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Magnetic Properties of Diruthenium(II,III) Carboxylate Compounds. Crystal Structures of $Ru_2Cl(\mu\text{-}O_2CCH{=}CHCH{=}CHMe)_4$ and $Ru_2Cl(\mu\text{-}O_2CCH_2OMe)_4$

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The reaction of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ with 2,4-hexadienoic and 2-methoxyacetic acids affords the compounds $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH=CHCH=CHCH$_3$ (**1**), CH$_2$OMe (**2**)]. The structures of both complexes have been determined by X-ray crystallography. **1** crystallizes in the triclinic space group *P*-1 with $a = 9.264(1)$ Å, $b = 12.661(8)$ Å, $c = 12.839(5)$ Å, $\alpha = 106.09(3)°$, $\beta = 77.89(2)°$, $\gamma = 97.73(3)°$, and $Z = 2$. **2** crystallizes in the nonstandard monoclinic space group *P*2(1)/*c* with $a = 12.132(4)$ Å, $b = 11.570(2)$ Å, $c = 13.674(2)$ Å, $\beta = 91.18(2)°$, and $Z = 4$. Complexes **1** and **2** show $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units linked by chloride ions, giving zigzag chains with Ru−Cl−Ru angles of 119.43(4)° and 110.11(7)°, respectively. The Ru−Ru bond distances are 2.2857(9) Å (**1**) and 2.290(1) Å (**2**). A magnetic study, in the 2−300 K temperature range, of the new compounds and the previously described $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CHMe$_2$ (**3**), CMe$_3$ (**4**), C$_4$H$_4$N (**5**)] is described. The polymeric complexes **1** and **2** and the nonpolymeric **3**−**5** show a large zero-field splitting which varies from 53.9 to 68.1 cm^{-1}. These complexes also show a weak, but not negligible, through-space intermolecular antiferromagnetic coupling not observed in the previous magnetic studies carried out on these types of compounds.

Introduction

The synthesis and properties of numerous mixed-valent diruthenium(II,III) carboxylates have been reported.[2−4] The crystal structure determination of several $Ru_2Cl(\mu\text{-}O_2CR)_4$ (R = alkyl or aryl) compounds shows usually a polymeric structure with the $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units linked by chloride ions, forming linear or zigzag chains.[5−13] However, arrangements giving discrete dinuclear molecules of the type $Ru_2Cl(\mu\text{-}O_2CR)_4(S)$ (S = solvent molecule)[14−16] have also been described. Zigzag chains and cationic and anionic units have been found in the ethoxyacetate derivative.[17] The different nature of the carboxylate bridging ligands is the cause of these arrangements in the solid state, but the relationship between the nature of the ligands and the polymeric/nonpolymeric structure in the solid state is not clear.

Among the properties of these complexes, the magnetic behavior is of particular interest. It is well-known that the magnetic properties of the diruthenium compounds are dependent on a large zero-field splitting. Some studies have been carried out to evaluate the possible antiferromagnetic exchange between the diruthenium units linked by chloride ligands. In the early studies[18,19] on the complex $Ru_2Cl(\mu\text{-}O_2CPr)_4$ only a large intramolecular antiferromagnetic interaction or zero-field splitting was considered, and the intermolecular antiferromagnetic coupling was not detected. Later, Cotton et al.[11] have observed that a very strong intermolecular antiferromagnetic exchange is possible, but only when the chains are linear or at least not bent at Cl$^-$ to angles as small as 125°. More recently, Cukiernik et al.[12] have established a correlation between the type of magnetic behavior and the Ru−Cl−Ru interdimer angle. Several magnetic studies on tetracarboxylatediruthenium(II,III) units, connected axially by other bridging ligands, have mainly shown weak or strong intermolecular antiferromagnetic coupling.[20−26]

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In our studies on the influence of the carboxylate ligand in the arrangement of the diruthenium(II,III) units, we present in this paper the role of 2,4-hexadienoic and 2-methoxyacetic acids. Thus, we describe here the new compounds $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH═CHCH═CHCH$_3$ (**1**), CH$_2$OMe (**2**)]. We have chosen the 2,4-hexadienoic acid because the influence of unsaturated chains in the carboxylate ligand has been little explored and only two crystal structures containing this type of carboxylate ligands have been described.[7,13] The 2-methoxyacetic acid has been chosen due to similarity with the 2-ethoxyacetic acid, which gives the most unusual arrangement described for these types of complexes.[17] The crystal structures of **1** and **2** are reported. We also describe in this paper a magnetic study on the new chlorocarboxylate complexes and the previously described[14,15] $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CHMe$_2$ (**3**), CMe$_3$ (**4**), C$_4$H$_4$N (**5**)], which give discrete molecular units in the solid state. A comparison of the magnetic properties between the polymeric **1** and **2** and molecular **3**−**5** complexes has also been carried out.

