*Inorg. Chem.* **2005**, *44*, 5770–5777

Inorganic Chemistry
Article

# Discrete and Monodimensional Heteropolynuclear Structures Formed by Tetracarboxylatodiruthenium(II,III) and Perrhenato Fragments

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Received May 12, 2005

Reaction between cationic units of carboxylate-bridged diruthenium complexes $[Ru_2(\mu\text{-}O_2CR)_4]^+$ (R = Me, $CMePh_2$, $CMe_3$, $CH_2CH_2OMe$, C(Me)═CHEt, $C_6H_4$-*p*-OMe, Ph) and tetrabutylammonium perrhenate gives complexes with different arrangements in the solid state. Thus, the compounds $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$ [R = Me (**1**), $CMePh_2$ (**2**), $CMe_3$ (**3**), $CH_2CH_2OMe$ (**4**), C(Me)═CHEt (**5**), $C_6H_4$-*p*-OMe (**6**), Ph (**7**)] have polymeric structures with the diruthenium units linked by perrhenate ligands in the axial positions. The structures of complexes **3**·THF and **4** were established by single-crystal X-ray diffraction. The tetrahedral geometry of the $ReO_4^-$ anion permits the formation of a chain close to the linearity. In contrast to the polymeric chains observed in complexes **1**–**7**, the reaction of $[Ru_2(\mu\text{-}O_2CPh)_4]^+$ with $NBu_4ReO_4$ also affords the compounds $Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)(H_2O)$ (**8**) and $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$ (**9**) depending on the reaction conditions. The structure of **8** consists of cationic and anionic units, $[Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2]^+$ and $[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]^-$, linked by hydrogen bonds, which give a three-dimensional net. The structure of complex **9**·$0.5H_2O$ has an anionic unit similar to that of **8**, whose counterion is $NBu_4^+$. The Ru–Ru bond distances are slightly longer in $[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]^-$ than in the polymeric compounds $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$. The magnetic behavior owes to the existence of zero-field splitting (ZFS) and a weak antiferromagnetic coupling. The experimental data are fitted with a model that considers the ZFS effect using the Hamiltonian $\hat{\mathcal{H}}_D = SDS$. The weak antiferromagnetic coupling is introduced as a perturbation, using the molecular field approximation.

## Introduction

The incorporation of dinuclear paddlewheel complexes into extended frameworks is a new, emergent area of supramolecular chemistry.[1,2] Among the dinuclear metal−metal complexes, the diruthenium compounds are especially interesting because of their variety of electronic configurations, which lead to singular electrochemical, electrical, or magnetic properties.[1,3,4] Numerous tetracarboxylatodiruthenium(II,III) monocations bonded to mononegative anions such as halide giving polymeric or molecular arrangements have been described.[1,3,5] Neutral molecules[6] or organic radicals such as nitroxides[7] have also been used to bind the cationic units.

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10.1021/ic050757x CCC: $30.25

However, heteropolynuclear compounds where tetracarboxylatodiruthenium units are bonded to another transition-metal complex are very scarce.[6e,8−10] Thus, the reaction of $Ru_2Cl(\mu\text{-}O_2CMe)_4$ with Cp(dppe)FeCN leads to the cyanide-linked tetranuclear cation $\{[Cp(dppe)FeCN]_2Ru_2(\mu\text{-}O_2CMe)_4\}^+$.[6e] Yoshioka and co-workers[8] have reported the formation of a two-dimensional layer structure[8] in the compound $[Ru_2(\mu\text{-}O_2CCMe_3)_4]_3[Fe(CN)_6]\cdot 4H_2O$. In contrast, Miller and co-workers[9a] have proposed a three-dimensional-network Prussian Blue-like structure for similar complexes $[Ru_2(\mu\text{-}O_2CMe)_4]_3[M(CN)_6]$ (M = Cr, Fe, Co). The three-dimensional structure was confirmed[9b] for the derivative $[Ru_2(\mu\text{-}O_2CMe)_4]_3[Cr(CN)_6]$ by a Reitveld analysis of the synchrotron powder data.[9b] Heteropolynuclear complexes containing diruthenium(II,III) units and ferrocenecarboxylate ligands have been also obtained.[10]

On the other hand, the perrhenate group is a weakly coordinating anion that has been used as a counterion in several complexes, although it can also be bonded to metal cations.[10−12] Three different modes of perrhenate coordination, monodentate,[13] chelate,[14] and bridging,[15] are known. However, no diruthenium paddlewheel complexes with coordinated or noncoordinated perrhenate ions are known.

In this paper, we describe the use of the perrhenate group to link tetracarboxylatodiruthenium(II,III) units in order to build new supramolecular structures. The arrangements observed in the new heteropolynuclear species vary from monodimensional chains in the complexes $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$ [R = Me, $CMePh_2$, $CMe_3$, $CH_2CH_2OMe$, C(Me)═CHEt, $C_6H_4$-*p*-OMe, Ph] to discrete polynuclear units in the derivative $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$. In the complex $Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)(H_2O)$, a supramolecular structure is observed as a result of the existence of hydrogen-bond interactions. The spectroscopic, magnetic, and structural properties of these complexes are described.

## Experimental Section

**General Procedures.** All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. The complexes $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = Me, $CMePh_2$, $CMe_3$, $CH_2CH_2OMe$, C(Me)═CHEt, $C_6H_4$-*p*-OMe, Ph] were prepared according to the literature procedures.[16−22] Other chemicals and solvents were obtained from commercial sources and used without further purification.

Elemental analyses were carried out by the Microanalytical Service of the Complutense University of Madrid. IR spectra were recorded on a Midac prospect FT-IR, a Shimadzu FT-IR Prestige-21, or a Perkin-Elmer 1330 IR spectrophotometer using KBr disks. 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. All data were 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. Mass spectra were obtained on a Bruker Esquire-LC with electrospray ionization (ESI) using methanol as a solvent. Nominal molecular masses and the distribution isotopic of all peaks were calculated with the MASAS[23] computer program, using a polynomial expansion based on natural abundances of the isotopes.

