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Notes

Diruthenium(II,III) Carboxylate Compounds: Existence of both Polymeric and Ionic Forms in Solution and Solid State

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Introduction

Numerous diruthenium(II,III) complexes of formula $Ru_2Cl(\mu\text{-}O_2CR)_4$ (R = alkyl, aryl) have been described[2] including several crystal structure determinations.[3−12] In these complexes two type of arrangements, in the solid state, are actually known: (i) $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units linked by bridging chloride ions[3−9] giving infinite linear or zigzag chains, (ii) discrete dinuclear molecules of $Ru_2Cl(\mu\text{-}O_2CR)_4(S)$ (S = solvent molecule, such as H_2O or THF) with packing only by hydrogen bonds or van der Waals forces.[10−12] The reasons for these different arrays in the solid state are not well-known, but the influence of a branched chain in the bridging ligand seems to be very important. As part of our recent studies[10−13] on the factors which determine the polymeric/nonpolymeric nature of these type of compounds, we have found a very unusual behavior with the ethoxyacetate ligand. The complex of stoichiometry $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4\cdot H_2O$ represents the first example in which the formation of chain and discrete anionic−cationic dinuclear units are present in the solid state. The reaction of this compound with $OPPh_3$ is also examined.

Experimental Section

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. Ruthenium trichloride and carboxylic acids were purchased from commercial sources. Solvents were used without previous purification. $Ru_2Cl(\mu\text{-}O_2CMe)_4$ was prepared by the literature procedure.[14] IR spectra were recorded, as KBr disks, on a Nicolet Magna-IR 550 infrared spectrophotometer. Molar conductivities were measured with a Philips PW 9526 digital conductivity meter using a Philips PW 9512/60 conductivity measuring cell. Elemental analyses for C and H were performed in the Microanalytical Service of the Complutense University of Madrid. Electronic spectra in the region 190−3300 nm were recorded on a Cary 5G spectrophotometer; the electronic spectra in solid state were recorded with a "Praying Mantis" accessory. Magnetic susceptibility measurements were made in the range 70−300 K using a fully automatic DSM 8 magneto-susceptometer, based on the Faraday methods. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG AutoSpec spectrometer. Nominal molecular masses and distribution isotopic of all peaks were calculated with the computer program MASAS[15] using polynomial expansion based on natural abundances of the isotopes. The experimental or calculated *m/z* value given for each peak, is the mass of the most abundant ion in the observed or calculated isotopic distribution.

Synthesis of $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4\cdot H_2O$ (1). To a solution of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ (0.14 g, 0.30 mmol) in methanol−water (1:1, 30 mL) was added an excess of HO_2CCH_2OEt (0.17 mL, 1.80 mmol). The reaction mixture was heated to reflux for 4 h, giving a red-brown solution. The solution was evaporated to dryness under vacuum giving a red-brown solid. The solid was washed twice with petroleum ether (40−60 °C), to eliminate the excess of ligand, and treated again with fresh HO_2CCH_2OEt under the same conditions to ensure the complete replacement of the acetate ligand. The red-brown solid obtained was dissolved in 20 mL of CH_2Cl_2 and layered with petroleum ether (40−60 °C) to give a red solid. This solid was filtered off and dried under vacuum. The evaporation in air of a solution of the compound in methanol/water gave red crystals of the title compound. Yield: 81%. Anal. Calcd for $C_{16}H_{30}O_{13}ClRu_2$: C, 28.77; H, 4.53. Found: C, 28.83; H, 4.44: IR data (KBr disk, cm^{-1}): 3450 m, br, 2977 m, 2934 w, 2880 m, 1633 w, 1474 vs, br, 1437 vs, br, 1420 s, sh, 1369 vs, 1121 vs, br, 1030 m, 889 w, 851 w, 729 s, 639 m, br, 480 m, 452 w, sh. UV−visible (THF solution; λ, nm (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)): 284 (3579), 336 (4657), 464 (1773). UV−visible (solid; λ, nm): 471, 1100. $\mu_{eff} = 4.19\ \mu_B$. Mass spectral data [*m/z* (fragment)]: LSIMS$^+$, 1265 ($[Ru_2(\mu\text{-}O_2CCH_2OEt)_4]_2Cl$), 650 ($Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4$), 616 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_4 + H$), 513 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_3 + H$), 410 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_2$); LSIMS$^-$, 686 ($Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4$), 650 ($Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4$).

$Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)$ (2). To a solution of **1** (0.20 g, 0.30 mmol) in acetone was added $OPPh_3$ (0.09 g, 0.30 mmol). The mixture was stirred at room temperature for 24 h. The solution was pumped to dryness to give a brown solid, which was washed with petroleum ether (40−60 °C) (10 mL). The solid was dissolved in CH_2Cl_2 and layered with petroleum ether (40−60 °C) giving brown microcrystals of **2**. Yield: 72%. Anal. Calcd for $C_{34}H_{43}O_{13}PClRu_2$: C, 43.99; H, 4.67. Found: C, 44.61; H, 4.39: IR data (KBr disk, cm^{-1}): 3060 w, 2980 m, 2930 w, 2870 w, 1490 s, 1430 vs, br, 1400 s, 1322 s, 1140 s, sh, 1105 vs, 1080 m, sh, 1070 m, sh, 1022 m, 995 m, 840 w, 750 m, 720 vs, 695 vs, 625 m, 540 vs. UV−visible (THF solution; λ, nm (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)): 288 (3955), 336 (4259), 460

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Table 1. Crystallographic Data and Structure Refinement for $Ru_2Cl(\mu\text{-}O_2CH_2OEt)_4\cdot H_2O$

empirical formula: $C_{64}H_{120}Cl_4O_{52}Ru_8$	$Z = 1$
fw = 2672	$V = 2526(1)$ Å^3
space group: $P\bar{1}$	$d_{calcd} = 1.76$ g cm^{-3}
$a = 13.826(5)$ Å	$F_{(000)} = 1340$
$b = 14.116(2)$ Å	temp = 295 K
$c = 14.636(4)$ Å	wavelength = 0.710 69 Å
$\alpha = 64.48(4)°$	μ(Mo Kα) = 13.36 cm^{-1}
$\beta = 101.34(4)°$	$R^a = 3.8$
$\gamma = 92.91(5)°$	$R_w{}^b = 4.3$

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

(1723). $\mu_{eff} = 3.74\ \mu_B$. Mass spectral data [m/z (fragment)]: LSIMS$^+$, 1265 ([$Ru_2(\mu\text{-}O_2CCH_2OEt)_4]_2Cl$), 1172 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)_2$), 929 ($Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)$), 894 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)$), 616 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_4 + H$), 410 ($Ru_2(\mu\text{-}O_2CCH_2OEt)_2$); LSIMS$^-$, 686 ($Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4$), 650 ($Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4$).

X-ray Structure Determination. A summary of the fundamental crystal data for **1** is given in Table 1. A reddish crystal of regular shape and dimensions 0.30 × 0.30 × 0.30 mm^3 was mounted on an Enraf-Nonius CAD4 diffractometer to be used for the structure determination. A graphite-monochromatic Mo Kα ($\lambda = 0.710\ 69$ Å) beam was used in the data collection carried out at room temperature. The unit cell parameters were determined by least-squares refinement of the 2θ values of 25 strong well-centered reflections in the range $13° < 2\theta < 27°$. The intensities of all 8897 unique reflections (after merging) were measured in the angular range $1° < 2\theta < 50°$ (*hkl* range −16, −16,0 to 16,16, 17) using the $\omega/2\theta$ scan technique. There was no appreciable change in the intensities of three standard reflections periodically monitored. The raw data were corrected for Lorentz and polarization effects, and 6611 reflections were considered as observed with $I > 2\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and Cl atoms were taken from ref 16.

The value of $Z = 1$ and the empirical formula $C_{64}H_{120}Cl_4O_{52}Ru_8$ for the compound **1** (Table 1) has been chosen to stress that four different Ru−Ru dimeric units are present in the structure. Thus, the empirical formula is given as twice the smallest one describing the cell content and, as a consequence, Z is given as half of the value expected from crystallographic only considerations.