Experimental Section

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 purified and distilled by standard methods, except methanol which was used without previous purification. The complexes $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = Me, CHMe$_2$, CMe$_3$, C$_4$H$_4$N] were prepared by literature procedures.[14,15,27] IR spectra were recorded, as KBr disks, on a Nicolet Magna-FTIR 550 spectrophotometer. Elemental analyses of C and H were performed by the Microanalytical Service of the Complutense University of Madrid. Electronic spectra in the range 200−2500 nm were recorded on a Cary 5G spectrophotometer. The electronic spectra in the solid state were recorded using a "Praying Mantis" accessory. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG AutoSpec spectrometer using *m*-nitrobenzyl alcohol as a liquid matrix. Nominal molecular masses and isotopic distribution of all peaks were calculated with the computer program MASAS, using polynomial expansions based on the natural abundance of the isotopes.[28] 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. The variable-temperature magnetic susceptibility data were measured on a Quantum Design MPMS*XL* SQUID (superconducting quantum interference device) susceptometer over a temperature range of 2−300 K. For each compound, measurements were taken using a field strength of 10 000, 5000, or 3000 G, and no field dependence was observed. 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.

Synthesis of $Ru_2Cl(\mu\text{-}O_2CR)_4$ Complexes 1 and 2. These compounds were obtained following a general method of preparation. To a solution (45 cm^3) of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ (0.30 g, 0.63 mmol) in methanol/water (2:1) was added an excess of carboxylic acid (3.78 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 20 cm^3 of diethyl ether and treated again with fresh carboxylic acid (3.78 mmol) in the same conditions to ensure the complete replacement of the acetate ligands. The solution was evaporated to dryness under vacuum, giving a red-brown solid.

Table 1. Crystal Data for $Ru_2(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$ (**1**) and for $Ru_2(\mu\text{-}O_2CCH_2OCH_3)_4$ (**2**)

	1	**2**
empirical formula	$C_{24}H_{28}ClO_8Ru_2$	$C_{12}H_{20}ClO_{12}Ru_2$
fw	682.08	593.87
space group	*P*−1	*P*2(1)/*c*
a (Å)	9.264(1)	12.132(4)
b (Å)	12.661(8)	11.570(2)
c (Å)	12.839(5)	12.674(2)
α (deg)	106.09(3)	
β (deg)	77.89(2)	91.18(2)
γ (deg)	97.73(3)	
Z	2	4
V (Å^3)	1410(1)	1919.0(7)
d_{calcd} (g cm^{-1})	1.606	2.056
F(000)	682	1172
temp (K)	295	295
wavelength	0.710 69	0.710 69
μ(Mo K) (cm^{-1})	13.36	13.36
R^a	2.4	3.47
$R_w{}^b$	6.8	10.21

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

The crude solid of compound **1** was washed three times with diethyl ether and dried under vacuum. The slow evaporation of a methanol/water (1:1) solution of **1** gave dark red crystals of the complex. Yield: 80%. Anal. Calcd for $C_{24}H_{28}O_8ClRu_2$: C, 42.26; H, 4.14. Found: C, 42.21, H 4.12. Main IR data (KBr disk, cm^{-1}): 2965w, 2934w, 2913w, 1645s, 1615s, 1436−1405vs. UV−vis (MeOH, solution; λ, nm; ε, dm^3 mol^{-1} cm^{-1}): 432 (887), 1025 (48), 1099 (52). UV−vis (solid; λ, nm): 407, 503, 980, 1164. $\mu_{eff} = 4.10\ \mu_B$ at room temperature. Mass spectral data [*m*/*z* (fragment)] (LSIMS$^+$): 683 ($Ru_2Cl(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$), 648 ($Ru_2(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$).

A THF solution of **2** was layered with petroleum ether (40−60 °C) to give red crystals of the title compound. Yield: 85%. Anal. Calcd for $C_{12}H_{20}O_{12}ClRu_2$: C, 24.27; H, 3.39. Found: C, 24.23; H 3.34. Main IR data (KBr disk, cm^{-1}): 2936m, 2830m, 1488−1408vs, 1115vs. UV−vis (MeOH, solution; λ, nm; ε, dm^3 mol^{-1} cm^{-1}): 432 (727), 966 (25), 1005 (25). UV−vis (solid; λ, nm): 464, 965, 1110. $\mu_{eff} = 4.07\ \mu_B$ at room temperature. Mass spectral data [*m*/*z* (fragment)] (LSIMS$^+$): 594 ($Ru_2Cl(\mu{-}O_2CCH_2OMe)_4$), 559 ($Ru_2(\mu{-}O_2CCH_2OMe)_4$), 470 ($Ru_2(\mu\text{-}O_2CCH_2OMe)_3$), 381 ($Ru_2(\mu\text{-}O_2CCH_2OMe)_2$).