**Synthesis of $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$, Complexes 1−6.** These compounds were obtained following a general method of preparation. Silver tetrafluoroborate (0.06 g, 0.30 mmol) was added to a suspension or solution of $Ru_2Cl(\mu\text{-}O_2CR)_4$ (0.30 mmol) in tetrahydrofuran (25 $cm^3$). The initial suspension, when R = Me, $C_6H_4$-*p*-OMe, or Ph, or the solution, when R = $CMePh_2$, $CMe_3$, $CH_2CH_2OMe$, or C(Me)═CHEt, was stirred for 24 h in the absence of light, giving a solid precipitate of AgCl and a brown solution. The precipitate was filtered over Celite, and the solution was pumped to dryness. The solid, $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$, was dissolved in methanol [R = Me, C(Me)═CHEt, $C_6H_4$-*p*-OMe, Ph], dichloromethane (R = $CMePh_2$), or tetrahydrofuran (R = $CMe_3$, $CH_2CH_2OMe$). Tetrabutylammonium perrhenate (0.15 g, 0.30 mmol) was added to the brown solution of $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$, and the reaction mixture was stirred for 16 h. The solution was evaporated to dryness under a vacuum, giving $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$ [R = Me (**1**), $CMePh_2$ (**2**), $CMe_3$ (**3**), $CH_2CH_2OMe$ (**4**), C(Me)═CHEt (**5**), or $C_6H_4$-*p*-OMe (**6**)] as red-brown solids.

**Complex 1.** Compound **1** was dissolved in methanol, and the solution was allowed to stand at −18 °C. After 2 days, red crystals were collected. Yield: 64%. Anal. Calcd for $C_8H_{12}O_{12}Ru_2Re$: C, 13.96; H, 1.76. Found: C, 14.03; H, 1.77. IR (KBr disk, $cm^{-1}$):

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**Table 1.** Crystal Data for **3**·THF, **4**, **8**, and **9**·0.5$H_2O$

| | **3**·THF | **4** | **8** | **9**·0.5$H_2O$ |
|---|---|---|---|---|
| empirical formula | $C_{24}H_{44}O_{13}ReRu_2$ | $C_{16}H_{28}O_{16}ReRu_2$ | $C_{28}H_{20}O_{13}ReRu_2$ | $C_{44}H_{56}NO_{16.50}Re_2Ru_2$ |
| fw | 928.93 | 864.72 | 952.78 | 1437.44 |
| cryst system | monoclinic | orthorhombic | monoclinic | triclinic |
| space group | *P*2(1)/*m* | *Pbca* | *P*2(1)/*c* | $P\bar{1}$ |
| *a* [Å] | 11.6763(8) | 8.3397(5) | 13.188(2) | 12.7800(8) |
| *b* [Å] | 9.5760(6) | 18.6714(11) | 17.524(3) | 13.2445(8) |
| *c* [Å] | 16.0089(11) | 33.578(2) | 14.150(2) | 18.7919(12) |
| α [deg] | 90 | 90 | 90 | 79.3560(10) |
| *β* [deg] | 109.7360(10) | 90 | 107.675(3) | 78.9200(10) |
| *γ* [deg] | 90 | 90 | 90 | 63.3590(10) |
| *V* [$Å^3$] | 1684.84(19) | 5228.6(5) | 3116.0(9) | 2772.5(3) |
| *Z* | 2 | 8 | 4 | 2 |
| $D_{calcd}$ [g $cm^{-3}$] | 1.831 | 2.197 | 2.031 | 1.722 |
| $\mu$ [$mm^{-1}$] | 4.523 | 5.830 | 4.896 | 4.947 |
| *F*(000) | 910 | 3320 | 1820 | 1394 |
| final R indices [$I > 2\sigma(I)$] | R1 = 0.0452 | R1 = 0.0641 | R1 = 0.0743 | R1 = 0.0437 |
| | wR2 = 0.1159 | wR2 = 0.1604 | wR2 = 0.1628 | wR2 = 0.1087 |
| R indices (all data) | R1 = 0.0626 | R1 = 0.1268 | R1 = 0.3575 | R1 = 0.0609 |
| | wR2 = 0.1236 | wR2 = 0.1876 | wR2 = 0.2434 | wR2 = 0.1166 |
| largest diff. peak/hole [$eÅ^{-3}$] | 2.488 and −1.256 | 4.915 and −2.006 | 1.394 and −1.691 | 1.462 and −1.065 |

2991w, 2937w, 1444−1349vs, 979w, 943s, 912vs, 883vs, 694vs, 320vw. $\mu_{eff}$ (rt) = 4.14 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 439 [$Ru_2(\mu\text{-}O_2CMe)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Complex 2.** A dichloromethane solution of compound **2** was layered with hexane to give red microcrystals of **2**·$CH_2Cl_2$. Yield: 40%. Anal. Calcd for $C_{61}H_{54}O_{12}Cl_2Ru_2Re$: C, 50.94; H, 3.78. Found: C, 50.64; H, 3.88. IR (KBr disk, $cm^{-1}$): 3057w, 2989w, 1494−1369vs, 979w, 948m, 929m, 898m, 848vs, 698vs, 668vs, 320vw. $\mu_{eff}$ (rt) = 4.21 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 1104 [$Ru_2(\mu\text{-}O_2CCMePh_2)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Complex 3·THF.** A tetrahydrofuran solution of compound **3** was layered with hexane to give red crystals of **3**·THF suitable for X-ray diffraction. Yield: 62%. Anal. Calcd for $C_{24}H_{44}O_{13}Ru_2Re$: C, 31.03; H, 4.77. Found: C, 28.72; H, 4.50. IR (KBr disk, $cm^{-1}$): 2968w, 1486−1421vs, 978w, 944m, 910w, 854vs, 315vw. $\mu_{eff}$ (rt) = 4.00 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 608 [$Ru_2(\mu\text{-}O_2CCMe_3)_4$]; ($ESI^-$): 251 ($ReO_4$). A satisfactory analysis for **3** was found when **3**·THF was treated for 24 h under a vacuum. Anal. Calcd for $C_{20}H_{36}O_{12}Ru_2Re$: C, 28.04; H, 4.23. Found: C, 28.19; H, 4.29.

