Polymeric, Molecular, and Cation/Anion Arrangements in Chloro-, Bromo-, and Iododiruthenium(II,III) Carboxylate Compounds

M. Carmen Barral,[a] Rodrigo González-Prieto,[a] Reyes Jiménez-Aparicio,*[a]
J. Luis Priego,[a] M. Rosario Torres,[b] and Francisco A. Urbanos[a]

Keywords: Carboxylate / Diruthenium / Metal−metal bonds / Multiple bonds / Ruthenium

The synthesis and characterization of the anhydrous compounds $[Ru_2X(\mu\text{-}O_2CR)_4]$ [R = CH_2CH_2OPh, X = Cl (**1a**), Br (**2a**), I (**3a**); R = $CMePh_2$, X = Br (**5a**), I (**6a**)] and of the solvated complexes $[Ru_2X(\mu\text{-}O_2CR)_4(H_2O)]$ [R = CH_2CH_2OPh, X = Cl (**1b**), I (**3b**); R = $CMePh_2$, X = Cl (**4b**), Br (**5b**), I (**6b**)] are described. Thermogravimetric analyses have been used to confirm the anhydrous or solvated natures of the complexes. The crystal structures of **1b·2MeOH**, **3b·0.5H$_2$O**, and **4b** have been investigated by X-ray diffraction and none of them shows the usual polymeric arrangement reported for tetracarboxylatodiruthenium(II,III) compounds. The structure of **3b·0.5H$_2$O** consists of cationic and anionic units, $[Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)_2][Ru_2I_2(\mu\text{-}O_2CCH_2CH_2OPh)_4]$, and represents the first reported crystal structure of a tetracarboxylato(iodo)diruthenium(II,III) derivative. The structures **1b·2MeOH** and **4b** each show the presence of discrete dinuclear molecules. The crystal structure of $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ demonstrates that diruthenium compounds with the same halide and carboxylate ligands may adopt polymeric or discrete molecular dispositions. Magnetic susceptibility measurements of the complexes in the 2–300 K range have been carried out. Complex **2a** shows a strong antiferromagnetic coupling, consistent with the existence of linear chains in the solid state. The complexes $[Ru_2X(\mu\text{-}O_2CR)_4(H_2O)]$ show weak through-space antiferromagnetic coupling, in accordance with non-polymeric structures. The magnetic behaviour of **1a**, **3a**, **5a**, and **6a** suggests a mixture of arrangements.
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Introduction

Since the synthesis of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ was first published,[1] numerous diruthenium(II,III) complexes of the formula $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = alkyl, aryl) have been described.[2−4] These complexes have attracted much attention, mainly due to interest in their electronic and magnetic properties.[2−4] More recently, many efforts have been devoted to the use of carboxylate complexes with metal−metal bonds as building blocks in the formation of supramolecular metallospecies.[5−8] In the $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ compounds, the diruthenium atoms are strongly bonded by four bridging carboxylate ligands, with one axial position occupied by one chlorine atom. In the solid state, most of them have polymeric structures with chloride ligands bridging the dinuclear units to give zigzag chains.[9−15] A similar structure with linear chains with four carboxylate ligands has been found.[16−19] Discrete dinuclear molecules in which a neutral ligand is coordinated to one of the axial positions have also been described,[20−22] as has a unique example showing zigzag chains made up jointly of cationic and anionic units.[13] The different arrangements observed in the diruthenium complexes are collected in Scheme 1.

The influence of the carboxylate ligand on the polymeric or molecular nature of the diruthenium complexes has been investigated and seems to be related to the presence of branched chains in the carboxylate ligand.[21,22] Few bromo and iodo derivatives have been reported,[23,24] and the influence of the halogen axial ligand on the structure has not been studied. $[Ru_2Br(\mu\text{-}O_2CH)_4]$ is the sole example of this kind of compounds whose crystal structure has been reported.[23]

In this paper we investigate the possibility of obtaining both discrete molecules and polymeric species with the same carboxylate ligand. The ligands 3-phenoxypropionate and 2,2-diphenylpropionate have been used. The preparation of new chloro, bromo, and iodo derivatives has been carried out and the influence of the halogen axial ligand on the arrangement of the complexes explored.

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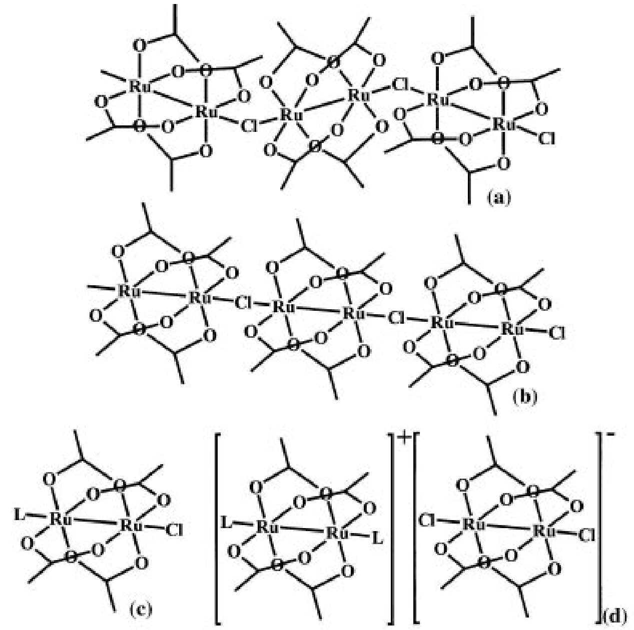
[a] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria, 28040 Madrid, Spain
Fax: (internat.) + 34-91/3944352
E-mail: qcmm@quim.ucm.es
[b] Centro de Asistencia a la Investigación de Rayos X, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria,
28040 Madrid, Spain

DOI: 10.1002/ejic.200300010



Scheme 1. Arrangement observed in diruthenium complexes: (a) zigzag chains, (b) linear chains, (c) discrete molecules, and (d) cation/anion species

Results and Discussion

Synthesis and Physicochemical Properties of the Compounds

The complex [$Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4$] (**1a**) was prepared by treatment of [$Ru_2Cl(\mu\text{-}O_2CMe)_4$] with 3-phenoxypropionic acid in methanol/water (1:1). Two metathesis cycles were carried out to ensure the complete replacement of the acetate ligands. $AgBF_4$ was added to a solution of **1a** in THF in order to obtain [$Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4(THF)_2$]$BF_4$, which was treated in ethanol with an aqueous solution of KBr to produce the precipitation of [$Ru_2Br(\mu\text{-}O_2CCH_2CH_2OPh)_4$] (**2a**). The synthesis of [$Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)$] (**3b**) was carried out by using KI in place of KBr. The hydrate [$Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)$] (**1b**) was obtained from a methanol solution of **1a**. The unsolvated [$Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4$] (**3a**) was prepared by prolonged heating of **3b** under vacuum. Attempts to obtain the analogous hydrated [$Ru_2Br(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)$] gave the polymeric **2a** in all cases.