The heavy atoms positions (four Ru atoms) were determined by a careful analysis of the three-dimensional Patterson function. The positions of the light atoms (C, O, and Cl) were obtained by Fourier synthesis. Most of the hydrogen atoms were included with fixed isotropic thermal parameters at the positions determined by the molecular geometry. The water molecule bonded to the Ru3 atom is involved in a hydrogen bond with a crystallization water molecule. This allowed us to locate their hydrogen atoms by Fourier synthesis, while it was not possible to determine the position of the hydrogen atoms of the crystallization water either by Fourier methods or by the molecular geometry. Since no trends in ΔF vs F_o or $(\sin\theta)/\lambda$ were observed, no special weighting scheme was used; i.e., unit weights were applied. An empirical absorption correction[17] was applied at the end of the isotropic refinements. A final full-matrix least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms, excepting the carbon atoms belonging to terminal ethoxy groups for which isotropic thermal parameters were used, led to agreement factors $R = 0.038$ and $R_w = 0.043$. The maximum and average shift-to-error ratios were 0.02 and 0.006, respectively, while the maximum residual electron density near to the Ru1 atom was 0.8 e Å^{-3}. Most of the calculations were carried out with the X-Ray 80 program.[18]

Results and Discussion

The reaction of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ with an excess of 2-ethoxyacetic acid in methanol/water (1/1) leads to the substitution of the acetate ligands and formation of $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4\cdot H_2O$ (**1**). This compound is soluble in organic solvents such as methanol, acetone, CH_2Cl_2, THF, etc., and insoluble in pentane or petroleum ether. The solubility of **1** is higher than those observed in the polymeric compounds and similar to those found in the nonpolymeric complexes. The conductivity measurements in methanol solution gave a value of conductivity of 44 S cm^2 mol^{-1}. This conductivity value is far from the values of conductivity predicted by Geary[19] for a 1:1 electrolyte. However, this value is higher than those observed in similar nonelectrolyte diruthenium compounds. This value is in accord with the presence in solution of units of the type $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(S)$ (S = solvent molecule), $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(H_2O)_2]^+$, and $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ consistent with the structure of this compound described below.

The magnetic susceptibility was measured in the range 70−300 K, showing that the compound obeys the Curie−Weiss law. The magnetic moment at room temperature (4.19 μ_B) is in accordance with the presence of three unpaired electron per dimer unit. This magnetic moment is also consistent with a ground state having S = $^3/_2$, which has been proposed for all previous diruthenium(II,III) compounds described in the literature.[3−13,20,21]

The LSIMS spectrum of $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4\cdot H_2O$ shows at $m/z = 650$ the peak assigned to $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4]^+$ and the base peak corresponding to $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4 + H]^+$ ($m/z = 616$). In this spectrum, similarly[12,22] to those observed in other $Ru_2Cl(\mu\text{-}O_2CR)_4$ compounds, sequential loss of carboxylate groups from the base peak and formation of clustering peak $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4]_2Cl^+$ ($m/z = 1265$) have been observed.

The LSIMS$^-$ spectrum shows two peaks: one signal at $m/z = 686$ due to $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ and another one at $m/z = 650$ due to $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4]^-$. The presence of these peaks indicates the existence of anionic units of the type $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ in the solid.

To know the precise structure of this compound, we have solved the crystal structure. Crystals suitable for this determination were obtained by evaporation in air of a methanol/water solution of the complex. Table 2 gives selected bond distances and angles. In compound **1** there are three types of dimer units:

(i) $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4]$ units are bonded by chlorine atoms giving zigzag chains with an angle Ru−Cl−Ru of 138.4(1)° similarly to the polymeric complexes. In these chains two crystallographic different units exit with one inversion center in the middle of the Ru−Ru bonds. The Ru−Ru and Ru−Cl distances in these units are very similar and also are analogous to those found in the other polymeric compounds of this type.[3−9] An ORTEP of these units is represented in Figure 1.

