthenium(II,III) derivatives are also polymers.[7,8] However, the amino- or hydroxy-pyridinate complexes present non-polymeric structures;[9–13] the presence of ligands with pendant groups, which could block one of the axial positions of the Ru_2^{5+} unit, has been suggested as the reason for this. However, the synthesis[14] of $[Ru_2(\mu\text{-pfap})_4(CCPh)_2]$ [Hpfap = 2-(2,3,4,5,6-pentafluoroanilino)pyridine] with two axial phenylacetylide ligands suggests that steric hindrance cannot be the cause of the molecular nature of these derivatives. Very recently the non-polymeric $[Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)]\cdot thf\cdot H_2O$ compound (thf = tetrahydrofuran) has been described and structurally characterized,[15] its molecular nature seems to be related to the presence of NH groups in the ligands and the formation of several hydrogen bonds.

In this paper we describe the preparation and properties of new compounds of the types $[Ru_2Cl(\mu\text{-}O_2CR)_4L]$ and $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CMe_3 or $CHMe_2$, L = H_2O or thf) which are the first examples of non-polymeric diruthenium(II,III) compounds with alkanecarboxylate ligands. The crystal structures of $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ are also reported.

Results and Discussion

The reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with trimethylacetic or isobutyric acid in methanol–water leads to total substitution of the acetate ligands and formation of $[Ru_2Cl(\mu\text{-}O_2CR)_4(H_2O)]$ (R = CMe_3 **1** or $CHMe_2$ **2**). Recrystallization of **1** and **2** from tetrahydrofuran or tetrahydrofuran–water gives $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(thf)]$ **3** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4** respectively. Compounds **1** and **2** are stable indefinitely in air, whereas **3** and **4** quickly lose crystallinity at room temperature, giving $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4]$ **5** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4]$ **6**. When **5** and **6** are dissolved in water or thf they give the corresponding solvated complexes. All these compounds are soluble in polar organic solvents such as thf, acetone, dichloromethane, *etc.*, but insoluble in light petroleum. This solubility contrasts with the usual high insolubility of the $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = alkyl or aryl) compounds and is similar to that observed in the case of a pyrrole-2-carboxylate derivative[15] which has a non-polymeric structure. The elemental analyses (C and H) for **1**, **2**, **5** and **6** are consistent with the proposed stoichiometries; good analyses for **3** and **4** could not be obtained due to facile loss of the weakly bonded thf ligand.[16,17]

The IR spectra of compounds **1**–**6** show in the CO_2 stretching region the typical pattern of bridging carboxylate ligands. For **1** and **2** bands corresponding to H_2O are observed whereas for **3** and **4** no bands corresponding to thf ligands are present, similarly to what is found[16,17] for other thf adducts of the type $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]^{n+}$ (n = 0 or 1).

The magnetic measurements, in the range 290–75 K, show that all these compounds obey the Curie–Weiss law with a magnetic moment corresponding to three unpaired electrons per dinuclear unit, in accordance with the ground-state configuration $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$, analogous to those found in $[Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)]\cdot thf\cdot H_2O$ and in polymeric complexes.[15,18]

Complexes **1**–**6** are non-electrolytes in methanol solution in contrast with the previously[1,18] described $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = alkyl or aryl) which are 1 : 1 electrolytes in methanol or dimethyl sulfoxide (dmso) solution. These conductivity data indicate that in these compounds the Ru–Cl bond is not

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

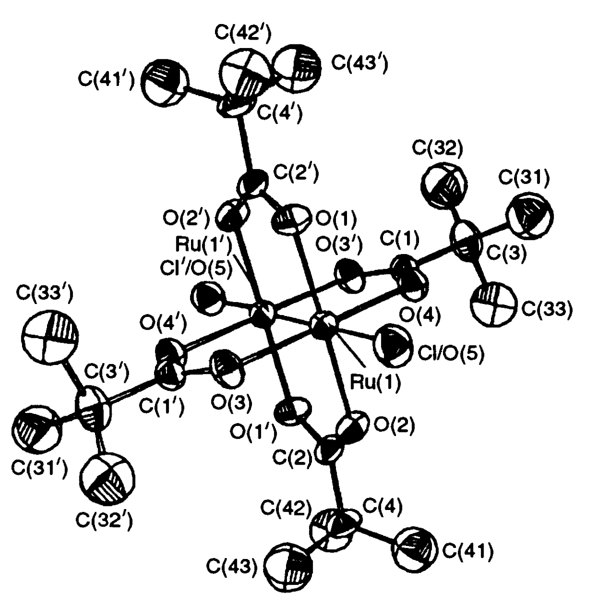

Fig. 1 An ORTEP view of $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1** with 50% probability ellipsoids showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1**