Treatment of [$Ru_2Cl(\mu\text{-}O_2CMe)_4$] with 2,2-diphenylpropionic acid in methanol/water (1:1) produced [$Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)$] (**4b**). The previously described compound [$Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4$][18] crystallized when petroleum ether was added to a solution of **4b** in CH_2Cl_2. The complexes [$Ru_2X(\mu\text{-}O_2CCMePh_2)_4(H_2O)$] [X = Br (**5b**), I (**6b**)] were obtained from [$Ru_2(\mu\text{-}O_2CCMePh_2)_4(THF)_2$]$BF_4$ and KBr or KI. The unsolvated **5a** and **6a** were prepared by heating **5b** and **6b**, respectively, under vacuum.

The cleavage of the polymeric chains of **1a**−**6a** by donor solvent molecules occurs in all cases except for that of the complex **2a**. The presence of coordinated water molecules in the complexes was inferred from analytical, IR, and thermogravimetric data.

Crystals of **1b·2MeOH** were formed by cooling of (−18 °C) methanol solutions of **1a** or **1b**. After several unsuccessful attempts to obtain crystals of the bromo and iodo derivatives, single crystals of **3b·0.5H₂O** suitable for an X-ray crystal structure analysis grew from a methanol solution containing [$Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4$]$^+$ and I^- over 48 h. Single crystals of **4b** were obtained by the same procedure from a solution containing [$Ru_2(\mu\text{-}O_2CCMePh_2)_4$]$^+$ and Cl^-.

The chloro complexes are quite soluble in polar organic solvents such as methanol or THF, but insoluble in petroleum ether or toluene. The solubilities of complexes **1**−**6** in polar organic solvents decrease along the series Cl, Br, and I, the iodo derivatives being only partially soluble in these solvents. The conductivities of these compounds in methanol (ca. 10^{-4} M) indicate that they are 1:1 electrolytes in this solvent.[25] The process of dissolution of the polymeric complexes **1a** and **3a**−**6a** in donor solvents results in the cleavage of the chains, giving discrete dinuclear units. Thus, from MeOH/H_2O solutions, molecular [$Ru_2Cl(\mu\text{-}O_2CR)_4(H_2O)$] complexes have been obtained.

Spectroscopic Properties

The IR spectra of all compounds show the pattern typical of bridging carboxylate ligands in the COO stretching region.[4] Other bands corresponding to the carboxylate ligands and attributable to CH or phenyl groups are also observed. The IR spectra of **1b** and **3b**−**6b** clearly show absorption bands due to the presence of water molecules.

The electronic spectra of all compounds in methanol are similar to those of other diruthenium(II,III) complexes,[2] showing two bands in the UV/Vis range at ca. 430 and ca. 290 nm and attributable to $\pi(RuO, Ru_2)\rightarrow\pi^*(Ru_2)$ and $\pi(\text{axial ligand})\rightarrow\pi^*(Ru_2)$ transitions, respectively, as proposed by Norman et al.[26] and by Miskowski and Gray.[27] All complexes also absorb in the near infrared region at ca. 1000 nm, due to a $\delta\rightarrow\delta^*$ transition.[28]

Thermogravimetric Studies

The thermogravimetric curves of the hydrated complexes **1b** and **3b**−**6b** each show weight loss between 145 and 210 °C, corresponding to one water molecule per complex. The assumption that this water molecule is bonded to one axial position of the diruthenium complexes was confirmed by the crystal structure determinations of **1b·2MeOH**, **3b·0.5H₂O** and **4b**. In a further experiment, the thermal decomposition of each compound was interrupted after the release of the water molecule, and their IR spectra were identical to those of the corresponding [$Ru_2X(\mu\text{-}O_2CR)_4$] species. Moreover, the anhydrous complexes do not display any weight loss before 250 °C. The loss of the halide ligand for **1a**, **2a**, **3b**, and **6b** is clearly observed in the 250−290 °C range, followed by the loss of the carboxylate groups in two steps. The thermogravimetric curves for the other compounds show that the release of the halide and of the first two carboxylate ligands takes place at the same time. These data are in accordance with previous studies[29] on the thermal decomposition of pentakis(alkanoato)diruthenium(II,III) complexes.

Magnetic Properties

Magnetic measurements on compounds **1**−**6** at room temperature each show magnetic moments of 3.86−4.18 μ_B, corresponding to the presence of three unpaired electrons per dimer unit.[2] These magnetic moments are in accordance with the $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ ground-state configuration proposed by Norman et al.[26] In all complexes the molar susceptibility χ_M increases continuously with decreasing temperature (300−2 K), except for complexes **1a** and **2a**. The magnetic moment in all cases exhibits a pronounced decrease with temperature. This behaviour has been ascribed to a large zero-field splitting (ZFS) and some degree of antiferromagnetic coupling between the diruthenium units.[14,15,18,30−33] The model of Cukiernik et al.[14] was successfully used to fit the magnetic data of complexes **1b** and **3b**−**6b**. In this model, we used the isotropic *g* parameter instead of $g_\parallel$ and $g_\perp$ in order to reduce the number of parameters and to obtain more accurate values of *D* and *zJ*. Figure 1 shows the experimentally measured and calculated curves for complex **4b** by this model. Similar fits are obtained for the complexes **1b** and **3b**−**6b**.

