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Article

Unligated Diruthenium(II,II) Tetra(trifluoroacetate): The First X-ray Structural Study, Thermal Compressibility, Lewis Acidity, and Magnetism

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The title compound, $[Ru_2(O_2CCF_3)_4]$ (**1**), has been obtained without any exogenous ligands and crystallized by deposition from the gas phase at 170 °C. Its crystal structure has been determined for the first time to confirm an infinite chain motif built on axial Ru···O interactions of the diruthenium(II,II) units. The X-ray diffraction studies at variable temperatures showed no phase transitions in the range of 295–100 K but revealed a significant decrease in the volume per atom from 14.2 to 13.3 Å^3. This noticeable thermal compressibility effect is discussed in connection with the solid-state packing of the $[Ru_2(O_2CCF_3)_4]_\infty$ chains. The highly electrophilic character of the diruthenium(II,II) units has been shown by the gas-phase deposition reaction of $[Ru_2(O_2CCF_3)_4]$ with an aromatic donor substrate, namely [2.2]paracyclophane ($C_{16}H_{16}$). As a result of the above reaction, a new arene adduct $[Ru_2(O_2CCF_3)_4 \cdot C_{16}H_{16}]$ (**2**) has been isolated in crystalline form. It has an extended one-dimensional (1D) chain structure comprised of alternating building units and based on the rare bridging mode of [2.2]paracyclophane, $[Ru_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]_\infty$. The magnetic susceptibility of **1** and **2** has been measured and compared in the range of 1.8–300 K. In addition, in the course of synthesis of **1** by the carboxylate exchange reactions, a new mixed-carboxylate diruthenium(II,II) core complex $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**), bearing no exogenous ligands, has also been isolated and structurally characterized. It exhibits an interesting polymeric structure in which the ruthenium(II) centers selectively form axial interdimer contacts with the O-atoms of the propionate groups only.

Introduction

Diruthenium tetracarboxylates represent an important class of transition-metal complexes[1] that display interesting magnetic,[2] electronic,[3] mesomorphic,[4] gas sorption,[5] and catalytic properties.[6] In contrast to the very extensive chemistry of the mixed-valent Ru_2^{5+} species,[1] far fewer complexes of the homovalent Ru_2^{4+} core are known,[7,8] with all structurally characterized examples having various axially coordinated

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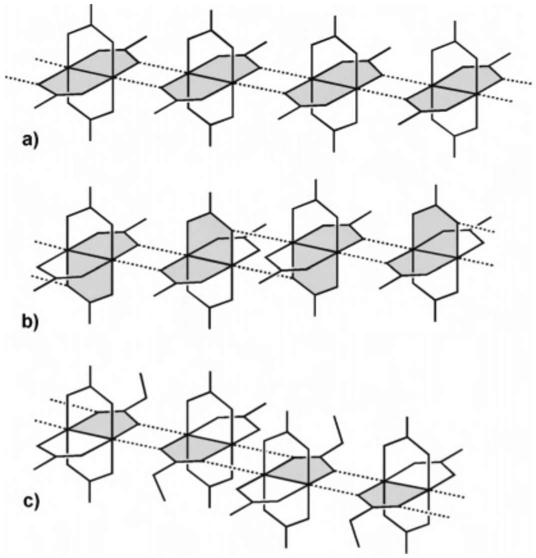
ligands.[9] In general, the preparation of dimetal tetracarboxylate complexes without exogenous ligands exhibiting extended or discreet structures represents a significant synthetic challenge.[10] For the former, the sublimation−deposition procedures have been successfully used to obtain solvent-free crystals of volatile complexes,[11] but the number of structurally characterized dimetal units having no exogenous ligands is still limited. For the diruthenium(II,II) core carboxylates, attempts to obtain unligated $[Ru_2(O_2CR)_4]$ complexes in noncoordinating solvents were unsuccessful,[12] and no crystallographic data for such complexes have been reported yet. Because such structural data were not available, the ground state for the $[Ru_2(O_2CR)_4]$ complexes having two unpaired electrons has been theoretically derived using molecular geometry and average geometrical parameters taken for known ligated compounds.[3,13] Moreover, the nature of the ground state of the doubly bonded paramagnetic $[Ru_2(O_2CCF_3)_4]$ species is still in question due to the fact that the δ^* and π^* HOMO orbitals are nearly degenerate.[13]