Ru(1)–Ru(1')	2.274(2)	O(1)–C(2')	1.27(1)
Ru(1)–O(1)	2.021(6)	O(2)–C(2)	1.26(1)
Ru(1)–O(2)	2.024(7)	O(3)–C(1')	1.26(1)
Ru(1)–O(3)	2.014(7)	O(4)–C(1)	1.28(1)
Ru(1)–O(4)	2.018(7)	C(1)–C(3)	1.50(1)
Ru(1)–Cl/O(5)	2.486(7)	C(2)–C(4)	1.51(1)
Cl/O(5)–Ru(1)–Ru(1')	176.4(2)	O(1)–Ru(1)–Cl/O(5)	91.8(3)
O(4)–Ru(1)–Ru(1')	89.4(2)	O(1)–Ru(1)–O(4)	89.1(3)
O(4)–Ru(1)–Cl/O(5)	93.9(3)	O(1)–Ru(1)–O(3)	91.1(3)
O(3)–Ru(1)–Ru(1')	89.1(2)	O(1)–Ru(1)–O(2)	178.6(3)
O(3)–Ru(1)–Cl/O(5)	87.5(2)	O(4)–C(1)–O(3')	122.8(9)
O(3)–Ru(1)–O(4)	178.5(3)	Ru(1)–O(1)–C(2')	118.8(7)
O(2)–Ru(1)–Ru(1')	89.1(2)	Ru(1)–O(2)–C(2)	119.3(7)
O(2)–Ru(1)–Cl/O(5)	89.5(3)	Ru(1)–O(3)–C(1')	119.8(6)
O(2)–Ru(1)–O(4)	90.4(3)	Ru(1)–O(4)–C(1)	118.9(7)
O(2)–Ru(1)–O(3)	89.3(3)	O(1)–C(2')–O(2')	123.0(9)
O(1)–Ru(1)–Ru(1')	89.6(2)		

dissociated and therefore discrete molecules are present in solution.

In accordance with all these data, in the solid state, complexes **1**–**4** seem to be non-polymeric having the axial positions occupied, whereas **5** and **6** could be polymeric. However, in solution, discrete molecules are present in all cases. The crystal structure determinations of **1** and **4** confirm in both cases their non-polymeric nature.

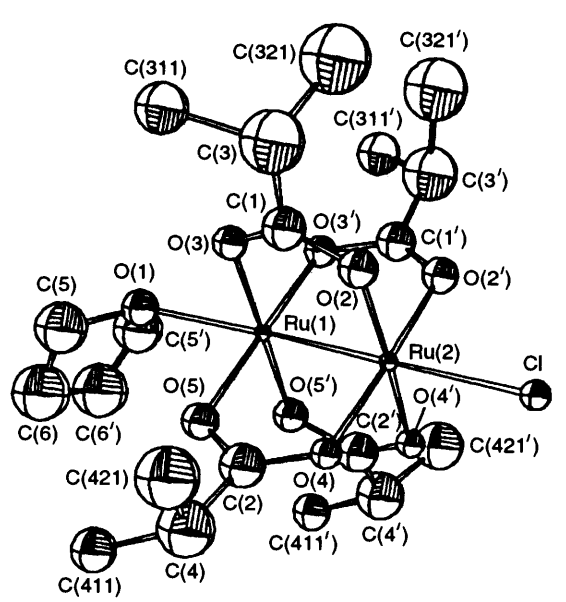

Fig. 2 An ORTEP view of $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4** with 40% probability isotropic ellipsoids showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. The prime atoms are obtained by the symmetry operation $x, \frac{1}{2} - y, z$