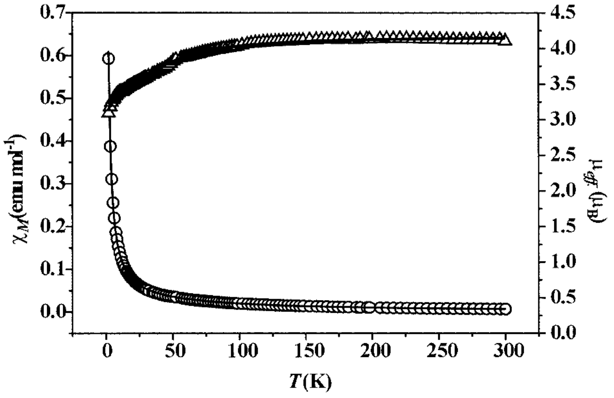


Figure 1. Temperature dependence of the molar susceptibility χ_M (circles) and $\mu_{eff.}$ (triangles) for complex **4b**; solid lines are the product of a least-squares fit to the model indicated in the text

Table 1 collects the calculated magnetic parameters (*g*, *D*, *zJ*, *TIP*, and *P*) for the complexes **1b**−**6b**, together with σ^2, which indicates the quality of the fits. All compounds show large zero-field splittings and low antiferromagnetic coupling values. The *D* values range from 50.60 to 64.72 cm^{-1}, similarly to those found previously for the analogous compounds.[8d,14,15,33−35] The molecular nature of the solvates **1b**−**6b** is in accordance with the low values (−0.04 to −1.33 cm^{-1}) of the antiferromagnetic coupling constants. Similar spin exchange by through-space pathways has recently observed in other molecular diruthenium complexes.[15]

Figure 2 displays the variation of the magnetic susceptibility with temperature for complex **2a**. A maximum is observed at 30 K. The paramagnetic tail and the turning point have been observed previously[18,33] in diruthenium(II,III) complexes with linear chain structures (Ru−Cl−Ru angle ca. 180°). In these cases strong antiferromagnetic coupling between the diruthenium(II,III) units through chlorine atoms gives rise to an inversion of the magnetic susceptibility curve and the approximation of the molecular field[14] cannot be used. Recently, we have developed a model[33] to fit this type of magnetic behaviour. A satisfactory agreement between experimentally measured and calculated curves of the molar susceptibility and the magnetic moment was obtained for complex **2a** (Figure 2) by use of this model.

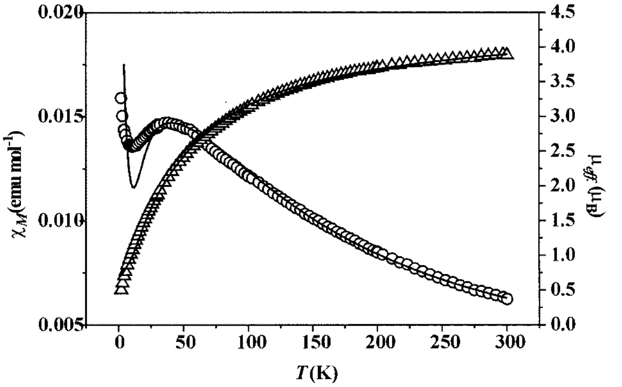


Figure 2. Temperature dependence of the molar susceptibility χ_M (circles) and $\mu_{eff.}$ (triangles) for complex **2a**; solid lines are the products of a least-squares fit to the model indicated in the text

The parameters obtained in the fit of the experimental data for complex **2a** are collected in Table 1. The *zJ* value calculated for complex **2a** is −9.08 cm^{-1}, analogous to those found[18,33] for $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ [R = $CMePh_2$, CH_2CH_3, C(Me)=CHEt]. The high paramagnetic impurity value (3.3%), slightly higher than those observed

Table 1. Magnetic parameters obtained in the fits to the magnetic moment as a function of temperature

Compound	g	*D* [cm^{-1}]	*zJ* [cm^{-1}]	*TIP* [mL/mol]	*P* [%]	σ^2 [a]
1b	2.00	64.03	−1.33	1.49 10^{-3}	0.12	1.50 10^{-4}
2a	2.00	62.99	−9.08	8.31 10^{-4}	3.35	1.45 10^{-4}
3b	2.02	64.72	−0.04	7.90 10^{-4}	$< 10^{-6}$	6.85 10^{-6}
4b	2.15	50.60	−0.07	$< 10^{-6}$	0.01	3.00 10^{-5}
5b	2.09	62.80	−0.08	7.87 10^{-5}	$< 10^{-4}$	5.15 10^{-6}
6b	2.02	62.80	−0.20	6.41 10^{-4}	$< 10^{-3}$	3.33 10^{-5}

[a] $\sigma^2 = \Sigma(\mu_{eff.\ calcd.} - \mu_{eff.\ exp.})^2/\Sigma\mu_{eff.\ exp.}{}^2$.

(1.7−2.7%) in the other linear chain compounds,[18,33] is probably due to the presence of the zigzag chain form in the solid.

In the variation of the magnetic susceptibility with temperature for complex **1a**, a maximum at 6 K and a shoulder at ca. 60 K are observed. These magnetic data cannot be fitted or the parameters obtained are anomalous. Since the elemental analysis and the spectroscopic and thermogravimetric data indicate that **1a** is a pure compound, the magnetic susceptibility data could indicate a mixture of two magnetically non-equivalent species. A similar mixture has been found previously[14] for the acetate complex.

As discussed above, the magnetic behaviour of complexes **3a**, **5a**, and **6a** cannot be fitted. These compounds were prepared by pumping the corresponding solvated complexes at 75 °C. If the anhydrous complexes have the usual polymeric structure through halogen bridging ligands, a rearrangement from the molecular to the polymeric structure must take place. In the solid state, however, this change could be difficult, and a mixture of arrays with different magnetic properties is possible. Complex **4b** may illustrate this behaviour. When this complex is heated to 75 °C under vacuum, the anhydrous $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4]$ is obtained. The variation of the magnetic susceptibility of this solid shows a maximum at the same temperature (67 K) as the maximum observed in the crystalline polymeric[18,33] $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4]$ (Figure 3), although the profile of the curves is different.