**Complex 4.** Crystals of **4** suitable for X-ray diffraction were obtained as mentioned above for **3**·THF. Yield: 68%. Anal. Calcd for $C_{16}H_{28}O_{16}Ru_2Re$: C, 22.22; H, 3.26. Found: C, 22.29; H, 3.09. IR (KBr disk, $cm^{-1}$): 2931−2927w, 1464−1429vs, 1111vs, 980w, 947s, 898m, 848vs, 330vw. $\mu_{eff}$ (rt) = 4.06 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 615 [$Ru_2(\mu\text{-}O_2CCH_2CH_2OMe)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Complex 5.** Crystals of **5** suitable for X-ray diffraction were obtained as mentioned above for **3**·THF. Yield: 51%. Anal. Calcd for $C_{24}H_{36}O_{12}Ru_2Re$: C, 31.86; H, 4.01. Found: C, 31.92; H, 3.98. IR (KBr disk, $cm^{-1}$): 2969−2879w, 1643m, 1460−1411vs, 976w, 943w, 914w, 893w, 851m, 315vw. $\mu_{eff}$ (rt) = 4.53 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 656 [$Ru_2(\mu\text{-}O_2CCMeCHEt)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Complex 6.** Compound **6** was dissolved in methanol and was allowed to evaporate at room temperature, giving red microcrystals. Yield: 65%. Anal. Calcd for $C_{32}H_{28}O_{16}Ru_2Re$: C, 36.37; H, 2.67. Found: C, 36.51; H, 2.81. IR (KBr disk, $cm^{-1}$): 3080−2840w, 1605vs, 1442−1396vs, 1262vs, 1172vs, 976w, 933w, 914w, 849m, 773m, 649m, 320vw. $\mu_{eff}$ (rt) = 3.67 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 808 [$Ru_2(\mu\text{-}O_2CC_6H_4\text{-}p\text{-}OMe)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Synthesis of $Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)$ (7) and $Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)(H_2O)$ (8).** The reaction of [$Ru_2(\mu\text{-}O_2CPh)_4$]$BF_4$ and $NBu_4ReO_4$ was carried out in methanol as described above for **1**−**6**, leading to a brown precipitate and a brown solution. The brown precipitate was filtered out, washed with methanol, and dried under a vacuum to give polymer **7**. Yield: 25%. Anal. Calcd for $C_{28}H_{20}O_{12}Ru_2Re$: C, 35.90; H, 2.15. Found: C, 35.67; H, 2.23. IR (KBr disk, $cm^{-1}$): 3200−3066w, 1600m, 1464−1407vs, 974, 933m, 910m, 872s, 845m, 721s, 714s, 690s, 315vw. $\mu_{eff}$ (rt) = 4.09 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 688 [$Ru_2(\mu\text{-}O_2CPh)_4$]; ($ESI^-$): 251 ($ReO_4$).

The brown solution was pumped to dryness. Red crystals suitable for X-ray diffraction of [$Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2$][$Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2$] (**8**) (Yield: 28%) were obtained by the evaporation of a dichloromethane solution of the solid residue at room temperature. Anal. Calcd for $C_{56}H_{44}O_{26}Ru_4Re_2$: C, 35.22; H, 2.32. Found: C, 35.19; H, 2.28. IR (KBr disk, $cm^{-1}$): 3066−2925w, 1600m, 1496−1408vs, 977w, 946m, 899m, 858s, 717s, 690s, 315vw. $\mu_{eff}$ (rt) = 3.77 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 688 [$Ru_2(\mu\text{-}O_2CPh)_4$]; ($ESI^-$): 251 ($ReO_4$).

**Synthesis of $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$ (9).** To a methanol solution of [$Ru_2(\mu\text{-}O_2CPh)_4$]$BF_4$ (0.23 g, 0.30 mmol) was added an excess of tetrabutylammonium perrhenate (0.75 g, 1.50 mmol). The reaction mixture was stirred for 16 h. A precipitate was formed together with a brown solution. The solid was filtered and identified as **7** (yield: 27%), and the solution was pumped to dryness. A dichloromethane solution of this residue solid was layered with hexane to give red-brown crystals of **9**·0.5$H_2O$, suitable for X-ray diffraction. Yield: 38%. Anal. Calcd for $C_{44}H_{57}O_{16.5}NRu_2Re_2$: C, 36.74; H, 3.99; N, 0.97. Found: C, 36.45; H, 3.90; N, 0.85. IR (KBr disk, $cm^{-1}$): 2962−2875m, 1600m, 1497−1407vs, 970w, 922s, 855s, 721s, 690s, 310vw. $\mu_{eff}$ (rt) = 3.97 $\mu_B$. Mass spectral data [*m*/*z* (fragment)] ($ESI^+$): 688 [$Ru_2(\mu\text{-}O_2CPh)_4$]; ($ESI^-$): 742 [$NBu_4(ReO_4)_2$].

**X-ray Crystallographic Procedures.** Details of the data collection and crystal structure refinement corrections for **3**·THF, **4**, **8**, and **9**·0.5$H_2O$ are summarized in Table 1. Representative crystals were mounted on a Bruker Smart-CCD diffractometer with graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation. Data were collected, at 293(2) K, over a hemisphere of the reciprocal space by a combination of three exposure sets. The cell parameters were refined by a least-squares fit of all the reflections collected. The

**Table 2.** Selected Bond Length (Å) and Angles (deg) for **3**·THF, **4**, **8**, and **9**·0.5$H_2O$

| **3**·THF | | **4** | |
|---|---|---|---|
| Ru(1)−Ru(1)#2 | 2.2667(9) | Ru(1)−Ru(2) | 2.2646(10) |
| Ru(1)−O(1) | 2.247(4) | Ru(1)−O(5) | 2.260(7) |
| Re(1)−O(1) | 1.741(4) | Ru(2)−O(8)#1 | 2.255(7) |
| O(1)−Ru(1)−Ru(1)#2 | 175.74(13) | Re(1)−O(5) | 1.735(7) |
| Re(1)−O(1)−Ru(1) | 148.6(3) | Re(1)−O(8) | 1.749(7) |
| | | Ru(2)−Ru(1)−O(5) | 176.67(19) |
| | | O(8)#1−Ru(2)−Ru(1) | 177.9(2) |
| | | Re(1)−O(5)−Ru(1) | 131.4(4) |
| | | Re(1)−O(8)−Ru(2)#2 | 140.3(4) |