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4**

Ru(1)–Ru(2)	2.272(2)	Ru(2)–O(4')	2.01(1)
Ru(1)–O(1)	2.37(2)	O(1)–C(5')	1.39(4)
Ru(1)–O(3)	2.00(1)	O(2)–C(1)	1.23(3)
Ru(1)–O(5)	2.00(2)	O(3)–C(1)	1.27(3)
Ru(1)–O(3')	2.00(1)	O(4)–C(2)	1.26(3)
Ru(1)–O(5')	2.00(2)	O(5)–C(2)	1.30(3)
Ru(2)–Cl	2.445(6)	O(1)–C(5)	1.39(4)
Ru(2)–O(2)	2.02(2)	C(6)–C(6')	1.65(7)
Ru(2)–O(4)	2.01(1)	C(5)–C(6)	1.26(6)
Ru(2)–O(2')	2.02(2)		
Ru(2)–Ru(1)–O(1)	178.6(6)	O(5)–Ru(1)–O(5')	90.7(6)
Ru(2)–Ru(1)–O(3)	90.2(3)	O(3')–Ru(1)–O(5')	88.5(6)
Ru(2)–Ru(1)–O(5)	89.8(3)	Cl–Ru(2)–Ru(1)	179.8(7)
Ru(2)–Ru(1)–O(3')	90.2(4)	Cl–Ru(2)–O(2)	91.6(4)
Ru(2)–Ru(1)–O(5')	89.8(3)	Cl–Ru(2)–O(4)	91.0(3)
O(1)–Ru(1)–O(3)	90.8(5)	Cl–Ru(2)–O(2')	91.6(4)
O(1)–Ru(1)–O(5)	89.2(5)	Cl–Ru(2)–O(4')	91.0(3)
O(1)–Ru(1)–O(3')	90.8(5)	Ru(1)–Ru(2)–O(2)	88.2(3)
O(1)–Ru(1)–O(5')	89.2(5)	O(2)–Ru(2)–O(2')	92.6(7)
O(3)–Ru(1)–O(5)	88.5(6)	O(2)–Ru(2)–O(4')	177.3(5)
O(3)–Ru(1)–O(3')	92.3(6)	O(4)–Ru(2)–O(2')	177.3(5)
O(3)–Ru(1)–O(5')	179.2(7)	O(4)–Ru(2)–O(4')	91.9(6)
O(5)–Ru(1)–O(3')	179.2(79)	O(2')–Ru(2)–O(4')	87.7(6)

The crystal structure of complexes **1** and **4** consists of discrete dinuclear molecules of $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ respectively separated by normal van der Waals distances. The molecular structure of **1** is illustrated in Fig. 1 and selected bond lengths and angles are listed in Table 1. An ORTEP[19] drawing of **4** appears in Fig. 2 and principal bond lengths and angles are summarized in Table 2. The dinuclear unit of **1** has two ruthenium atoms linked by four bridging trimethylacetate ligands with one chlorine atom and one water molecule in the axial positions. The molecular structure of **4** is similar, having one axial position occupied by one thf molecule instead of one water molecule. In both compounds the ruthenium atoms have a distorted-octahedral co-ordination geometry. The distortion arises essentially from the longer $Ru–L_{axial}$ and Ru–Ru distances with respect to $Ru–O_{eq}$. The absence of steric forces that would produce a twist in the molecules is evident for the low values of the torsion angles about the metal–metal bond (0.29–0.44 and 0.00–0.73° for **1** and **4** respectively).

The Ru–Ru distances of 2.274(2) and 2.272(2) Å for complexes **1** and **4** respectively are of the same order as that found[15] in $[Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)]\cdot thf\cdot H_2O$ [2.275(1) Å] and there are no appreciable differences from those found in the polymeric carboxylatodiruthenium(II,III) compounds;[2–6] this is not surprising because the Ru–Ru distance is very similar in all diruthenium(II,III) compounds of this type and also in compounds with Ru_2^{4+} units.[17,20] However, in **4** the axial Ru–Cl bond length, 2.445(6) Å, is the shortest Ru–Cl distance found in $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ compounds [2.5016(6)–2.587(5) Å].[2–6,15] It is consistent with the presence of a Ru–Cl terminal bond, compared with the bridging Ru–Cl···Ru bonds in the polymeric compounds. On the contrary, the opposite Ru–O_{thf} distance [2.37(2) Å] is the longest Ru–O_{ax} distance found when compared with those in other axial O-donor complexes of the $[Ru_2(\mu\text{-}O_2CR)_4]^+$ unit [2.017(2)–2.34(1)].[2,15,21] In **1** the axial positions are shared by the O_{water} and Cl atoms, the Ru–L_{axial} distance being 2.486(7) Å. In agreement with that found in **4**, this value suggests a short Ru–Cl distance and a long Ru–O_{water} bond.