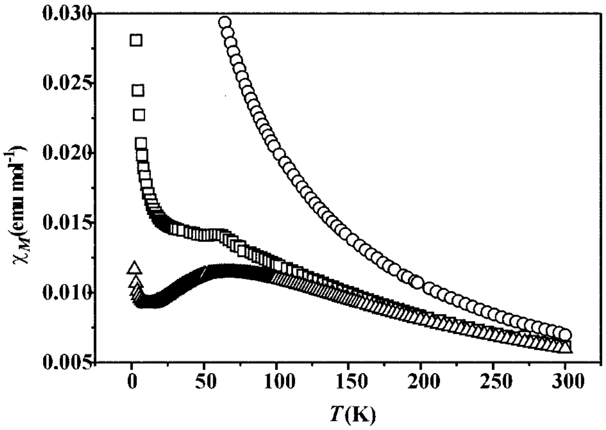


Figure 3. Temperature dependence of the molar susceptibility χ_M for complexes **4b** (circles), **4b** heated at 75 °C under vacuum (squares), and the polymeric $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4]$ (triangles)

Crystal Structure of $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 2MeOH$ (1b·2MeOH)

In the structure of **1b·2MeOH**, the asymmetric unit is composed of halves of two different crystallographically independent centrosymmetric molecules (A and B) with the inversion centre in the middle of the Ru−Ru bonds. A PLUTO view of the molecule (A) is shown in Figure 4. Table 2 gives selected bond lengths and angles of the complex. Each dinuclear unit of **1b·2MeOH** has two ruthenium atoms linked by four bridging 3-phenoxypropionoate ligands. Each axial position is shared by the O_{water} and Cl atoms with a 50% occupancy. The same situation has been found[21] for the complex $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$. The ruthenium atoms have a distorted octahedral coordination geometry. The distortion arises essentially from the longer $Ru-L_{axial}$ and Ru−Ru distances with respect to $Ru-O_{eq}$.

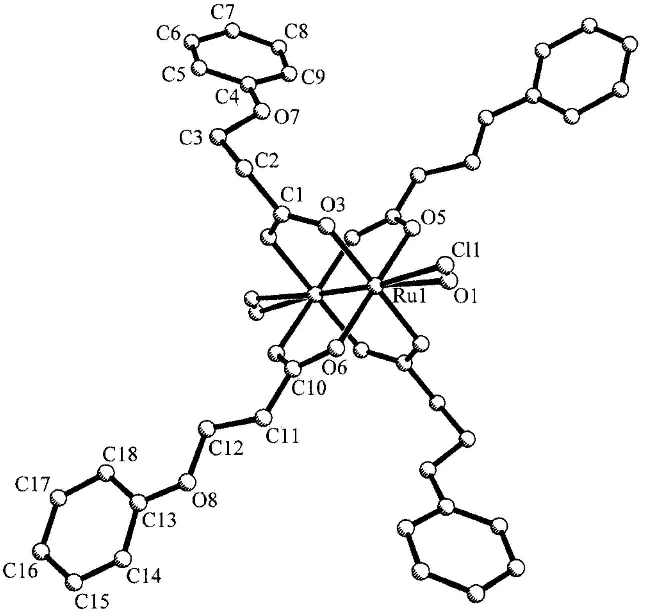


Figure 4. PLUTO view of the molecule (A) of the complex $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 2MeOH$ (**1b·2MeOH**); hydrogen atoms and MeOH molecules are omitted for clarity

The Ru−Ru distances in the two molecules are 2.278(2) and 2.280(2) Å. These distances are of the same order as those found in the other carboxylatodiruthenium(II,III) compounds.[2−4] The molecules are packed only by normal van der Waals forces.

The most important feature of these structures is their molecular nature. Only four crystal structures of molecular tetracarboxylato(chloro)diruthenium(II,III) complexes have been reported,[20−22] and their molecular natures have been attributed to the carboxylate bridges. The importance of the carboxylate ligands in the arrangement is illustrated by the structures of the compounds with O_2CCH_2OEt, O_2CCH_2OMe, and $O_2CCH_2CH_2OPh$. In the first case[13] a singular arrangement with formation of anionic, cationic, and polymeric units is formed. In the second case[15] a polymeric structure is observed, whereas in the last case a molecular arrangement is adopted.

Crystal Structure of $[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 0.5H_2O$ (3b·0.5H₂O)

Crystals of **3b·0.5H₂O** were grown from a methanol solution containing $[Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4]^+$ and I^-. The crystal structure determination shows packing of cationic $\{[Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)_2]^+\}$ and anionic $\{[Ru_2I_2(\mu\text{-}O_2CCH_2CH_2OPh)_4]^-\}$ species, and water molecules. The asymmetric unit is composed of halves of the anion and the cation, with an inversion centre in the middle of the ruthenium−ruthenium bonds and half a molecule of

Table 2. Selected bond lengths [Å] and angles [°] for $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 2MeOH$ (**1b·2MeOH**), $[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 0.5H_2O$ (**3b·0.5H₂O**), and $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (**4b**)

1b·2MeOH		**3b**·0.5H₂O		**4b**	
Ru(1)−Ru(1A)	2.278(2)	Ru(1)−Ru(1A)	2.310(2)	Ru(1)−Ru(1A)	2.2844(9)
Ru(1)−Cl(1)	2.468(6)	Ru(1)−I(1)	2.875(1)	Ru(1)−O(5)	2.37(1)
Ru(1)−O1	2.291(1)	Ru(1)−O(1)	2.038(7)	Ru(1)−Cl(1)	2.502(4)
Ru(1)−O(3)	2.030(6)	Ru(1)−O(2)	2.028(6)	Ru(1)−O(1)	2.026(4)
Ru(1)−O(4)	2.026(6)	Ru(1)−O(3)	2.026(7)	Ru(1)−O(2)	2.022(3)
Ru(1)−O(5)	2.032(6)	Ru(1)−O(4)	2.026(6)	Ru(1)−O(3)	2.029(4)
Ru(1)−O(6)	2.032(6)	Ru(2)−Ru(2A)	2.265(2)	Ru(1)−O(4)	2.029(3)
Ru(2)−Ru(2A)	2.280(2)	Ru(2)−O(9)	2.271(7)		
Ru(2)−Cl(2)	2.515(5)	Ru(2)−O(5)	2.026(8)		
Ru(2)−O2	2.290(1)	Ru(2)−O(6)	2.025(7)		
Ru(2)−O(9)	2.022(6)	Ru(2)−O(7)	2.002(8)		
Ru(2)−O(10)	2.021(6)	Ru(2)−O(8)	2.017(7)		
Ru(2)−O(11)	2.025(6)				
Ru(2)−O(12)	2.014(6)				
Ru(1A)−Ru(1)−Cl(1)	174.2(2)	Ru(1A)−Ru(1)−I(1)	177.56(6)	Ru(1A)−Ru(1)−Cl(1)	175.49(9)
Ru(1A)−Ru(1)−O(1)	173.2(4)	O(1)−Ru(1)−Ru(1A)	88.8(2)	Ru(1A)−Ru(1)−O(5)	174.9(3)
Ru(1A)−Ru(1)−O(3)	89.4(2)	O(2)−Ru(1)−Ru(1A)	88.7(2)	O(1)−Ru(1)−Ru(1A)	89.9(1)
Ru(1A)−Ru(1)−O(4)	89.3(2)	O(3)−Ru(1)−Ru(1A)	89.3(2)	O(2)−Ru(1)−Ru(1A)	88.8(1)
Ru(1A)−Ru(1)−O(5)	88.8(2)	O(4)−Ru(1)−Ru(1A)	89.0(2)	O(3)−Ru(1)−Ru(1A)	88.8(1)
Ru(1A)−Ru(1)−O(6)	90.1(2)	O(2)−Ru(1)−O(1)	88.5(3)	O(4)−Ru(1)−Ru(1A)	89.5(1)
O(3)−Ru(1)−O(4)	178.7(2)	O(3)−Ru(1)−O(1)	177.9(3)	O(2)−Ru(1)−O(1)	89.0(2)
O(3)−Ru(1)−O(5)	89.2(2)	O(4)−Ru(1)−O(1)	91.2(3)	O(1)−Ru(1)−O(3)	178.6(2)
O(3)−Ru(1)−O(6)	91.7(2)	Ru(2A)−Ru(2)−O(9)	176.4(2)	O(1)−Ru(1)−O(4)	89.4(2)
Ru(2A)−Ru(2)−Cl(2)	175.6(2)	O(5)−Ru(2)−Ru(2A)	89.6(2)		
Ru(2A)−Ru(2)−O(2)	173.1(5)	O(6)−Ru(2)−Ru(2A)	89.6(2)		
Ru(2A)−Ru(2)−O(9)	89.8(2)	O(7)−Ru(2)−Ru(2A)	89.5(2)		
Ru(2A)−Ru(2)−O(10)	89.3(2)	O(8)−Ru(2)−Ru(2A)	89.3(2)		
Ru(2A)−Ru(2)−O(11)	89.0(2)	O(5)−Ru(2)−O(6)	90.6(3)		
Ru(2A)−Ru(2)−O(12)	89.2(2)	O(7)−Ru(2)−O(5)	179.0(3)		
O(9)−Ru(2)−O(10)	90.9(2)	O(8)−Ru(2)−O(5)	89.3(3)		
O(9)−Ru(2)−O(11)	178.7(2)				
O(9)−Ru(2)−O(12)	89.0(2)				