The synthesis of diruthenium(II,II) tetra(trifluoroacetate) has been accomplished by Wilkinson and co-workers in 1987 with three of its bis-adducts being structurally characterized since then.[7,14] More recently, the electrophilic $[Ru_2(O_2CCF_3)_4]$ unit has been used as a paramagnetic electron-rich building block for the formation of extended hybrid materials,[2a,b] but the crystal structure of the parent $[Ru_2(O_2CCF_3)_4]$ unit remained unknown. Therefore, we carried out the preparation of diruthenium(II,II) tetra(trifluoroacetate) free of exogenous axial ligands and achieved its crystallization from the gas phase. Single-crystal X-ray diffraction studies of the title complex have been performed at six different temperatures in the range 295−100 K to show a noticeable thermal compressibility effect. We have also tested the reactivity of two-ended Lewis acidic $[Ru_2(O_2CCF_3)_4]$ units in the gas phase toward an aromatic donor substrate, [2.2]paracyclophane ($C_{16}H_{16}$). The resulting organometallic product has been structurally characterized, and its magnetic susceptibility has been compared with that of the parent diruthenium(II,II) trifluoroacetate complex. The results of these studies are discussed below.

Scheme 1



Results and Discussion

Metal carboxylates are known to exhibit a variety of structures. The main-group metal trifluoroacetate complex, $[Bi_2(O_2CCF_3)_4]$, has recently been shown to have a structure based on isolated dimetal units in the solid state.[15] Dimetal tetracarboxylates of transition metals in the absence of external donor molecules exhibit chain polymeric structures having axial interdimer interactions of metal centers with the carboxylate oxygen atoms of neighboring units. Within this common motif, two major packing patterns of dimetal units have been clearly distinguished, namely "flat ribbon" and "venetian blind" (Scheme 1; a and b, respectively). Whereas isomorphous dirhodium(II,II)[11a] and dimolybdenum(II,II)[16] tetra(trifluoroacetates) belong to the former type, copper(II) trifluoroacetate was found to be structurally unique.[11b] This diversity prompted us to pursue the X-ray diffraction study of the ruthenium(II) trifluoroacetate complex that was not structurally characterized in its "unsolvated" form before. Moreover, the Ru_2^{4+} core species deserve special attention due to their interesting electronic properties, because they exhibit, in addition to an electron-rich double metal−metal bond, a triplet ground state. Because the δ^* and the π^* antibonding orbitals lie very close in energy for the Ru_2^{4+} core,[3] they can be both occupied, and that can

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result in different electronic configurations. The latter are determined, in part, by the ligand environment at the Ru_2^{4+} core but can also be temperature dependent.[17] X-ray photoelectron spectroscopic studies performed on the $[Ru_2(O_2CCF_3)_4]$ complex did not allow for a definitive assignment of the ground state.[13] Therefore, we attempted to correlate here structural data on $[Ru_2(O_2CCF_3)_4]$ with magnetic susceptibility measurements and performed X-ray crystallographic studies at variable temperatures.