The most noticeable feature in the structure of these compounds is their molecular nature in contrast with the polymeric nature of all alkane- or arene-carboxylate complexes of this type described. The absence of pendant or NH groups in the ligands makes this behaviour more interesting because, in this case, the volume of the *tert*-butyl and isopropyl groups of the bridging ligands does not affect the axial positions of the Ru_2^{5+} unit and there is no special cause for the formation of isolated dinuclear molecules. Thus, we have not found any good reason to explain why the trimethylacetato and isobutyrato derivatives are non-polymeric, whereas, for example, the propionato[5a] and the 2-methylpropenoato[4] derivatives are polymeric.

The results described in this paper suggest that the polymeric or non-polymeric character of the chlorotetracarboxylatodiruthenium(II,III) compounds depends mainly on the nature of the bridging ligand and therefore many other compounds of this type should be also non-polymeric in contrast with the widespread belief that all these compounds are polymeric. The non-polymeric compounds **1**–**6** have the ruthenium atoms in different formal oxidation states and although we have not observed any significant difference in the magnetic behaviour with respect to those observed in the polymeric compounds, the substitution of the aqua or thf axial ligands could permit one to obtain other unsymmetrical complexes with singular magnetical properties; efforts are currently underway to explore this possibility.

Experimental

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. Ruthenium trichloride and carboxylic acids were obtained from commercial sources. Solvents were used without previous purification. The complex $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ was prepared by the literature procedure.[2] Infrared spectra were recorded, as KBr discs, on a Perkin-Elmer 1330 spectrophotometer. Magnetic susceptibility measurements were made using a fully automatic DSM 8 magnetosusceptometer, based on the Faraday method. Molar conductivities were measured with a Philips PW 9526 digital conductivity meter using a PW 9512/60 conductivity measuring cell. Elemental analyses for C and H were performed by the Microanalytical Service of the Complutense University of Madrid.

Synthesis.—$[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1**. To a solution of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ (0.3 g, 0.63 mmol) in methanol–water (1 : 1, 60 cm^3) was added an excess of trimethylacetic acid (0.39 g, 3.79 mmol). The reaction mixture was heated under reflux for 4 h, giving a brown-red solution. This was cooled slowly to room temperature giving a crop of red-brown crystals, which were washed twice with hexane (0.31 g, 74%) (Found: C, 36.6; H, 5.6. $C_{20}H_{38}ClO_9Ru_2$ requires C, 36.4; H, 5.8%); $\tilde{\nu}_{max}/cm^{-1}$ 3380 (br) (OH), 2980m, 2940m (CH), 1490–1420s (CO_2); μ_{eff} = 4.07 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(H_2O)]$ **2**. This complex was prepared by the method described for **1**, giving a brown-red solution. The solution was concentrated under vacuum to 40 cm^3 and cooling overnight to 4 °C gave red crystals of **2**. The crystals were filtered off, washed twice with hexane and diethyl ether and dried in a stream of nitrogen (0.31 g, 82%) (Found: C, 32.3; H, 4.4. $C_{16}H_{26}ClO_9Ru_2$ requires C, 32.0; H, 4.4%); $\tilde{\nu}_{max}/cm^{-1}$ 3440 (br) (OH), 2980m, 2960m (CH), 1470–1420s (CO_2); μ_{eff} = 4.01 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(thf)]$ **3**. Complex **1** (0.2 g) was dissolved in thf (40 cm^3) giving a red solution. This was concentrated under vacuum to 10 cm^3 and cooling to −18 °C gave red crystals of **3**. The crystals were filtered off and dried in a stream of nitrogen (0.2 g, 91%) (Found: C, 38.6; H, 5.8. $C_{24}H_{44}ClO_9Ru_2$ requires C, 40.4; H, 6.2%); $\tilde{\nu}_{max}/cm^{-1}$ 2980m, 2940m (CH), 1490–1420s (CO_2); μ_{eff} = 4.21 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4**. Complex **2** (0.2 g) was dissolved in thf (40 cm^3) giving a red solution. Water was added until turbidity and then the solution was cooled to −18 °C to give crystals of **4**. These were filtered off and dried in a stream of nitrogen (0.21 g, 95%) (Found: C, 34.6; H, 4.95. $C_{20}H_{36}ClO_9Ru_2$ requires C, 36.5; H, 5.5%); $\tilde{\nu}_{max}/cm^{-1}$ 2980m, 2940m (CH), 1480–1420vs (CO_2); μ_{eff} = 4.20 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CMe_3 **5** *or* $CHMe_2$ **6**). When complex **3** or **4** was pumped to vacuum for 1 h quantitatively **5** or **6** was obtained: **5** (Found: C, 37.2; H, 5.5. $C_{20}H_{36}ClO_8Ru_2$ requires C, 37.4; H, 5.65%); $\tilde{\nu}_{max}/cm^{-1}$ 2980m, 2940m (CH), 1480–1420vs (CO_2); μ_{eff} = 4.15 μ_B; **6** (Found: C, 32.6; H, 4.7. $C_{16}H_{28}ClO_8Ru_2$ requires C, 32.8; H, 4.8%); $\tilde{\nu}_{max}/cm^{-1}$ 2980m, 2940m (CH), 1460–1440s (CO_2); μ_{eff} = 4.24 μ_B.