water of crystallization. A PLUTO view of the compound is shown in Figure 5.

Both ions contain a diruthenium(II,III) unit with four 3-phenoxypropionate moieties as bridging ligands. The cationic complexes have two axially coordinated water molecules, and the anions two iodide ligands. Compound **3b·0.5H₂O** could thus be formulated as $[Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)_2][Ru_2I_2(\mu\text{-}O_2CCH_2CH_2OPh)_4]\cdot H_2O$.

There are only two known complexes in which both cationic and anionic units possess diruthenium cores:[13,36] $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(H_2O)]$ and $[Ru_2(\mu\text{-}O_2CPh)_4(HSO_4)(EtOH)]$. Complex **3b·0.5H₂O** is the first tetracarboxylato(iodo)diruthenium complex whose crystal structure has been determined.

The Ru−Ru bond length in the cation unit [2.265(2) Å] is analogous to that found in complex **1b·2MeOH**, which is typical of these types of compounds.[4,37] In the anionic unit, however, the Ru−Ru distance is 2.310(2) Å. This bond is longer than those observed in the analogous chloro derivatives[13,16,38] $[Ru_2Cl_2(\mu\text{-}O_2CR)_4]^-$ (R = CH_2OEt, Me, H, C_6H_4-*p*-OMe) but shorter than the longest Ru−Ru distance [2.427(1) Å] found in the cation[39] $[Ru_2(\mu\text{-}O_2CMe)_4(PCy_3)_2]^+$ which has the very strong axial donor ligand PCy_3. The Ru−I bond length in the anionic unit [2.875(1) Å] is longer than any other $Ru-L_{axial}$ bond in diruthenium complexes, including the compound[23] $[Ru_2Br(\mu\text{-}O_2CH)_4]$ [2.7170(8)−2.7313(9) Å]. This large Ru−I bond length is in accordance with the large size of the iodide ligand. The $Ru-O_{axial}$ bond length in the cationic unit [2.271(7) Å] is similar to that found in other $[Ru_2(\mu\text{-}O_2CR)_4(H_2O)_2]^+$ cations.[8c,13,16,40,41]

Crystal Structure of $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (4b)

The molecular structure of **4b** is depicted in Figure 6, and selected bond lengths and angles are given in Table 2. This molecule has two Ru atoms linked by four 2,2-diphenylpropionate bridging ligands, with the axial positions occupied by one water molecule and one chloride ligand. Analogously to those described above for complex **1b·2MeOH**, the axial positions are shared by the O_{water} and Cl atoms with occupation factors of 50%. Although the hydrogen atoms of the axial water molecules were not located, the distances between the Cl and the O_{axial} atoms of the neighbouring molecule [3.04(1) Å] suggest hydrogen-bond interactions between them. Thus, the $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ molecules are packed, giving chains.

The molecular structure of complex **4b** contrasts with the polymeric structure reported[18] for $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4]$. In spite of their different arrangements in the solid state, all distances, including the Ru−Cl bond length, are very similar in both complexes.

The synthesis and X-ray analysis of the molecular $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ demonstrates that different arrays are possible with the same carboxylate ligand.