The target complex was prepared by the carboxylate-exchange reaction starting from diruthenium(II,II) tetra(acetate) using the literature methods.[7a,b] However, the preparation of the pure crystalline compound $[Ru_2(O_2CCF_3)_4]$, free of all exogenous ligands, was proved to be more difficult than was originally reported. The title molecule has a great avidity for axial ligands, and all our attempts to completely remove THF from the bis-adduct $[Ru_2(O_2CCF_3)_4 \cdot (THF)_2]$, as suggested,[7b] were unsuccessful. A lack of lability of the axial THF ligands in $[Ru_2(O_2CCF_3)_4 \cdot (THF)_2]$ in contrast to its rhodium analogue has also been noticed before.[2a] Our successful procedure was based on the extraction of the crude ruthenium trifluoroacetate product by diethyl ether,[18] followed by its recrystallization from acetone/hexanes to form $[Ru_2(O_2CCF_3)_4 \cdot (Me_2CO)_2]$.[19] Acetone was then removed by heating the bis-adduct at temperatures around 120 °C for 3 days under reduced pressure. Even such treatment was insufficient to completely eliminate the coordinated solvent, and multiple separations of the more volatile acetone adduct by sublimation at 140−160 °C were added to obtain the title product without any detectable traces of acetone, as it was confirmed by IR and by elemental analysis. It was a challenge to grow crystals of diruthenium(II,II) tetra(trifluoroacetate) and to handle those, because the compound is highly hydroscopic and rapidly absorbs moisture from the air or from incompletely dried glassware. In addition to that, the ruthenium(II) complex was found to be not as volatile as analogous rhodium(II), molybdenum(II), and copper(II) trifluoroacetates. Sublimation of the powder, obtained as described above, was performed at 170−175 °C in an evacuated sealed tube to afford very thin, red-brown needles of “unligated” $[Ru_2(O_2CCF_3)_4]$ (**1**).

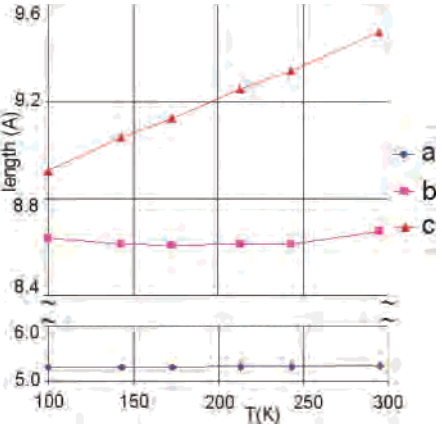

Figure 1. Temperature dependence of the unit cell parameters (*a*, *b*, and *c*) in the structure of **1**.

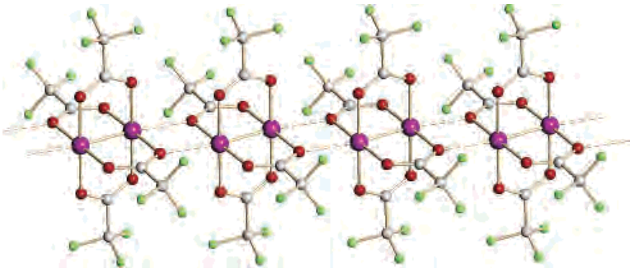

Figure 2. Fragment of the 1D polymeric chain in $[Ru_2(O_2CCF_3)_4]$ (**1**). Ru purple, O red, F green, C gray.

The single-crystal X-ray diffraction studies of the $[Ru_2(O_2CCF_3)_4]$ complex have been performed at six different temperatures ranging from 295 to 100 K. The title compound is isostructural to dirhodium(II,II)[11a] and dimolybdenum(II,II)[16] tetra(trifluoroacetates) and crystallizes in the triclinic $P\bar{1}$ space group. Although no phase transitions in this temperature range were observed for the ruthenium complex, a noticeable decrease of the unit cell volume from 425.1(2) Å^3 at 295 K to 398.77(8) Å^3 at 100 K has been detected. The overall effect of temperature on the lattice parameters of **1** has been examined. The plot shown in Figure 1 indicates that there is a substantial gradual increase of the parameter c in the range 100−295 K, whereas the parameters a and b do not exhibit a temperature dependence. The angle α steadily decreases from 83.493(2) to 79.456(5)°, whereas β increases from 83.698(2) to 85.705(5)°, and γ is almost constant (86.921(2) and 86.776(5)°) in the same temperature range (see Supporting Information). This results in the significant overall thermal compressibility in the structure of $[Ru_2(O_2CCF_3)_4]$ to give a calculated volume per atom of 14.2 and 13.3 Å^3 at 295 and 100 K, respectively. Similar behavior has been detected in the variable-temperature X-ray diffraction study of bismuth(II) trifluoroacetate that showed the 1.9% volume contraction in the same temperature range.[15] The effect is even more pronounced for $[Ru_2(O_2CCF_3)_4]$, with a 6.3% volume decrease.