X-Ray Data Collection and Structure Determination.—Brown-reddish (**1**) and pale reddish (**4**) crystals of prismatic shape were coated with epoxy resin and mounted in an Enraf-Nonius diffractometer, equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections with a 2θ range of 13–32° for **1** and 16–27° for **4**. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and Cl were taken from ref. 23. The crystal data are shown in Table 3.

The data collection for complex **4** was performed at low temperature (250 K) in order to minimize both the thermal disorder and the decomposition of the crystal due to the loss of tetrahydrofuran molecules. However, an intensity decay of 7% was observed.

The structures were solved by Patterson and Fourier methods. An empirical absorption correction[24] was applied at the end of the isotropic refinements.

According to common practice, the structure of complex **1** was refined, in a first step, using the space group of highest symmetry among those allowed by the extinction group of the diffraction data. In this case, only two triclinic space groups were possible: *P*1 (no. 1) and $P\bar{1}$ (no. 2). Thus, the first choice was the centrosymmetric group. Difference synthesis showed some electron densities near the oxygen and carbon atoms suggesting a slight, but significant, distortion of the molecular skeleton. However, a non-centrosymmetric structural model yielded unrealistic Ru–O_{water} and Ru–Cl distances and unusually high standard errors in the atomic coordinates. Thus, a centrosymmetric structural model with partial occupation (50%) of chlorine and oxygen in the Cl and O_{water} positions was used. A final refinement with the weighting scheme shown in Table 3 and anisotropic thermal parameters for the non-hydrogen atoms, except for those carbon atoms belonging to the terminal methyl groups in CMe_3 which were isotropically refined due to their high thermal disorder. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by the molecular geometry. Since final difference synthesis showed no significant electron densities, it was not possible to locate the hydrogen atoms of the water molecule. This is probably due to the free rotation of that molecule around the Ru–O bond and to the positional disorder of the O_{water} and Cl atoms.

For complex **4** a final refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms, except for some carbon atoms belonging to the terminal groups

Table 3 Crystal data for $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1** and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4** [a]

	1	**4**
Formula	$C_{20}H_{38}ClO_9Ru_2$	$C_{20}H_{36}ClO_9Ru_2$
M	660.1	658.1
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/m$ (no. 11)
a/Å	9.353(3)	10.996(5)
b/Å	9.469(6)	11.120(4)
c/Å	9.804(4)	13.102(2)
α/°	72.57(4)	
β/°	83.21(3)	95.69(2)
γ/°	73.88(4)	
Z	1	2
$U/Å^3$	795.3(7)	1605(1)
$D_c/g\ cm^{-3}$	1.38	1.36
F(000)	335	666
T/K	295	250
μ(Mo-Kα)/cm^{-1}	10.5	10.4
Crystal dimensions/mm	0.25 × 0.3 × 0.4	0.3 × 0.3 × 0.4
Data collected	−12, −12, 0 to 12, 12, 12	−14, 0, 0 to 14, 14, 17
Unique data	3816	4067
Observed reflections $[I > 3\sigma(I)]$	3195	2693
R_{int}	0.018	0.038
Decay (%)	< 1	≈ 7
Weighting scheme	*b*	Unit
R	0.068	0.106
R'	0.093	0.111
Absorption correction range	0.95–1.02	0.87–1.09