| **8** | | **9**·0.5$H_2O$ | |
|---|---|---|---|
| Ru(1)−Ru(1)#1 | 2.272(3) | Ru(1)−Ru(1)#2 | 2.270(5) |
| Ru(1)−O(2) | 2.247(13) | O(5)−Ru(1) | 2.22(2) |
| Re(1)−O(2) | 1.697(12) | O(5)−Re(1) | 1.751(18) |
| Ru(2)−Ru(2)#2 | 2.251(4) | O(5)−Ru(1)−Ru(1)#2 | 175.9(5) |
| Ru(2)−O(12) | 2.276(13) | Re(1)−O(5)−Ru(1) | 131.3(10) |
| O(2)−Ru(1)−Ru(1)#1 | 177.6(4) | Ru(2)−Ru(2)#1 | 2.273(5) |
| Re(1)−O(2)−Ru(1) | 145.6(9) | O(13)−Ru(2) | 2.233(18) |
| Ru(2)#2−Ru(2)−O(12) | 176.8(4) | O(13)−Re(2) | 1.735(18) |
| | | O(13)−Ru(2)−Ru(2)#1 | 172.8(5) |
| | | Re(2)−O(13)−Ru(2) | 144.0(11) |

structures were solved by direct methods and refined by the full-matrix least-squares methods against $F^2$ of all data. Calculations were performed with the aid of the SHELXS and SHELXL programs.[24,25] A final mixed refinement for complexes **3**·THF, **4**, **8**, and **9**·0.5$H_2O$ was undertaken with anisotropic thermal parameters for the non-hydrogen atoms with some exceptions. For **3**·THF, the carbon atoms of the methyl groups were isotropically refined. For **4**, the carbon atom of three of the four methyl groups, some of the oxygen atoms of the methoxy groups, and some of the oxygen atoms of the perrhenate ligand were also isotropically refined. For **8**, the hydrogen atoms of the coordination water molecules were not found by Fourier synthesis. However, the distances O(12)···O(7) [2.79(2) Å] and O(12)···O(8)# [2.647(18) Å] suggest the presence of hydrogen-bond interactions. For **9**·0.5$H_2O$, the tetrabutylammonium groups are disordered and the butyl chains were refined with geometrical restraints and a variable common carbon−carbon distance. For the noncoordinated oxygen, atoms of the perrhenate ion were the only refined coordinates.

Figures 2, 4, and S4 (Supporting Information) have been generated using the Mercury 1.3 Program.

## Results and Discussion

**Synthetic Aspects.** The abstraction of the chloride ligand in $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = Me, CMePh$_2$, CMe$_3$, CH$_2$CH$_2$OMe, C(Me)=CHEt, C$_6$H$_4$-*p*-OMe, Ph] with AgBF$_4$ in tetrahydrofuran leads to the compounds $[Ru_2(\mu\text{-}O_2CR)_4(THF)_2]BF_4$. The reaction of these complexes with NBu$_4$ReO$_4$ in a 1:1 molar ratio gives different species depending on the carboxylate bridging ligand. Thus, polymeric compounds, $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$ where R = Me (**1**), CMePh$_2$ (**2**), CMe$_3$ (**3**), CH$_2$CH$_2$OMe (**4**), C(Me)=CHEt (**5**), C$_6$H$_4$-*p*-OMe (**6**), and Ph (**7**), were obtained. In these complexes, the $ReO_4^-$ anions connect the dimetallic units through the axial positions. Complexes **1**−**6** were also obtained when an excess of NBu$_4$ReO$_4$ was used. In contrast, in the reaction of $[Ru_2(\mu\text{-}O_2CPh)_4(THF)_2]BF_4$ with NBu$_4$ReO$_4$ in a 1:1 molar ratio, in addition to the polymeric **7**, the cation/anion complex $[Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2][Ru_2(O_2CPh)_4(ReO_4)_2]$ (**8**) was also isolated. However, in a similar reaction with an excess of perrhenato ions, complexes **7** and $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$ (**9**) were obtained.

On the other hand, the substitution of the acetate ligands in $Ru_2Cl(\mu\text{-}O_2CMe)_4$ by perrhenate ions has not been observed. The Ru−Ru distances in complexes **3**·THF, **4**, **8**, and **9**·0.5$H_2O$ are in the range 2.251(4)−2.273(5) Å, whereas the oxygen−oxygen distances of the perrhenato ligands, in the same complexes, vary from 2.700 to 2.857 Å. Therefore, the O···O distance in the perrhenate ligands is too large and could not be appropriated for the substitution of the carboxylate group in $Ru_2Cl(\mu\text{-}O_2CR)_4$. Attempts to obtain heteropolynuclear complexes by substitution of the carboxylate ligands by perrhenate groups in dinuclear complexes such as $Cu_2(\mu\text{-}O_2CR)_4$ with a metal−metal length similar to the O−O distance in the perrhenate ion are currently under study.

**Crystal Structures of $Ru_2(\mu\text{-}O_2CCMe_3)_4(ReO_4)$·THF (3·THF) and $Ru_2(\mu\text{-}O_2CCH_2CH_2OMe)_4(ReO_4)$ (4).** Both complexes have four carboxylate ligands surrounding a diruthenium core with the axial positions occupied by bridging perrhenate groups giving chains. Selected bond lengths and angles are listed in Table 2. The Ru−Ru distances in **3**·THF and **4** were found to be 2.2667(9) and 2.2646(10) Å, respectively. These distances are typical for tetracarboxylatodiruthenium(II,III) units.[3] The Ru−O$_{ax}$ bond lengths, 2.247(4) Å in **3**·THF and 2.260(7) and 2.255(7) Å in **4**, are similar to those found[26,27] in other polymeric complexes with O-donor ligands bridging the diruthenium units, such as $Ru_2(\mu\text{-}O_2CEt)_4(O_2CEt)$ [2.157(10) and 2.172(10) Å], $Ru_2(\mu\text{-}O_2CCF_3)_4(O_2CCF_3)$ [2.157(10) Å], and $Ru_2(\mu\text{-}O_2CPh)_4(O_2CPh)\cdot(HO_2CPh)$ [2.244(3) and 2.214(3) Å]. In both complexes, the rhenium atoms are pseudotetrahedral and are surrounded by two bridging and two terminal oxygen