X-ray Crystallographic Procedures. A summary of the fundamental crystal data for **1** and **2** is given in Table 1. Representative brown-red prismatic crystals of approximate dimensions 0.10 × 0.15 × 0.20 (**1**) and 0.4 × 0.05 × 0.05 mm (**2**) were mounted in an Enraf-Nonius CAD4 diffractometer. A graphite-monochromatic Mo Kα (λ = 0.710 70 Å) beam was used in the data collection carried out at 295 K. The cell dimensions were refined from least-squares fitting of the θ values of 25 reflections with a 2θ range of 15−30°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion correction for Ru and Cl were taken from the *International Tables for X-ray Crystallography*.[29] The structure was solved by Patterson and Fourier methods.[30,31] Final mixed refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms, except for the carbon atoms belonging to the terminal −CH$_3$ groups for **2**, which have been refined only isotropically. Atomic parameters for **1** and **2** are given in Tables 2 and 3, respectively. The hydrogen atoms were included with fixed isotropic contributions at their

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Ru_2(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$ (**1**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	0.0598(1)	0.5182(1)	0.5731(1)	0.029(1)
Ru(2)	0.0615(1)	0.5063(1)	0.9146(1)	0.034(1)
Cl	0.2009(1)	0.5428(1)	0.7312(1)	0.042(1)
O(1)	−0.1262(3)	0.5749(2)	0.6748(2)	0.037(1)
O(2)	−0.0051(3)	0.3630(2)	0.5861(2)	0.037(1)
O(3)	0.1213(3)	0.6727(2)	0.5575(2)	0.039(1)
O(4)	0.2454(3)	0.4659(2)	0.4674(2)	0.038(1)
O(5)	0.1097(3)	0.3473(2)	0.8778(2)	0.044(1)
O(6)	0.0105(3)	0.6653(2)	0.9553(2)	0.046(1)
O(7)	−0.1278(3)	0.4551(2)	0.8566(2)	0.043(1)
O(8)	0.2501(3)	0.5523(2)	0.9756(2)	0.042(1)
C(1)	−0.2401(4)	0.5729(3)	0.6347(3)	0.034(1)
C(2)	−0.3748(4)	0.6168(3)	0.7075(3)	0.039(1)
C(3)	−0.3740(4)	0.6785(3)	0.8088(3)	0.043(1)
C(4)	−0.5003(5)	0.7294(4)	0.8819(3)	0.051(1)
C(5)	−0.4945(5)	0.8038(4)	0.9764(4)	0.064(1)
C(6)	−0.6238(7)	0.8588(5)	1.0512(5)	0.097(2)
C(7)	−0.0802(4)	0.2979(3)	0.5185(3)	0.036(1)
C(8)	−0.1237(4)	0.1856(3)	0.5284(3)	0.046(1)
C(9)	−0.1020(4)	0.1500(3)	0.6111(3)	0.045(1)
C(10)	−0.1404(5)	0.0395(4)	0.6236(4)	0.054(1)
C(11)	−0.1188(5)	0.0061(4)	0.7073(4)	0.061(1)
C(12)	−0.1559(7)	−0.1063(4)	0.7233(5)	0.083(2)
C(13)	0.0666(4)	0.2942(3)	0.9509(3)	0.044(1)
C(14)	0.1070(5)	0.1824(4)	0.9298(4)	0.058(1)
C(15)	0.1950(5)	0.1329(4)	0.8392(4)	0.063(1)
C(16)	0.2420(7)	0.0225(4)	0.8147(5)	0.079(2)
C(17)	0.3368(8)	−0.0207(6)	0.7263(5)	0.105(2)
C(18)	0.3861(10)	−0.1348(6)	0.6999(7)	0.161(1)
C(19)	−0.2464(4)	0.4369(3)	0.9221(3)	0.039(1)
C(20)	−0.3833(4)	0.4026(3)	0.8796(3)	0.043(1)
C(21)	−0.3884(4)	0.3729(3)	0.7738(3)	0.042(1)
C(22)	−0.5207(4)	0.3398(4)	0.7277(3)	0.048(1)
C(23)	−0.5234(5)	0.3024(4)	0.6216(4)	0.057(1)
C(24)	−0.6589(6)	0.2673(5)	0.5725(4)	0.076(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Ru_2(\mu\text{-}O_2CCH_2OCH_3)_4$ (**2**)