(ii) Cationic units of the type $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(H_2O)_2]^+\cdot 2H_2O$ are found in which the axial positions are occupied by water molecules with a Ru−O$_{water}$ distance of 2.238(8) Å. This distance is similar to that found[5] in $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]BF_4$ and in other diruthenium compounds with O-donor ligands in the axial positions.[13,23−25] Two additional water molecules

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4{\cdot}H_2O$

$Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4$ Unit			
Ru1−Ru1′	2.277(1)	Ru1−O3	1.999(6)
Ru2−Ru2′	2.280(1)	Ru1−O4′	2.030(6)
Ru1−Cl1	2.563(2)	Ru2−O5	2.029(6)
Ru2−Cl1	2.558(2)	Ru2−O6'	2.004(5)
Ru1−O1	2.036(4)	Ru2−O7'	2.023(6)
Ru1−O2'	2.012(4)	Ru2−O8	2.012(6)
Ru1′−Ru1−O3	89.0(2)	Ru2′−Ru2−O8	89.2(2)
Ru1'−Ru1−O1	89.0(2)	Ru2′−Ru2−O5	89.2(2)
Ru1′−Ru1−Cl1	177.9(2)	Ru2′−Ru2−Cl1	179.3(1)
Ru1−Ru1′−O4	89.5(2)	Ru2′−Ru2−O7	89.3(2)
Ru1−Ru1′−O2	89.6(2)	Ru2′−Ru2−O6	89.2(2)
O1−Ru1−O3	89.0(3)	O5−Ru2−O8	92.2(3)
Cl1−Ru1−O3	89.2(2)	Cl1−Ru2−O8	91.4(2)
Cl1−Ru1−O1	89.7(2)	Cl1−Ru2−O5	91.2(2)
O2−Ru1′−O4	88.9(3)	O6−Ru2′−O7	91.6(3)
Ru1−O1−C1	118.0(5)	Ru2−O5−C9	117.9(5)
Ru1′−O2−C1	119.0(6)	Ru2′−O6−C9	119.3(6)
Ru1−O3−C5	119.4(6)	Ru2′−O7−C13	118.6(6)
Ru1′−O4−C5	117.5(5)	Ru2−O8−C13	119.0(6)
Ru1−Cl1−Ru2	138.4(1)		
$[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(H_2O)_2]^+$ Unit			
Ru3−Ru3′	2.261(1)	Ru3−O12'	2.017(5)
Ru3−O9	2.017(5)	Ru3−O13	2.238(8)
Ru3−O10'	2.016(5)	O13−H0131	0.907(5)
Ru3−011	2.026(5)	O13−H0132	0.773(6)
Ru3′−Ru3−O13	177.7(2)	O9−Ru3−O11	88.4(3)
Ru3′−Ru3−O11	89.4(2)	Ru3−O9−C17	118.8(5)
Ru3′−Ru3−O9	89.6(2)	Ru3′−O10−C17	119.1(6)
Ru3−Ru3′−O12	89.6(2)	Ru3−O11−C21	118.5(6)
Ru3−Ru3′−O10	89.4(2)	Ru3′−O12−C21	118.5(6)
O11−Ru3−O13	88.3(3)	Ru3−O13−H0132	116.1(7)
O9−Ru3−O13	90.3(2)	Ru3−O13−H0131	119.5(5)
$[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ Unit			
Ru4−Ru4'	2.294(2)	Ru4−O15'	2.018(6)
Ru4−Cl2	2.499(2)	Ru4−O16	2.031(7)
Ru4−O14	2.026(6)	Ru4−O17'	2.028(7)
Ru4'−Ru4−O16	89.2(2)	Cl2−Ru4−O14	94.0(2)
Ru4'−Ru4−O14	89.7(2)	O15−Ru4'−O17	89.6(3)
Ru4'−Ru4−Cl2	176.3(2)	Ru4−O14−C25	117.4(6)
Ru4−Ru4'−O17	89.0(2)	Ru4'−O15−C25	119.2(6)
Ru4−Ru4'−O15	88.6(2)	Ru4−O16−C29	117.6(6)
O14−Ru4−O16	88.9(3)	Ru4'−O17−C29	118.2(6)
Cl2−Ru4−O16	91.1(2)		

bonded by hydrogen bonds to the axial water molecules are also present in the crystal. An ORTEP of the cationic unit is represented in Figure 2.