[a] Details in common: 2θ range 1–56°; ω–2θ scan mode; three standard reflections every 100; maximum shift/error 0.2; $R = \Sigma|\Delta F|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2 F/\Sigma w|F_o|^2)^{\frac{1}{2}}$; $\Delta = |F_o| - |F_c|$. [b] Weighting coefficients *a*, *b* in the expression $w^{-1} = (a + b|F_o|)^2$ for $|F_o| < 8$, 2.627, −0.235; for $8 < |F_o| < 18$, 1.106, −0.010; for $18 < |F_o| < 140$, −0.199, 0.061.

Table 4 Coordinates for $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.0431(1)	0.0241(1)	0.0921(1)
O(1)	0.0697(8)	−0.2470(7)	−0.0224(7)
O(2)	0.1540(7)	−0.1993(8)	0.1570(7)
O(3)	−0.1349(8)	−0.0273(8)	0.2128(7)
O(4)	0.2194(7)	0.0748(8)	−0.0326(7)
C(1)	0.2281(10)	0.0642(11)	−0.1605(10)
C(2)	0.1426(10)	−0.2908(10)	0.0914(11)
C(3)	0.3632(13)	0.1001(14)	−0.2601(13)
C(4)	0.2109(12)	−0.4581(11)	0.1543(13)
C(31)	0.4500(18)	0.1834(18)	−0.1960(18)
C(32)	0.3186(20)	0.1894(20)	−0.4111(19)
C(33)	0.4728(20)	−0.0650(21)	−0.2540(19)
C(41)	0.3498(18)	−0.4862(19)	0.2295(18)
C(42)	0.2264(18)	−0.5472(19)	0.0419(18)
C(43)	0.1005(19)	−0.5099(20)	0.2690(19)
Cl	0.1282(6)	0.0670(7)	0.3038(6)
O(5)	0.1282(6)	0.0670(7)	0.3038(6)

Table 5 Coordinates for $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ **4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.2212(1)	0.75	0.2588(1)
Ru(2)	0.2421(1)	0.75	0.4319(1)
Cl	0.2636(6)	0.75	0.6181(5)
O(1)	0.2045(22)	0.75	0.0785(15)
O(2)	0.1149(15)	0.6189(17)	0.4273(9)
O(3)	0.0945(12)	0.6197(14)	0.2585(9)
O(4)	0.3692(12)	0.6198(12)	0.4294(8)
O(5)	0.3490(14)	0.6221(15)	0.2592(9)
C(1)	0.0693(23)	0.5802(27)	0.3443(14)
C(2)	0.3985(25)	0.5818(26)	0.3448(16)
C(3)	−0.0414(34)	0.5082(38)	0.3457(28)
C(311)	−0.0733(21)	0.4385(23)	0.2381(18)
C(321)	−0.1626(27)	0.5918(29)	0.3649(22)
C(4)	0.4769(35)	0.4686(40)	0.3433(30)
C(411)	0.5244(23)	0.4527(26)	0.2405(19)
C(421)	0.3953(35)	0.3526(39)	0.3704(29)
C(5)	0.2423(36)	0.6516(40)	0.0254(30)
C(6)	0.3457(42)	0.6757(43)	−0.0027(34)

$CHMe_2$ and those of the thf molecules. The thermal parameters of these atoms are strongly affected by thermal disorder and the partial decomposition of the crystal. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. A final difference synthesis showed no significant electron density. The final agreement factors are unusually high due to the crystal decomposition and the thermal disorder.

Most of the calculations were carried out with the X-RAY 80 system.[25] The atomic positional parameters for complex **1** and **4**, are given in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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