atom	*x*	*y*	*z*	*U*(eq)[a]
Ru(1)	0.4217(1)	0.0078(1)	0.4523(1)	0.022(1)
Ru(2)	0.0748(1)	0.0027(1)	0.4505(1)	0.022(1)
Cl(1)	0.2461(2)	0.0172(2)	0.3444(1)	0.032(1)
O(1)	0.5064(4)	−0.0392(5)	0.3333(4)	0.030(1)
O(2)	0.1618(4)	−0.0802(4)	0.5573(4)	0.027(1)
O(3)	0.3414(4)	0.0614(4)	0.5724(4)	0.029(1)
O(4)	0.4577(4)	0.1752(4)	0.4250(4)	0.030(1)
O(5)	0.1102(4)	0.1616(4)	0.5044(4)	0.029(1)
O(6)	0.0331(4)	−0.1540(4)	0.3949(4)	0.032(1)
C(1)	0.3912(6)	0.0650(6)	0.6546(5)	0.029(2)
C(2)	0.3340(6)	0.1036(8)	0.7437(6)	0.035(2)
C(3)	0.1630(9)	0.1403(9)	0.8135(7)	0.060(3)
C(4)	0.5426(6)	0.2188(6)	0.4678(6)	0.029(2)
C(5)	0.5614(7)	0.3449(7)	0.4489(6)	0.041(2)
C(6)	0.7524(8)	0.3650(9)	0.4718(8)	0.060(3)
C(7)	0.1180(6)	−0.1015(6)	0.6375(5)	0.029(2)
C(8)	0.1813(6)	−0.1615(8)	0.7161(6)	0.039(2)
C(9)	0.3589(8)	−0.2130(9)	0.7729(7)	0.054(2)
C(10)	0.0491(6)	0.2039(7)	0.5677(5)	0.031(2)
C(11)	0.0719(8)	0.3248(7)	0.6051(7)	0.046(2)
C(12)	0.2625(9)	0.3493(9)	0.5855(8)	0.060(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

calculated positions determined by molecular geometry. The final discrepancy factor was $R = \sum||F_0| - |F_c||/\sum|F_0| = 0.024$ (**1**) and 0.0347 (**2**). No trend in ΔF versus sin θ/λ was observed. A final difference synthesis showed no significant electron density (1.069 (**1**) and 1.323 (**2**) $e^- Å^{-3}$ near the Ru atom).

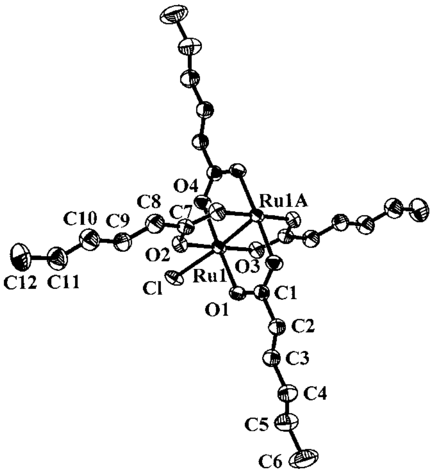

Figure 1. ORTEP view of the binuclear unit of **1** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **1** and **2**[a]

1		2	
Ru1−Ru1A	2.2857(9)	Ru1−Ru1A	2.2890(1)
Ru1−O1	2.015(2)	Ru1−O1	2.018(5)
Ru1−O2	2.018(3)	Ru1−O3	2.023(5)
Ru1−O3	2.015(3)	Ru1−O4	2.022(5)
Ru1−O4	2.017(2)	Ru1−O7	2.029(5)
Ru1−Cl	2.564(1)	Ru1−Cl1	2.569(2)
Ru1−Cl−Ru1A′	119.43(4)	Ru1−Cl1−Ru1A′	110.11(7)
Ru1A−Ru1−Cl	175.24(3)	Ru1A−Ru1−Cl1	177.87(6)
O1−Ru1−Ru1A	89.46(7)	O1−Ru1−Ru1A	90.4(1)
O2−Ru1−Ru1A	88.41(8)	O3−Ru1−Ru1A	88.3(1)
O3−Ru1−Ru1A	90.18(8)	O4−Ru1−Ru1A	90.1(1)
O4−Ru1−Ru1A	89.03(7)	O7−Ru1−Ru1A	88.3(1)
O1−Ru1−Cl	93.63(7)	O1−Ru1−Cl1	88.7(2)
O2−Ru1−Cl	87.89(8)	O3−Ru1−Cl1	92.7(1)
O3−Ru1−Cl	93.53(8)	O4−Ru1−Cl1	91.9(1)
O4−Ru1−C1	88.01(7)	O7−Ru1−Cl1	89.8(1)
O1−Ru1−O2	91.4(1)	O1−Ru1−O3	177.3(2)
O1−Ru1−O3	88.3(1)	O1−Ru1−O4	89.6(2)
O1−Ru1−O4	177.5(1)	O1−Ru1−O7	88.6(2)