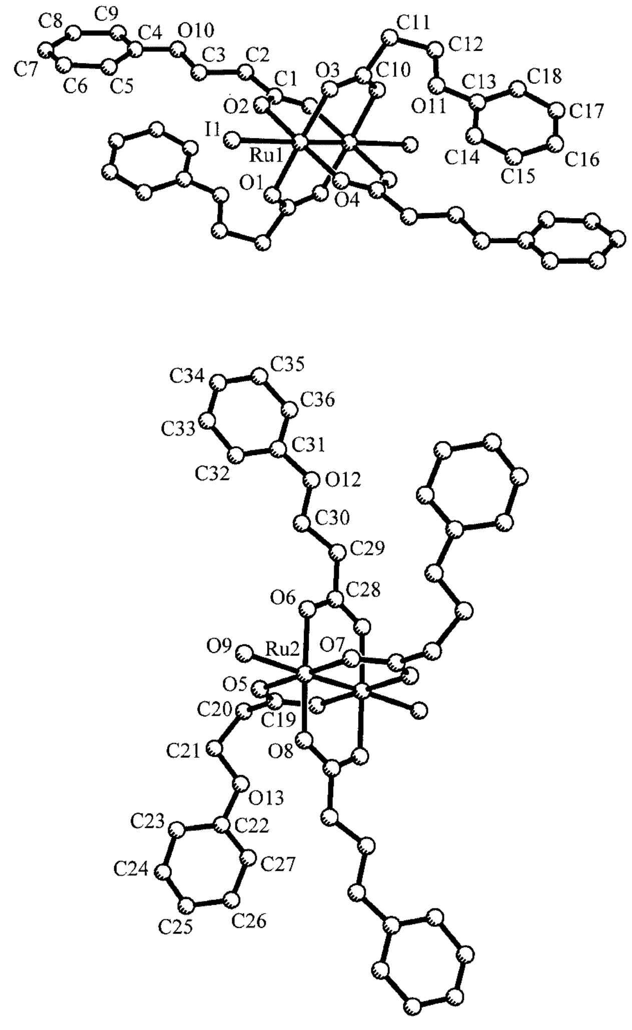


Figure 5. PLUTO view of $[Ru_2(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)_2][Ru_2I_2(\mu\text{-}O_2CCH_2CH_2OPh)_4]\cdot H_2O$ (**3b·0.5H₂O**); the water of hydration and hydrogen atoms have been omitted for clarity

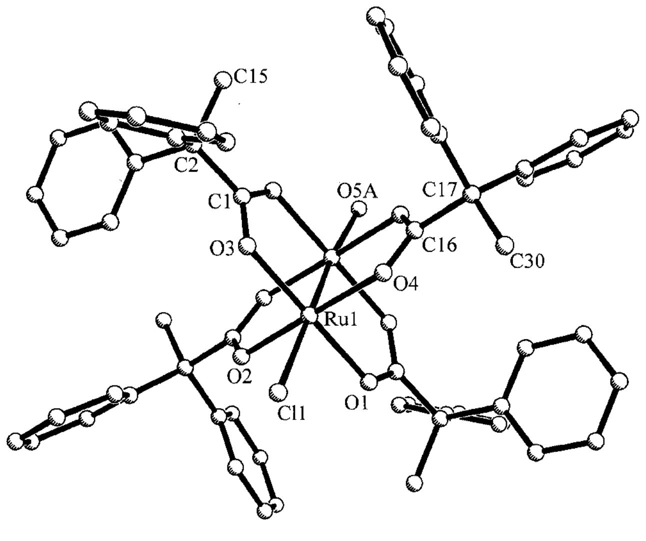


Figure 6. PLUTO view of $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (**4b**); hydrogen atoms are omitted for clarity

Conclusion

The crystal structure determination of two new molecular diruthenium(II,III) compounds indicates that the usual polymeric structure of the tetracarboxylato(chloro)diruthenium(II,III) complexes can be broken by neutral molecules, giving discrete dinuclear species. These results also confirm that small differences in the electronic or steric requirements of the carboxylate ligand can have important consequences in the arrangement in the solid state, as illustrated by the different arrays found in the complexes with the ligands O_2CCH_2OEt, O_2CCH_2OMe, and $O_2CCH_2CH_2OPh$.

The synthesis of derivatives with different halide ligands reveals that the nature of the axial ligand has a great influence on the arrangement in the solid state. Thus, the chloro complex with 3-phenoxypropionate ligands displays a molecular structure, whereas the iodo derivative shows a less usual cation/anion array.

Nevertheless, compound $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4]$ was known to have a polymeric structure while complex $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$, with the same halide and carboxylate ligands, has a molecular structure. There must therefore be other factors that play a role in the arrangement of the diruthenium(II,III) compounds. Efforts to study these factors and their influence on diruthenium chemistry are currently underway.

Experimental Section

General Remarks: All reactions were carried out under inert gases, by use of standard Schlenk techniques. Ruthenium trichloride and carboxylic acids were obtained from commercial sources. Solvents were used without previous purification. The complexes $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CMePh₂, Me) were prepared by literature procedures.[18,42] IR spectra were recorded as KBr discs with a Nicolet Magna-FTIR 550 spectrophotometer. Elemental analysis of C and H were performed by the Microanalytical Service of Complutense University, Madrid. Electronic spectra in the range 200−2500 nm were recorded with a Cary 5G spectrophotometer in methanol solutions (10^{-4} M). The thermogravimetric analyses were carried out with a Perkin−Elmer Pyris 1 TGA thermogravimetric analyzer. The samples were heated up to 600 °C in platinum crucibles, with a heating rate of 5 °C min^{-1}, and purged in a nitrogen stream. The variable-temperature magnetic susceptibility data were measured with a Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) susceptometer over a temperature range of 2−300 K. Each raw data field was corrected for the diamagnetic contribution of both the sample holder and the compound to the susceptibility. The molar diamagnetic corrections for the complexes were calculated on the basis of Pascal's constants. The fit of experimental data was carried out using the commercial MATLAB V.5.1.0.421 program.

Preparation of $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (1a) and $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]$ (1b): An excess of 3-phenoxypropionic acid (0.50 g, 3.00 mmol) was added to a solution (30 mL) of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ (0.24 g, 0.50 mmol) in methanol/water (1:1, 24 mL). The reaction mixture was heated at reflux for 4 h, giving a red-brown solid. The solution was filtered, and the solid was washed with diethyl ether (3 × 20 mL) and again treated with fresh carboxylic acid (3.00 mmol) under the same conditions to ensure the complete replacement of the acetate ligands. The red-brown solid was isolated by filtration, washed again with diethyl ether, and dried under vacuum to give **1a**. A solution of the above red-brown solid in hot methanol (20 mL) was allowed to stand at room temperature and later at −18 °C, yielding red-brown crystals of **1b·2MeOH**. These crystals were dried under vacuum at room temperature to give **1b**.

$[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (1a): Yield: 0.34 g (75%). $C_{36}H_{36}ClO_{12}Ru_2$ (898.27): calcd. C 48.14, H 4.04; found C 48.32, H 4.04. IR (KBr): $\tilde{\nu}$ = 3061 w, 3040 w, 2933 w, 2892 w, 1599 m, 1587 m, 1529 m, 1497 s, 1460 vs, 1439 vs, 1418 s, 1317 m, 1244 s, 1225 s, 1039 m, 752 s, 703 m, 690 m cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 297 (1653), 429 (786), 988 (18 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 3.86 μ_B at room temperature.