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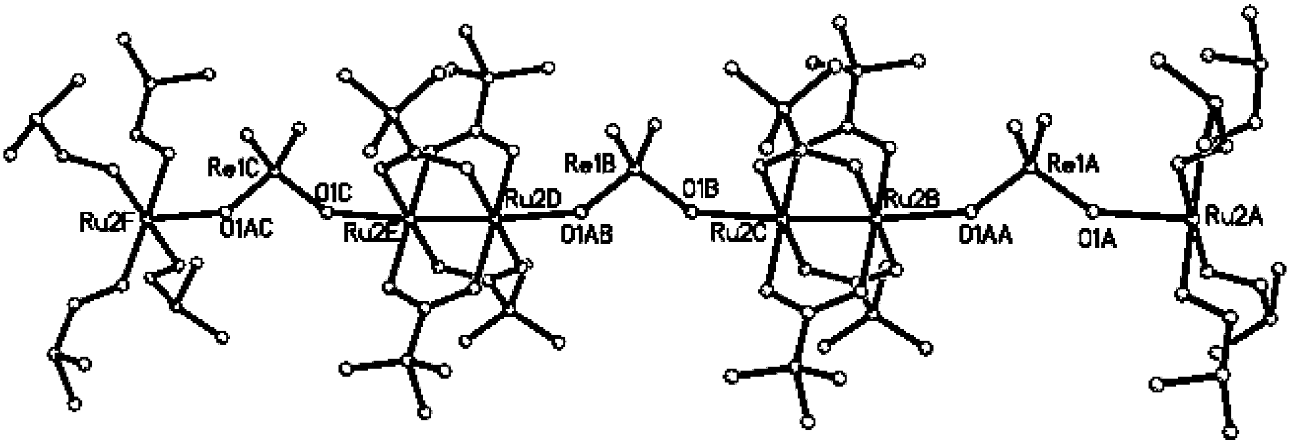

**Figure 1.** Linear chain, in the solid state, of $Ru_2(\mu\text{-}O_2CCMe_3)_4(ReO_4)\cdot THF$ (**3**·THF). Hydrogen atoms and the crystallization molecule are omitted for clarity.

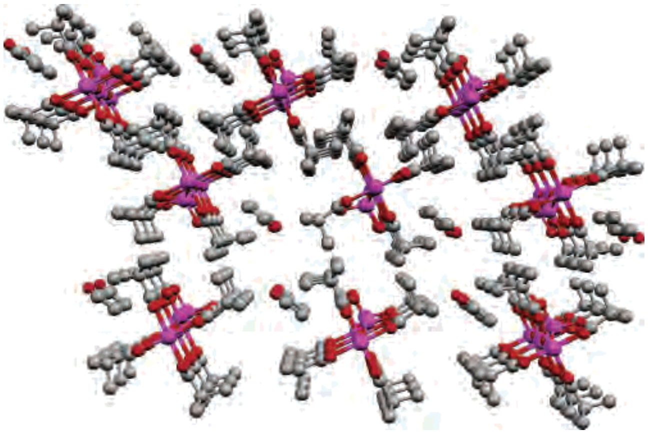

**Figure 2.** Packing of the eclipsed linear chains of $Ru_2(\mu\text{-}O_2CCMe_3)_4(ReO_4)\cdot THF$ (**3**·THF) along the *b* axis. Hydrogen atoms are omitted for clarity.

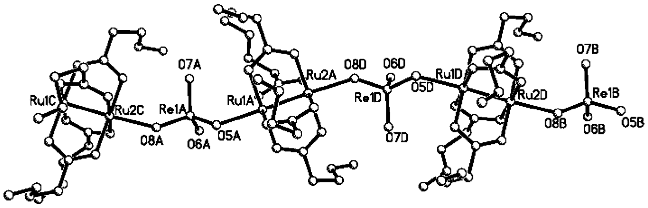

**Figure 3.** Nonlinear chain, in the solid state, of $Ru_2(\mu\text{-}O_2CCH_2CH_2OMe)_4(ReO_4)$ (**4**). Hydrogen atoms are omitted for clarity.

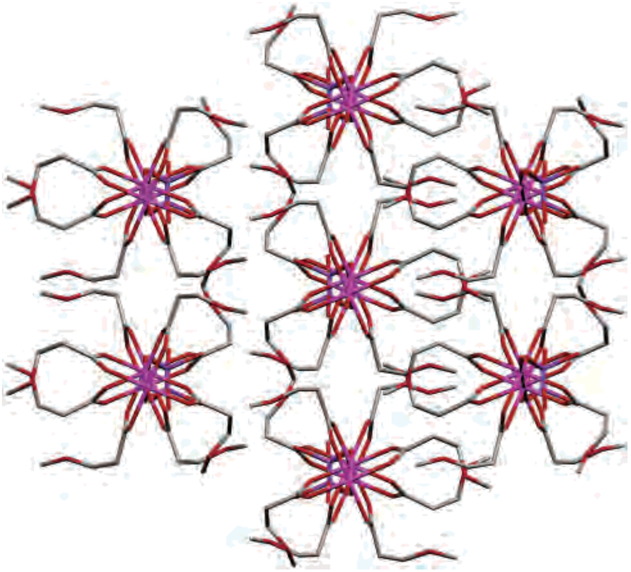

**Figure 4.** View of the staggered conformation of the chains in complex $Ru_2(\mu\text{-}O_2CCH_2CH_2OMe)_4(ReO_4)$ (**4**). Hydrogen atoms are omitted for clarity.

atoms. Thus, the bridging perrhenate groups show a small and similar degree of deviation from tetrahedral geometry. In **3**·THF, the Re−O bond distances are in the range 1.674(8)−1.741(4) Å and the O−Re−O angles vary from 108.7(3) to 110.1(5)°, whereas in **4**, the ranges are 1.677(16)−1.755(11) Å and 107.3(6)−111.8(6)°, respectively.

In complex **3**·THF, the angle Re(1)−O(1)−Ru(1) is 148.6(3)°. However, the diruthenium units are connected by the perrhenate groups, giving Ru−Ru···Ru angles of 180°, leading to a 1D supramolecular structure (Figure 1). The linearity of the chains can be observed in the packing view along the *b* axis displayed in Figure 2, where the compound shows a total eclipsed geometry. The chain axes are parallel to each other in the crystal and are packed only by normal van der Waals forces.