[a] Symmetry transformations used to generate equivalent atoms: (A) −*x*, −*y*, −*z*; (A′) −*x* + 1, −*y*, −*z*.

Results and Discussion

Crystal Structures of $Ru_2Cl(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$ (1) and $Ru_2Cl(\mu\text{-}O_2CCH_2OMe)_4$ (2). Figure 1 shows an ORTEP view of compound **1**. Table 4 gives selected bond distances and angles of the complex. The asymmetric unit consists of half of **1** related to the other half *via* a crystallographic inversion center located in the middle of the Ru−Ru bond. The dinuclear unit of **1** has two ruthenium atoms linked by four bridging 2,4-hexadienoate ligands. The $[Ru_2(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4]^+$ units are connected by chloride ions, giving zigzag chains. The Ru−Ru distance 2.2857(9) Å is on the same order as that found in the other polymeric carboxylatediruthenium(II,III) compounds. The Ru−Cl bond length [2.564(1) Å] is similar to that found in analogous polymeric complexes [2.5016(6)−2.587(5) Å] and is longer than the corresponding bond length in nonpolymeric compounds [2.445(6)−2.523(3) Å].[2,4] The Ru−Cl−Ru angle of 119.43(4)° is similar to that observed[6] in one of the three crystallographically independent $[Ru_2(O_2CR)_4]^+$ units found in $[Ru_2Cl(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}OCH_3)_4]$. No significant interactions are seen between the zigzag chains of $[Ru_2Cl(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4]_n$.

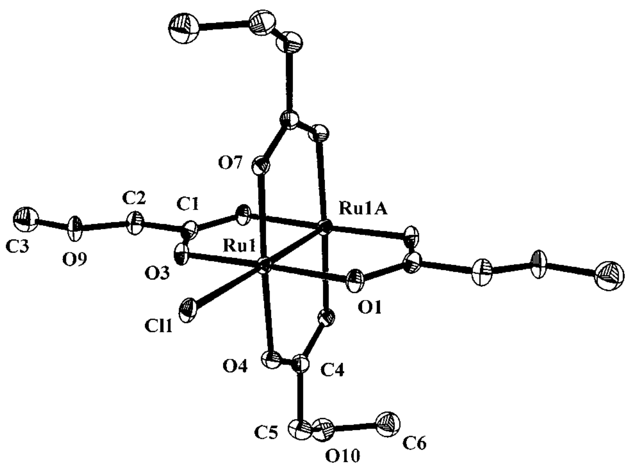

Figure 2. ORTEP view of the binuclear unit of **2** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

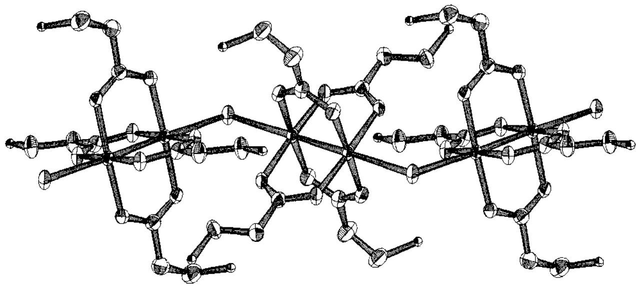

Figure 3. ORTEP drawing showing the chain structure of **2**.

Figure 2 shows the ORTEP structure of compound **2.** Selected bond lengths and angles are collected in Table 4. The asymmetric unit consists of half of **2** related to the other half via a crystallographic inversion center located in the middle of the Ru−Ru bond. Ru−Ru [2.2890(1) Å], Ru−Cl [2.569(2) Å], and the other bond distances of the [$Ru_2Cl(\mu\text{-}O_2C\text{-})_4$] unit are very similar to those of compound **1** and other diruthenium carboxylate complexes.[2−4] The Ru−Cl−Ru angle of 110.11(7)° is the most acute Ru−Cl−Ru angle found in chlorotetra(carboxylate)diruthenium(II,III) complexes.[2,3] As in **1**, interactions between the zigzag chains in the solid are limited to van der Waals forces. Figure 3 shows an ORTEP drawing of the zigzag chain in **2**.