$[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]$ (1b): Yield: 0.32 g (69%). $C_{36}H_{38}ClO_{13}Ru_2$ (916.29): calcd. C 47.19, H 4.18; found C 47.31, H 4.22. IR (KBr): $\tilde{\nu}$ = 3445 s, 3065 w, 3041 w, 2932 w, 1600 m, 1588 m, 1497 m, 1466 s, 1437 vs, 1243 s, 1041 m, 755 m, 693 m cm^{-1}. UV/Vis: identical to data of **1a**. $\mu_{eff.}$ = 3.98 μ_B at room temperature.

Preparation of $[Ru_2Br(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (2a): Silver tetrafluoroborate (0.07 g, 0.35 mmol) was added to a solution of $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (0.31 g, 0.35 mmol) in THF (30 mL). The reaction mixture was stirred for 24 h, giving a solid precipitate of AgCl and a brown solution. The precipitate was filtered through Celite and the solution was pumped to dryness. The solid was dissolved in ethanol (10 mL) and treated with an aqueous solution (10 mL) of KBr (0.42 g, 3.50 mmol), giving a dark brown precipitate, which was filtered, washed with water (3 × 20 mL) and dried under vacuum. Yield 0.24 g (72%). $C_{36}H_{36}BrO_{12}Ru_2$ (942.73): calcd. C 45.87, H 3.85; found C 45.77, H 3.86. IR (KBr): $\tilde{\nu}$ = 3060 w, 3041 w, 2930 w, 2888 w, 1599 s, 1587 s, 1470 vs, 1440 vs, 1419 s, 1243 vs, 1043 s, 753 s, 692 m cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 291 (1857), 429 (829), 1004 (25 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 3.88 μ_B at room temperature.

Preparation of $[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (3a) and $[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]$ (3b): The preparation was carried out as described above for **2a**, but with KI (0.58 g, 3.50 mmol) in place of KBr. The solid isolated by this procedure was characterized as **3b**. Complex **3a** was obtained after **3b** had been heated under vacuum at 75 °C for 24 h. Single crystals of **3b·0.5H₂O** were obtained by the following procedure: $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (0.09 g, 0.10 mmol) was dissolved in methanol (15 mL) and treated with an aqueous solution of $AgNO_3$ (0.017 g, 0.10 mmol). The solution was filtered and treated with an excess of PPh_4I (0.26 g, 0.50 mmol). Crystals grew over 48 h.

$[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4]$ (3a): Yield 0.24 g (70%). $C_{36}H_{36}IO_{12}Ru_2$ (989.73): calcd. C 43.69, H 3.67; found C 43.58, H 3.62. IR (KBr): $\tilde{\nu}$ = 3066 w, 3040 w, 2936 w, 2889 w, 1599 m, 1588 m, 1496 m, 1466 s, 1437 vs, 1318 m, 1243 s, 1040 m, 756 m, 692 m cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 288 (1836), 427 (748), 976 (19 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 3.96 μ_B at room temperature.

$[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]$ (3b): Yield 0.25 g (70%). $C_{36}H_{38}IO_{13}Ru_2$ (1007.74): calcd. C 42.91, H 3.80; found C 42.78, H 3.75. IR (KBr): $\tilde{\nu}$ = 3431 m, 3066 w, 3040 w, 2936 w, 2889 w, 1599 m, 1588 m, 1496 m, 1466 s, 1437 v s, 1318 m, 1243 s, 1040 m, 756 m, 692 m cm^{-1}. UV/Vis: identical to data of **3a**. $\mu_{eff.}$ = 4.18 μ_B at room temperature.

Preparation of $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (4b): An excess of 2,2-diphenylpropionic acid (0.68 g, 3.00 mmol) was added to a solution (25 mL) of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ (0.24 g, 0.50 mmol) in methanol/water (24 mL, 1:1). The reaction mixture was heated at reflux for 4 h, giving a red-brown solid. The solution was filtered, and the solid was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Single crystals of **4b** were obtaining by the procedure described above for **3b·0.5H₂O**, with PPh_4Cl (0.19 g, 0.50 mmol) in place of PPh_4I.

$[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (4b): Yield 0.44 g (76%). $C_{60}H_{54}ClO_9Ru_2$ (1156.69): calcd. C 62.30, H 4.71; found C 62.20, H 4.69. IR (KBr): $\tilde{\nu}$ = 3446 w, 3141 w, 3057 w, 3021 w, 2994 w, 2941 w, 1598 w, 1494 m, 1464 s, 1436 s, 1394 vs, 1367 vs, 1029 m, 998 w, 760 m, 737 m, 731 m, 697 vs, 668 s cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 287 (2962), 426 (818), 968 (21 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 4.12 μ_B at room temperature.

Preparation of $[Ru_2Br(\mu\text{-}O_2CCMePh_2)_4]$ (5a) and $[Ru_2Br(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (5b): The preparation was carried out similarly to that described for **2a**, with $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (0.40 g, 0.35 mmol). The brown solid was characterized as **5b**. Complex **5a** was obtained after **5b** had been heated under vacuum at 75 °C for 24 h.

$[Ru_2Br(\mu\text{-}O_2CCMePh_2)_4]$ (5a): Yield 0.30 g (73%). $C_{60}H_{52}BrO_8Ru_2$ (1183.13): calcd. C 60.91, H 4.43; found C 60.80, H 4.39. IR (KBr): $\tilde{\nu}$ = 3088 w, 3058 w, 3031 w, 2984 w, 2940 w, 1599 w, 1494 m, 1466 m, 1440 m, 1392 vs, 1368 s, 1029 m, 751 m, 735 m, 698 s, 668 m cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 330 (983), 425 (709), 944 (213 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 4.13 μ_B at room temperature.

$[Ru_2Br(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (5b): Yield 0.31 g (73%). $C_{60}H_{54}BrO_9Ru_2$ (1201.14): calcd. C 60.00, H 4.53; found C 59.92, H 4.50. IR (KBr): $\tilde{\nu}$ = 3435 m, 3088 w, 3058 w, 3031 w, 2984 w, 2940 w, 1599 w, 1494 m, 1466 m, 1440 m, 1392 vs, 1368 s, 1029 m, 751 m, 735 m, 698 s, 668 m cm^{-1}. UV/Vis: identical to data of **5a**. $\mu_{eff.}$ = 4.06 μ_B at room temperature.