In complex **4**, the diruthenium units and the perrhenate groups are situated in a similar way to that of complex **3**·THF but the angle Ru−Ru···Ru is 162.07°, and therefore, the monodimensional supramolecular structure is formed by nonlinear chains (Figure 3). Another difference in the arrangement, in the solid state, in complexes **3**·THF and **4**, is that in complex **4**, although each diruthenium unit has an eclipsed conformation, the disposition of the diruthenium blocks have a staggered conformation with a deviation ~45° from eclipsed (Figure 4). In this case, the chains are also packed only by normal van der Waals forces. The carboxylate ligand nature with different steric requirements could be the reason for the differences in the arrangement of these complexes. ORTEP views of compounds **3**·THF and **4** are available in the Supporting Information (Figures S1 and S2).

**Crystal Structure of $Ru_2[\mu\text{-}O_2CC(Me){=}CHEt]_4(ReO_4)$ (5).** The structure of this complex can only be discussed qualitatively because of its poor nature.[28] Despite everything, it is clear that the structure of this complex is similar to that found for compounds **3**·THF and **4**. The dinuclear unit has

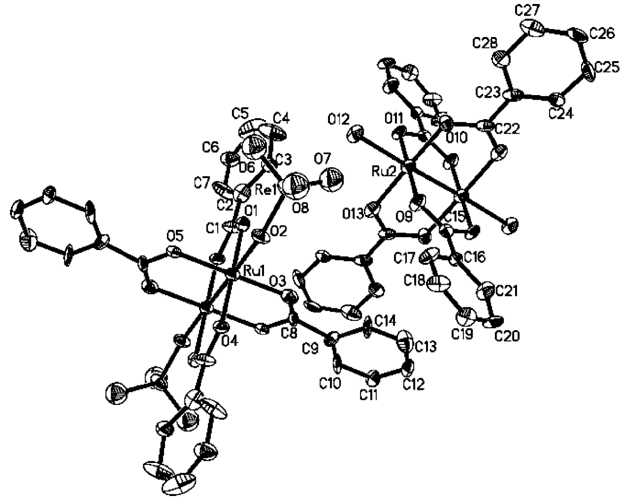

**Figure 5.** ORTEP view of $[Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2][Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$ (**8**). Hydrogen atoms are omitted for clarity.

two ruthenium atoms linked by four *trans*-2-methyl-2-pentenoate ligands. The axial positions are occupied by bridging perrhenate ligands, giving chains (Figure S3, Supporting Information). Complex **5** shows, in the solid state, monodimensional zigzag chains analogous to complex **4**.

**Crystal Structures of $Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)(H_2O)$ (8) and $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]\cdot 0.5H_2O$ (9·0.5H₂O).** The crystal structure determination of complex **8** shows the presence of cationic $[Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2]^+$ and anionic $[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]^-$ species (Figure 5). Therefore, compound **8** should be formulated as $[Ru_2(\mu\text{-}O_2CPh)_4(H_2O)_2][Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]$. Both ions contain a diruthenium(II,III) unit with four benzoates as equatorial bridging ligands. The cationic species has two axially coordinated water molecules, similar to those found[5a,29] in $Ru_2I(\mu\text{-}O_2CCH_2CH_2OPh)_4(H_2O)\cdot 0.5H_2O$ and $Ru_2Cl(\mu\text{-}O_2CCH_2OEt)_4\cdot(H_2O)$. On the contrary, the anionic unit has two O-bonded perrhenate ligands. There is only one other complex[30] structurally characterized with cationic/anionic units, $[Ru_2(\mu\text{-}O_2CPh)_4(EtOH)_2][Ru_2(\mu\text{-}O_2CPh)_4(HSO_4)_2]$. To our knowledge, complex **8** is the first heteropolynuclear tetracarboxylatodiruthenium(II,III) complex with an anion/cation arrangement.

In complex **8**, a three-dimensional network via hydrogen-bond interactions between cationic and anionic units is observed. Each axial water molecule of the cationic units is hydrogen bonded to two different $ReO_4^-$ groups of the adjacent anionic units. Thus, oxygen atom O12 of the water molecule is linked to O7 and O8 of two different anionic units. The distances O(12)···O(7) and O(12)···O(8)#3 are 2.79(2) and 2.647(18) Å, respectively. The environment of the rhenium atoms is distorted tetrahedral, being coordinated to one free oxygen, to two oxygens hydrogen bonded to water molecules, and to one oxygen bonded to a ruthenium atom. As a consequence, the whole molecular structure can be seen as a 3D structure (Figure S4, Supporting Information).

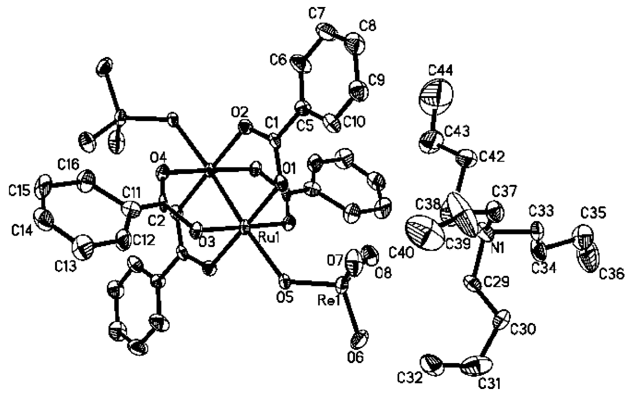

**Figure 6.** ORTEP view of $NBu_4[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]\cdot 0.5H_2O$ (**9**·0.5H₂O). Hydrogen atoms and the crystallization solvent are omitted for clarity.

The crystal structure of complex **9**·$0.5H_2O$ shows anionic units $[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]^-$, $NBu_4^+$ cations, and half a molecule of crystallization water. An ORTEP view of this complex is depicted in Figure 6. The asymmetric unit consists of half of **9**·$0.5H_2O$ related to the other half via a crystallographic inversion center located in the middle of the Ru−Ru bond. The dimetallic $[Ru_2(\mu\text{-}O_2CPh)_4(ReO_4)_2]^-$ anions are analogous to those observed in complex **8**, having two perrhenato groups in the axial positions and four carboxylate bridging groups. In this case, the rhenium atoms are coordinated to three terminal oxygens and to one oxygen bonded to the ruthenium atom.

Selected bond lengths and angles, for **8** and **9**·$0.5H_2O$, are given in Table 2. The Ru−Ru bond lengths are 2.251(4) Å (cation) and 2.272(3) Å (anion) in **8** and 2.270(5) and 2.273(5) Å in **9**·$0.5H_2O$. These distances are similar to those found[5b,27,30,31] in $Ru_2(\mu\text{-}O_2CPh)_4X$ [X = Cl, 2.290(1); Br, 2.2906(7); I, 2.2965(6); $O_2CPh$, 2.277(1) and 2.278(1) Å] and $[Ru_2(\mu\text{-}O_2CPh)_4(HSO_4)(EtOH)]$ [2.265(2) (cation) and 2.272(2) Å (anion)].