Thus, the unsaturated 2,4-hexadienoate ligand gives a compound with polymeric structure similar to those of the compounds obtained with 2-methylpropenoate[7] and 2-methyl-2-pentenoate[13] ligands, although the two former ligands give zigzag chains and the third leads to linear chains. The main difference between these unsaturated ligands and the isobutyrate and trimethyl acetate[15] is probably the greater rigidity of the alkenecarboxylate ligands. This could lead to a lower interaction with the solvents, and probably this prevents the formation of discrete molecules in the crystallization process.

With the 2-methoxyacetate ligand, zigzag chains have been obtained, and these results contrast those described for the 2-ethoxyacetate[17] ligand which shows zigzag chains and cationic and anionic units. Thus, the change of the Et group by the Me group in the carboxylate ligand leads to a dramatic change in the arrangement. We have carefully studied both complexes, and we have no explanation of the differences in the behavior of these complexes.

Physicochemical Properties of the Compounds. The reaction of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ with 2,4-hexadienoic and 2-methoxyacetic acids in methanol/water (2:1) leads to $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH=CHCH=CHCH$_3$ (**1**), CH$_2$OMe (**2**)]. Two metathesis cycles were carried out to ensure the complete replacement of the acetate ligands. The mass spectra of **1** and **2** after two metathesis cycles show only peaks corresponding to the tetrasubstituted compounds showing that the metathesis was complete. Compound **1** is less soluble than **2** in organic solvents such as dichloromethane or acetone, while both are soluble in polar solvents, such as methanol or THF, and insoluble in petroleum ether, diethyl ether, or toluene. The conductivity measurements in methanol solution (*ca.* 10^{-3} M) indicate that these compounds are nonelectrolytes in this solvent,[32] and therefore the Ru−Cl bond remains intact in solution. This behavior has been found previously in the nonpolymeric complexes[14−16] and in the case of the 2-methyl-2-pentenoate derivative, which is polymeric in the solid state, but forms discrete dimeric molecules in solution.[13]

Spectroscopic Properties. The IR spectra of **1** and **2** show the typical pattern of the bridging carboxylate ligand in the COO stretching region.[4] The peaks and the fragmentation pathways observed in the LSIMS spectra of **1** and **2** are similar to those described previously for other diruthenium carboxylate complexes. In accordance with previous studies,[33] the LSIMS spectrum of compound **2** clearly suggests the formation of discrete dinuclear molecules in solution. The LSIMS spectrum of **1** shows fewer signals than **2**, although the presence of the molecular peak also suggests the formation of molecules in solution.[13]

The electronic spectra of **1** and **2** in methanol solution are similar to those of other diruthenium(II,III) complexes showing both a band in the visible range[34,35] at 432 nm, due to a π(RuO, Ru$_2$) → π^*(Ru$_2$) transition and another split one in the near-infrared, at ca. 1050 nm assigned to a $\delta \rightarrow \delta^*$ transition.[35−37] The electronic spectra in the solid state are similar, showing minor shifts in the absorption frequencies.

Magnetic Properties. Magnetic measurements of compounds **1**−**5** show in all cases magnetic moments at room temperature of 4.0−4.2 μ_B corresponding to the presence of three unpaired electrons per dimer unit. The representation of the magnetic moment versus temperature shows a pronounced decrease of the magnetic moment, mainly at very low temperatures. This pronounced decrease has also been observed in all similar compounds when the measurements were carried out in liquid helium and has been ascribed to a large zero-field splitting (ZFS).[12,18,19] The following equation described by O'Connor[38] and corrected later by Telser and Drago[39] for an $S = 3/2$ spin system with an axial ZFS has been used previously for similar complexes[12,21,26]

$$\chi_{\parallel} = (Ng^2\beta^2/kT)(1 + 9e^{-2D/kT})/4(1 + e^{-2D/kT})$$

$$\chi_{\perp} = (Ng^2\beta^2/kT)(4 + (3kT/D)(1 - e^{-2D/kT})/4(1 + e^{-2D/kT}))$$

giving the average molar magnetic susceptibility of a powder sample

$$\chi_M = (\chi_{\parallel} + 2\chi_{\perp})/3$$

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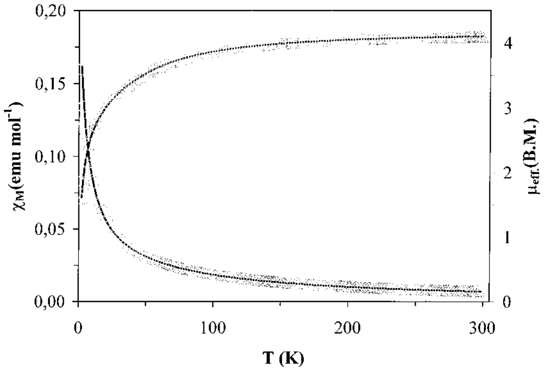

Figure 4. Temperature dependence of the molar susceptibility χ'_{mol} (○) and μ_{eff} (△) for complex **1**. Solid lines result from least-squares fits using the model described in the text.