(iii) Anionic units of the type $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ exist. The Ru−Ru [2.294(2) Å] and Ru−Cl [2.499(2) Å] distances are similar to those found[6,26] in $Cs[Ru_2Cl_2(\mu\text{-}O_2CMe)_4]$, $K[Ru_2Cl_2(\mu\text{-}O_2CH)_4]$, and $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}OMe)_4]$. The Ru−Cl distance is slightly shorter that found in the polymeric units. These anionic units also present an inversion center in the middle of the diruthenium unit. An ORTEP of this anion is represented in Figure 2.

On the basis of these data, compound **1** could be formulated as $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4]_n[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(H_2O)_2]_{n/2}[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]_{n/2}{\cdot}nH_2O$.

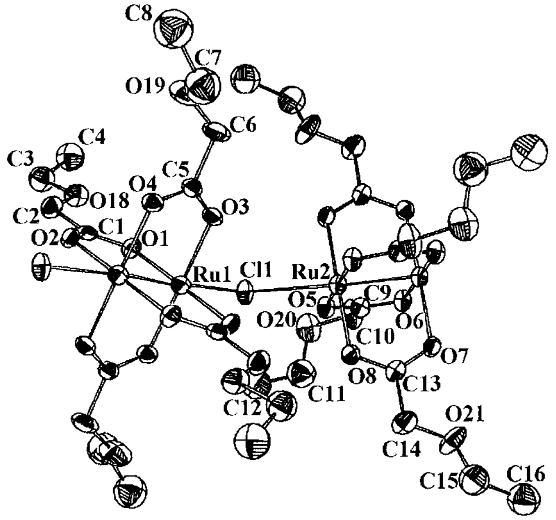

Figure 1. ORTEP view of $Ru_2(\mu\text{-}O_2CCH_2OEt)_4$ units linked by chlorine atoms showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

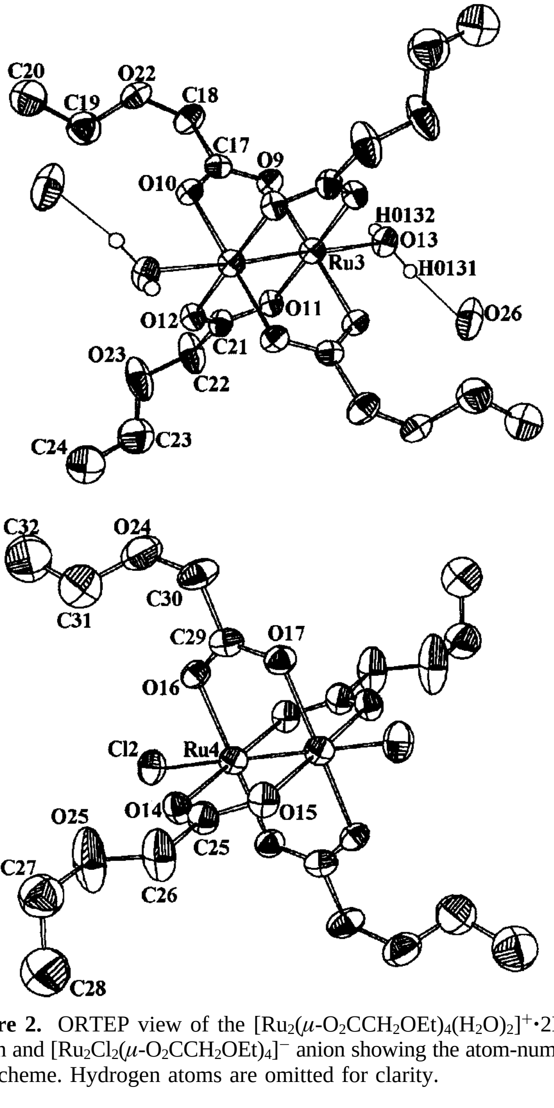

Figure 2. ORTEP view of the $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(H_2O)_2]^+{\cdot}2H_2O$ cation and $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ anion showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

In the solid state all these dimetallic units are arranged as shown in Figure 3. The polymeric chains alternates with cationic−anionic units bonded by electrostatic forces. In this arrangement also there are two water molecules per asymmetric unit bonded by hydrogen bonds to the axial water molecules. Thus, the compound **1** represents the first example in which anionic and cationic units of the type $[Ru_2Cl_2(\mu\text{-}O_2CR)_4]^-$ and $[Ru_2(\mu\text{-}O_2CR)_4]^+$ are present together in the same complex. In