On the other hand, the distances $Ru-O_{perrhenate}$ are 2.247(13) Å in **8** and 2.22(2) and 2.233(18) Å in **9**·$0.5H_2O$. The metal−oxygen perrhenate bond lengths in these complexes are slightly shorter in the anionic units, with two perrhenate ions at the axial positions, than in polymeric arrangements. This fact was also observed[32] very recently in mono- and dihalotetracarboxylatodiruthenium(II,III) compounds.

The distortion of the tetrahedral environment of these monodentate perrhenate groups is bigger than that found in **3**·THF and **4**. Thus, in complex **8**, the Re−O bond distances are in the range 1.619(7)−1.697(12) Å and the O−Re−O angles vary from 105.7(11) to 115.0(9)°. In complex **9**·$0.5H_2O$, the ranges are 1.686(12)−1.751(18) Å and 104.8(15)−111.8(10)°, respectively. The more strained tetrahedral environment in **8** could be due to the hydrogen bonds

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(28) Complex **5** crystallizes in the monoclinic system, *C*2/*c*, with cell dimesions $a = 13.3017(18)$ Å, $b = 15.573(2)$ Å, $c = 15.150(2)$ Å, $\beta = 90.649(3)°$; $V = 3138.1(7)$ Å$^3$, $Z = 4$. Of the 8052 reflections collected, 2757 were unique [R(int) = 0.0974]. The final R indices [$I > \sigma(I)$] are R1 = 0.0868 and wR2 = 0.1851.

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between the perrhenate groups and the water molecules. A distortion caused by hydrogen bonds was also observed in the complex[33] $[\{(UO_2)(OPPh_3)_3\}_2(\mu_2\text{-}O_2)][ReO_4]_2$.

The $Re-O_{bridging}$ distances in **3**, **8**, and **9**·$0.5H_2O$ are somewhat longer than the $Re-O_{terminal}$ distances, whereas in complex **4**, these distances are similar. Examples of both behaviors have been described in the literature.[15,33]

**Spectroscopic Properties.** The IR spectra of all compounds show in the COO stretching region the typical pattern of bridging carboxylate ligands. Complex **9** exhibits characteristic bands due to the $NBu_4^+$ cation. The tetrahedral perrhenate ion has four normal modes of vibration, although only $\upsilon_3$ and $\upsilon_4$ are infrared-active.[34] These modes for monodentate and bidentate (or bridging bidentate) bonding should split into two and three bands, respectively, while $\upsilon_1$ and $\upsilon_2$ become IR-active for unidentate coordination.[12,33−35] The bands corresponding to $\upsilon_1$ and $\upsilon_3$ appear, approximately, at 970 and 920 $cm^{-1}$, respectively, and $\upsilon_2$ and $\upsilon_4$ at ca. 330 $cm^{-1}$.[12,34] In the infrared spectra of complexes $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$ (**1**−**7**), $\upsilon_1$ is a weak band at 974−980 $cm^{-1}$, whereas $\upsilon_3$ splits into three or four bands between 845 and 948 $cm^{-1}$, attributed to bridging bidentate $ReO_4^-$ groups. For compound **9**, where the perrhenate ligand is monodentate, there are only two bands (922 and 855 $cm^{-1}$) corresponding to $\upsilon_3$. However, the $\upsilon_3$ of **8** splits into three bands at 946, 899, and 858 $cm^{-1}$. The crystalline structure of this complex shows significant distortion in the perrhenate anions due to the hydrogen bonds with adjacent water molecules, which could modify the tetrahedral symmetry, increasing the number of bands. A weak absorption corresponding to $\upsilon_1$, at 977 (**8**) and 970 (**9**) $cm^{-1}$, is also observed. For all complexes, a very weak band is observed in the range 310−330 $cm^{-1}$. This absorbance can be assigned to $\upsilon_4$, although $\upsilon_2$ also appears at these wavenumbers.

All mass spectra ($ESI^+$) show the base peak corresponding to the ion $[Ru_2(\mu\text{-}O_2CR)_4]^+$.

**Magnetic Properties.** Magnetic measurements of all the compounds show magnetic moments at room temperature corresponding to the presence of three unpaired electrons per dimetallic unit. These magnetic moments (3.67−4.53 $\mu_B$) are in accordance with the ground-state configuration $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ proposed by Norman et al.[36] The representation of the magnetic moment versus temperature shows a pronounced decrease of the magnetic moment, mainly at very low temperatures, whereas the molar susceptibility increases continuously with decreasing temperature and no maximum is observed. This behavior has been observed in other molecular and zigzag polymeric diruthenium(II,III) compounds and has been ascribed[5,17,19,21,32,37,38] to a large zero-field splitting (ZFS) and a weak degree of antiferromagnetic coupling between the dimetallic units.

The ZFS effect on the susceptibility can be quantified by considering the Hamiltonian $\hat{\mathscr{H}}_D = SDS$, as described by O'Connor.[39] The perturbation of a weak antiferromagnetic coupling over the ZFS system can be considered by using the molecular field approximation.[39] Thus, for an $S = {}^3/_2$ spin system, the magnetic susceptibility can be expressed as

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

where $\chi'_M$ includes the temperature-independent paramagnetism (TIP):

$$\chi'_M = \chi_M + TIP$$

and $\chi_M$ considers the ZFS in the parallel and perpendicular components as

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

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

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

Finally, the consideration of a paramagnetic impurity ($P$) leads to the expression

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

Complexes **8** and **9** have a molecular nature, whereas **1**−**7** are polymeric. In complex **3**·THF, an arrangement in the solid state in linear chains with respect to the axis Ru−Ru···Ru was observed. In linear chlorotetracarboxylatodiruthenium(II,III) compounds, a maximum in the molar susceptibility versus temperature curve has been found.[5a,40] In this case, strong antiferromagnetic coupling between the diruthenium(II,III) units through chlorine atoms gives rise to an inversion of the magnetic susceptibility curve. However, in complexes $Ru_2(\mu\text{-}O_2CR)_4(ReO_4)$, although there are linear chains with respect to the diruthenium units and the rhenium atoms have vacant d orbitals, the tetrahedral geometry of the bridging perrhenate ligands prevents a strong antiferromagnetic coupling.