Compounds **1** and **2** have a polymeric structure with a Ru−Cl−Ru angle lower than 125°, and compounds **3**−**5** are nonpolymeric. As a consequence, according to the previous studies, in these complexes very weak or inexistent antiferromagnetic coupling are expected to show.[11,12] The fits carried out with the above-mentioned model give g and D values analogous to those found in similar compounds.[12,21,26] However, the experimental and calculated curves differ, mainly at very low temperature. In addition, in compounds **1** and **2**, the σ^2 values are too high, indicating the poor quality of the fits.

In several previously studied systems, it was necessary to include in the expression of the molar susceptibility other terms corresponding to temperature-independent paramagnetism (TIP)

$$\chi'_M = \chi_M + \text{TIP}$$

and a paramagnetic impurity (P)

$$\chi'_{mol} = (1 - P)\chi'_M + PNg_{mo}{}^2\beta^2/4kT$$

Fits of compounds **1**−**5** using these equations result in poor correlation or anomalous parameter values. The pronounced decrease of the magnetic moment with temperature suggests an antiferromagnetic interaction between $S = 3/2$ units, and we have made use of the molecular field approximation used by Cukiernik *et al.*,[12] which incorporates both the strong ZFS as well as a weak intermolecular antiferromagnetism

$$\chi' = \chi'_M/1 - (2zJ/Ng^2\beta^2)\,\chi'_M$$

and

$$\chi'_{mol} = (1 - P)\chi' + PNg_{mo}{}^2\beta^2/4kT$$

being

$$\mu_{eff} = 2.84(T\chi'_{mol})^{1/2}$$

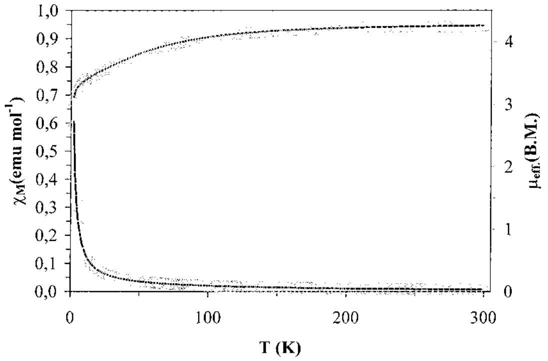

Figure 5. Temperature dependence of the molar susceptibility χ'_{mol} (○) and μ_{eff} (△) for complex **5**. Solid lines result from least-squares fits using the model described in the text.

The quality of the fits increases considerably using this model. We have observed some differences in the magnetic parameter values depending on the mode of the experimental data fits. Thus, the best fits were obtained when the magnetic parameters were fit to the magnetic moment as a function of temperature. With the parameters obtained in these fits, a very good agreement was observed between experimental and calculated curves of the magnetic moment and the molar magnetic susceptibility. Figures 4 and 5 show the experimental and calculated curves for the polymeric (**1**) and molecular (**5**) complexes using this model. On the other hand, if the magnetic parameters were obtained from a fit to the molar magnetic susceptibility curves, poorer agreement was obtained. As a consequence the magnetic parameters obtained in the first case could be more accurate. Table 5 collects the magnetic parameters (g, D, zJ, TIP, and P) obtained in the fit of the magnetic moment and magnetic susceptibility curves. In both fits all compounds show large zero-field splitting values and antiferromagnetic coupling. As one can observe in Table 5, the D values range from 53.9 to 68.1 cm^{-1} and from 50.0 to 100.9 cm^{-1} depending on the fit method. Anyway, all these values are similar to those described for the previous analogous compounds.[12,21,25,26] The antiferromagnetic coupling constants also vary from −0.09 to −2.84 cm^{-1} and from −0.19 to −3.01 cm^{-1}. The polymeric compounds **1** and **2** show a similar Ru−Cl−Ru angle lower than 125°, and however, they have an antiferromagnetic coupling of −2.84 (or −3.01) cm^{-1} and −0.69 (or 0.68) cm^{-1}, respectively. The existence of antiferromagnetic coupling between the diruthenium units in these compounds is unexpected according to the previous studies, due to the low Ru−Cl−Ru angles. The crystal structure determination of compounds **3**−**5** has shown a molecular structure and, therefore, the existence of isolated molecules in the solid state.[14,15] In compound **5**, the molecular units are linked by a hydrogen bond, but in compounds **3** and **4** there are only van der Waals forces between the molecules. However, the fits of the magnetic data of these three compounds show the existence of a weak, but not negligible, antiferromagnetic coupling. These results indicate that, in the polymeric or