Preparation of $[Ru_2I(\mu\text{-}O_2CCMePh_2)_4]$ (6a) and $[Ru_2I(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (6b): The preparation was carried out as described previously for **3a** and **3b**, with $Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)$ (0.40 g, 0.35 mmol).

$[Ru_2I(\mu\text{-}O_2CCMePh_2)_4]$ (6a): Yield 0.29 g (67%). $C_{60}H_{52}IO_8Ru_2$ (1230.12): calcd. C 58.59, H 4.26; found C 58.51, H 4.22. IR (KBr): $\tilde{\nu}$ = 3088 w, 3059 w, 3024 w, 2983 w, 2940 w, 1582 w, 1494 m, 1467 m, 1440 m, 1392 vs, 1368 s, 1030 m, 752 w, 733 w, 698 s, 668 m cm^{-1}. UV/Vis (MeOH): $\lambda_{max.}$ (ε) = 328 (1160), 426 (820), 968 (25 L·mol^{-1}·cm^{-1}) nm. $\mu_{eff.}$ = 4.09 μ_B at room temperature.

$[Ru_2I(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (6b): Yield 0.29 g (67%). $C_{60}H_{54}IO_9Ru_2$ (1248.14): calcd. C 57.75, H 4.36; found C 57.65, H 4.32. IR (KBr): $\tilde{\nu}$ = 3436 m, 3088 w, 3059 w, 3024 w, 2983 w, 2940 w, 1582 w, 1494 m, 1467 m, 1440 m, 1392 vs, 1368 s, 1030 m, 752 w, 733 w, 698 s, 668 m cm^{-1}. UV/Vis: identical to data of **6a**. $\mu_{eff.}$ = 4.06 μ_B at room temperature.

X-ray Crystallographic Study: Details of the data collection and crystal structure refinement for **1b·2MeOH**, **3b·0.5H₂O** and **4b** are

Table 3. Crystal data for $[Ru_2Cl(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 2MeOH$ (**1b·2MeOH**), $[Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)]\cdot 0.5H_2O$ (**3b·0.5H$_2$O**), and $[Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4(H_2O)]$ (**4b**)

	1b·2MeOH	**3b**·0.5H$_2$O	**4b**
Empirical formula	$C_{38}H_{46}ClO_{15}Ru_2$	$C_{72}H_{78}I_2O_{27}Ru_4$	$C_{60}H_{54}ClO_9Ru_2$
Formula mass	980.37	2033.50	1156.69
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.947(2)	13.128(2)	8.8056(7)
b [Å]	14.102(2)	13.357(2)	11.5292(9)
c [Å]	14.471(2)	14.601(2)	14.525(1)
α [°]	65.395(3)	91.861(3)	111.253(2)
β [°]	79.742(3)	115.779(3)	96.898(2)
γ [°]	79.961(3)	115.269(3)	95.949(1)
V [Å^3]	2167.5(6)	2008.7(6)	1347.0(2)
Z	2	2	1
$D_{calcd.}$ [g cm^{-3}]	1.499	1.689	1.423
μ [mm^{-1}]	0.822	1.583	0.666
F(000)	994	1010	589
Crystal size [mm]	0.07 × 0.10 × 0.6	0.06 × 0.22 × 0.40	0.16 × 0.18 × 0.60
Crystal colour	red-brown	red-brown	red-brown
θ range [°]	1.60−25.00	1.61−25.00	1.53−25.00
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 8$, $-17 \le l \le 16$	$-15 \le h \le 15$, $-11 \le k \le 15$, $-17 \le l \le 14$	$-10 \le h \le 9$, $-10 \le k \le 13$, $-17 \le l \le 12$
Collected reflections	11355	10260	7064
Independent reflections	7539 [R(int) = 0.0815]	6981 [R(int) = 0.0528]	4706 [R(int) = 0.0328]
Completeness to θ = 25.00° [%]	98.7	98.6	98.9
Absorption correction	none	none	none
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/restraints/parameters	7539/2/463	6981/0/469	4706/0/326
Goodness-of-fit on F^2	0.907	1.000	1.115
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0644$, $wR2 = 0.1539$	$R1 = 0.0582$, $wR2 = 0.1307$	$R1 = 0.0503$, $wR2 = 0.1354$
R indices (all data)	$R1 = 0.1423$, $wR2 = 0.1791$	$R1 = 0.1437$, $wR2 = 0.1759$	$R1 = 0.0664$, $wR2 = 0.1416$
Largest diff. peak/hole [e·Å^{-3}]	1.311/−0.558	1.632/−0.909	2.242/−0.355

summarised in Table 3. Representative crystals were mounted on a Bruker Smart-CCD diffractometer with graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. For **1b·2MeOH**, data were collected over a quadrant of the reciprocal space by combination of two exposure sets. For **3b·0.5H$_2$O** and **4b**, data were collected over a hemisphere of the reciprocal space by combination of three exposures sets. The cell parameters were determined and refined by least-squares fitting of all reflections collected. The structures of **1b·2MeOH** and **3b·0.5H$_2$O** were solved by Patterson (Ru atoms, SHELXS)[43] and conventional Fourier techniques and refined by full-matrix, least-squares on F^2 (SHELXL).[44] The structure of **4b** was solved by direct methods and all calculations were performed with the aid of the SHELXS and SHELXL.[43,44] Final mixed refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms, except for the solvent molecules, which were refined only isotropically. The hydrogen atoms were included with fixed isotropic contributions at their geometrically calculated positions, except for **1b·2MeOH** (the hydrogen atoms of the OH group of the methanol molecules, which were located in a Fourier synthesis and refined together with the oxygen atom) and for **3b·0.5H$_2$O** (the hydrogen atoms of the coordination water molecules were not found by Fourier synthesis or geometrically). For **1b·2MeOH** the positional disorder of Cl and O_{water} was resolved by refining with geometric restraints and a variable $Ru-O_{water}$ distance.[45] For **3b·0.5H$_2$O**, one residual peak was found in the last cycles of refinement, and was assigned as a solvent water molecule and refined isotropically as oxygen atom. It was not possible to locate the hydrogen atoms of this molecule. For **4b**, the refinement was carried out in both the centric ($P\bar{1}$) and noncentric ($P1$) space groups. In spite of having more refinable parameters in the acentric model the thermal parameters of several atoms became negative. Thus, the centric space group ($P\bar{1}$) was chosen. CCDC-199023 to -199025 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Ministerio de Ciencia y Tecnología (Dirección General de Investigación, project no. BQU 2000-0643) for financial support.

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Received January 8, 2003