The above-mentioned model has been successfully used to fit the magnetic data of complexes **1**−**9**. A very good agreement between the experimental and calculated curves of the magnetic moment and the molar susceptibility for complexes **1**−**9** was observed. The parameters obtained in these fits (Table 3) are similar to those described[5,17,19,21,32,37] for other diruthenium(II,III) species, with very low $zJ$ values (from −0.04 to −1.74 $cm^{-1}$). Figure 7 shows the experimental and calculated curves for complex **3**·THF. Similar curves have been obtained for the other complexes, with $D$

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**Table 3.** Magnetic Parameters for Complexes **1**−**9** Obtained in the Fits to the Magnetic Moment as a Function of Temperature

| compound | g | $D$ (cm$^{-1}$) | $zJ$ (cm$^{-1}$) | TIP (mL/mol) | $P$ (%) | $\sigma^{2\,a}$ |
|---|---|---|---|---|---|---|
| **1** | 2.18 | 50.86 | −1.74 | $7.53 \times 10^{-10}$ | 0.03 | $9.44 \times 10^{-5}$ |
| **2** | 2.21 | 50.03 | −1.38 | $2.57 \times 10^{-12}$ | $6.82 \times 10^{-3}$ | $7.21 \times 10^{-5}$ |
| **3** | 2.12 | 53.32 | −1.38 | $2.84 \times 10^{-10}$ | $6.35 \times 10^{-5}$ | $9.70 \times 10^{-5}$ |
| **4** | 2.08 | 63.29 | −0.38 | $3.59 \times 10^{-4}$ | $<10^{-6}$ | $4.83 \times 10^{-5}$ |
| **5** | 2.31 | 77.13 | −0.74 | $5.41 \times 10^{-4}$ | $2.24 \times 10^{-2}$ | $2.26 \times 10^{-5}$ |
| **6** | 2.06 | 42.23 | −0.18 | $1.06 \times 10^{-19}$ | 0.14 | $8.82 \times 10^{-5}$ |
| **7** | 2.14 | 58.98 | −0.07 | $7.56 \times 10^{-10}$ | 0.82 | $3.77 \times 10^{-5}$ |
| **8** | 2.06 | 50.00 | −0.07 | $1.10 \times 10^{-10}$ | $2.20 \times 10^{-3}$ | $9.79 \times 10^{-4}$ |
| **9** | 2.10 | 53.84 | −0.04 | $3.05 \times 10^{-9}$ | $4.62 \times 10^{-5}$ | $1.73 \times 10^{-4}$ |

[a] $\sigma^2 = \sum(\mu_{\text{eff calc}} - \mu_{\text{eff exp}})^2/\sum\mu_{\text{eff exp}}^2$.

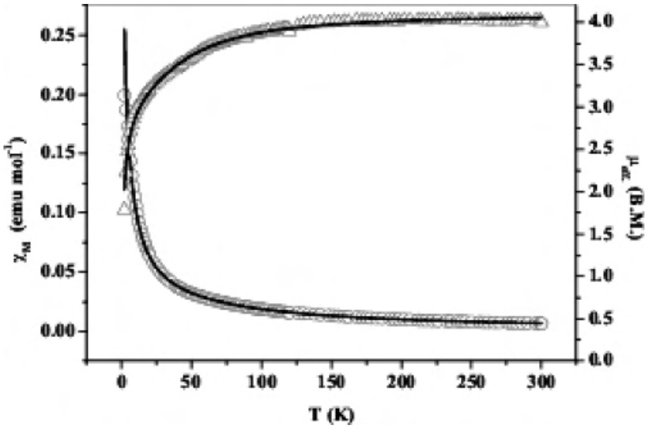

**Figure 7.** Temperature dependence of the molar susceptibility $\chi_M$ (○) and $\mu_{\text{eff}}$ (△) for $Ru_2(\mu\text{-}O_2CCMe_3)_4(ReO_4)$ (**3**·THF). Solid lines result from least-squares fits using the model described in the text.

values ranging from 42.23 to 77.13 cm$^{-1}$. Analogous $D$ values have been calculated for other tetracarboxylato complexes.[5,17,19,21,32,37] The $zJ$ values (from −0.04 to −1.74 cm$^{-1}$) are very low according to the presence of diruthenium(II,III) units connected by diamagnetic tetrahedral perrhenate groups in polymeric complexes **1**−**7**. Similar $zJ$ values are calculated for complexes **8** and **9**, which are nonpolymeric.[5,17,19,21,32,37] In these cases, a through-space antiferromagnetic interaction similar to that found in other molecular diruthenium complexes must be occurring.[5,19,21,32,] The existence of this through-space antiferromagnetic interaction, at very low temperatures, in polymeric complexes **1**−**7** instead of magnetic communication through perrhenate groups cannot be discarded.

## Conclusions

Replacement of the chloride ligand in the complexes $Ru_2Cl(\mu\text{-}O_2CR)_4$ by the perrhenate group results in heteropolynuclear compounds. Depending on the bridging ligand's nature, discrete heteropolynuclear species or monodimensional supramolecular structures were formed by alternating diruthenium units and perrhenate groups. A 3D supramolecular assembly via hydrogen bonds is also obtained with the benzoate ligand in an anion/cation complex. This study demonstrates that the tetracarboxylatodiruthenium(II,III) units have a very high tendency to coordinate axially with the perrhenate group. The most usual arrangement of these tetracarboxylatoperrhenatodiruthenium(II,III) complexes is as monodimensional linear or zigzag chains, but the formation of anionic or anion/cation complexes is also possible. The large O−O distance in the perrhenate group could prevent the replacement of the carboxylate ligands.

**Acknowledgment.** We are grateful to the Ministerio de Educación y Ciencia (Dirección General de Investigación, Project No. MAT2004-22102-E) for financial support.

**Supporting Information Available:** X-ray crystallographic data for **3**·THF, **4**, **5**, **8**, and **9**·0.5$H_2O$ in CIF format; ORTEP diagrams of **3**·THF (Figures S1 and S2) and **4**; a PLUTO diagram of the zigzag chain in **5** (Figure S3), and a packing diagram of **8** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050757X