Table 5. Magnetic Parameters for Complexes **1**−**5** Obtained in the Fits to the Magnetic Moment as a Function of Temperature[a]

compd	g	D (cm^{-1})	zJ (cm^{-1})	TIP (cm^3/mol)	P (%)	$\sigma^{2\,b}$	$\sigma^{2\,c}$
1	2.16 (2.17)	53.9 (50.0)	−2.84 (−3.01)	$<10^{-8}$ ($<10^{-8}$)	0.44 (0.08)	1.07×10^{-5}	(6.23×10^{-4})
2	2.07 (2.08)	67.5 (70.1)	−0.69 (−0.68)	2.8 10^{-4} (3.3 10^{-4})	$<10^{-2}$ ($<10^{-2}$)	4.07×10^{-6}	(1.22×10^{-5})
3	2.07 (2.13)	61.7 (84.2)	−0.09 (−0.19)	$<10^{-8}$ ($<10^{-8}$)	0.04 ($<10^{-2}$)	4.63×10^{-6}	(3.85×10^{-5})
4	2.04 (2.12)	65.2 (97.6)	−0.09 (−0.20)	$<10^{-8}$ ($<10^{-8}$)	0.09 ($<10^{-2}$)	9.05×10^{-6}	(3.58×10^{-5})
5	2.21 (2.28)	68.1 (100.9)	−0.13 (−0.24)	$<10^{-8}$ ($<10^{-8}$)	$<10^{-2}$ ($<10^{-2}$)	7.94×10^{-6}	(6.31×10^{-5})

[a] Values obtained from fits to the molar susceptibility curves are given in parentheses. [b] $\sigma^2 = \sum(\mu_{eff,calc} - \mu_{eff,exp})^2/\sum\mu_{eff,exp}{}^2$. [c] $\sigma^2 = \sum(\chi'_{mol,calc} - \chi'_{mol,exp})^2/\sum\chi'_{mol,exp}{}^2$.

molecular chlorotetracarboxylatediruthenium(II,III) at very low temperatures, a spin exchange between dimer units may occur *via* a through-space pathway. The results described above for compounds **1** and **2** could be compatible with those proposed by Cotton *et al.*[11] because although the Ru−Cl−Ru angles are lower than 125° the antiferromagnetic coupling could be produced through-space.

On the other hand, the correlation between the type of magnetic behavior and the interdimer Ru−Cl−Ru angle, established by Cukiernik *et al.*[12] for the chlorotetracarboxylatediruthenium(II,III) [(i) type I (inexistent or extremely weak antiferromagnetic coupling, $|zJ| < 0.2$ cm^{-1}, Ru−Cl−Ru angle $< 125°$), (ii) type II (weak antiferromagnetic coupling, $125° <$ Ru−Cl−Ru angle $< 180°$), and (iii) type III (large antiferromagnetic coupling, $|zJ| > 10$ cm^{-1}, Ru−Cl−Ru angle $\cong 180°$) could not be valid because the compounds of type I could have a coupling constant through-space similar to that of the compounds of type II through chloro atoms. As a consequence, the three types of magnetic behavior proposed by Cukiernik *et al.*[12] could be classified only as a function of the antiferromagnetic coupling as (i) compounds without antiferromagnetic coupling, (ii) compounds with weak antiferromagnetic coupling, and (iii) compounds with a large antiferromagnetic coupling (Ru−Cl−Ru angle $\cong 180°$).

Conclusion

In this work, we have reported two new diruthenium(II,III) carboxylate compounds, which show a polymeric structure. The present study shows that in nonpolymeric diruthenium(II,III) complexes a through-space antiferromagnetic exchange is produced. A similar through-space antiferromagnetic exchange, instead of a spin exchange between adjacent dimers through the bridging chlorine atoms, can be produced in those polymeric complexes with Ru−Cl−Ru angles lower than 125°. This through-space antiferromagnetic exchange has not been observed in previous magnetic studies carried out on these types of complexes.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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