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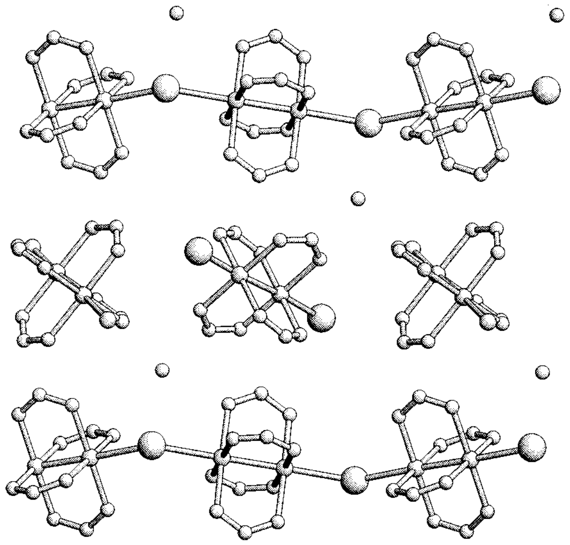

Figure 3. Arrangement in the solid state of compound **1**. Hydrogen atoms and CH_2OEt groups are omitted for clarity.

addition, this complex also shows simultaneously a polymeric chain through chlorine atoms. To our knowledge this is the first diruthenium compound containing three different diruthenium units with an anionic−cationic complex.

Compound **1** reacts with $OPPh_3$ in acetone to give a new compound of stoichiometry $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)$ (**2**). This compound has physical properties similar to those of **1**, being soluble in many solvents, with a conductivity measurements in methanol solution of 39 S cm^2 mol^{-1}. The magnetic moment at room temperature is 3.7 μ_B, corresponding to the presence of 3 unpaired electron per dimer unit. The IR spectrum of this compound shows the absence of bands due to water molecules, present in the starting compound, and the presence of bands due to coordinated $OPPh_3$. The positive LSIMS spectrum shows that the base peak corresponds to $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4 + H]^+$ (*m*/*z* 616), and peaks containing $OPPh_3$ molecules are detected at the following *m*/*z* values: (i) at 1172 and 929 corresponding to the fragments $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)_2]^+$ and $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)]^+$ respectively (these fragments indicate the presence of $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)_2]^+$ cations and $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)]$ molecules in the complex); (ii) at 894 corresponding to $[Ru_2(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)]^+$, which can be formed from the abovementioned fragments.

The negative LSIMS spectrum is similar to **1** and shows only two peaks assigned to $[Ru_2Cl_2(\mu\text{-}O_2CCH_2OEt)_4]^-$ ($m/z = 686$) and $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4]^-$ ($m/z = 650$).

All these data indicate that the addition of $OPPh_3$ to **1** gives a new compound in which the initial structure is preserved with the only difference that the chain observed in **1** is broken, giving discrete $[Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4(OPPh_3)]$ molecules, and the water molecules are replaced by $OPPh_3$. Several complexes containing discrete molecules of the type $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)]$ have been described very recently.[12]

In summary, in the compounds **1** and **2** an unusual arrangement has been found. The difference in the bridging ligand with respect to other polymeric compounds, such as the butanoato derivative, or with respect to nonpolymeric complexes, such as the isobutyrato complex, is the presence of an oxygen atom in the alkyl chain of the ethoxyacetate ligand. This oxygen atom forces an angle C−O−C of 111.50−115.34° in the carboxylate chain ligand, which has some influence in the packing in the solid state and also permits the possibility of hydrogen bonds in solution with solvents such as methanol/water. In the solid state, however, we have not found any interaction involving the OEt groups, and we cannot explain why, in this case, the arrangement is so different from those observed in the other compounds of this type described in the literature.

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Supporting Information Available: A figure showing LSIMS-induced fragmentation of **2** (1 page). An X-ray crystallographic file, in CIF format, for the structure determination of **1** is available on the Internet only. Ordering and access information is given on any current masthead page.

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