The title ruthenium complex exhibits the expected one-dimensional (1D) polymeric structure based on axial Ru$\cdots$O interactions (Figure 2). It is now proved that $[Ru_2(O_2CCF_3)_4]$ forms “flat ribbon” chains similar to those of rhodium(II) and molybdenum(II) trifluoroacetates and common for many other dimetal tetracarboxylates (Scheme 1a).

The dimetal $[Ru_2(O_2CCF_3)_4]$ unit is centrosymmetric, having an inversion center at the midpoint of the metal−

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[17] Cotton, F. A.; Murillo, C. A.; Reibenspies, J. H.; Villagran, D.; Wang, X.; Wilkinson, C. C. *Inorg. Chem.* **2004**, *43*, 8373−8378.

[18] Crystal data for $[Ru_2(O_2CCF_3)_4(Et_2O)_2]$: formula $C_{16}H_{20}F_{12}O_{10}Ru_2$; fw = 802.46; $P\bar{1}$; $a = 8.5253(5)$ Å, $b = 9.9951(5)$ Å, $c = 9.7803(5)$ Å; $\alpha = 67.5940(10)°$, $\beta = 88.5460(10)°$, $\gamma = 77.3920(10)°$; $V = 675.28(6)$ Å^3; $Z = 1$; $T = 173$ K; $D_{calcd} = 1.973$ g/cm^3; $\mu = 1.247$ mm^{-1}; 5909 reflections measured, final R1 and wR2 values are 0.0213 and 0.0527 for 3034 independent reflections [$I > 2\sigma(I)$]. Selected distances and angles: Ru−Ru, 2.2920(3) Å; Ru$\cdots$O$_{ax}$, 2.3152(13) Å; Ru−Ru$\cdots$O$_{ax}$, 176.96(4)°.

[19] Crystal data for $[Ru_2(O_2CCF_3)_4(Me_2CO)_2]$: formula $C_{14}H_{12}F_{12}O_{10}Ru_2$; fw = 770.38; $P2_1/n$; $a = 8.7288(6)$ Å, $b = 8.9709(7)$ Å, $c = 15.1089(11)$ Å; $\beta = 96.7520(10)°$; $V = 1174.90(15)$ Å^3; $Z = 2$; $T = 173$ K; $D_c = 2.178$ g/cm^3; $\mu = 1.428$ mm^{-1}; 9831 reflections measured, final R1 and wR2 values are 0.0399 and 0.0944 for 2751 independent reflections [$I > 2\sigma(I)$]. Selected distances and angles: Ru−Ru, 2.2866(6) Å; Ru$\cdots$O$_{ax}$, 2.288(3) Å; Ru−Ru$\cdots$O$_{ax}$, 176.76(8)°.

Table 1. Selected Distances (Å) and Angles (deg) in the Structures of $[Ru_2(O_2CCF_3)_4]$ (**1**), $[Ru_2(O_2CCF_3)_4 \cdot C_{16}H_{16}]$ (**2**), and $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**)

	1	**1**	**2**	**3**
T, K	100	243	213	243
Ru−Ru	2.2679(5)	2.2627(5)	2.2993(5)	2.2613(7)
$Ru-O_{eq}$ (av)	2.066(2)	2.061(3)	2.064(3)	2.064(3)
$Ru-O_{eq}$ (···Ru)	2.091(2)	2.085(3)		2.084(3)
$Ru \cdots O_{ax}$	2.363(2)	2.377(3)		2.347(3)
$Ru-Ru-O_{ax}$	167.07(6)	167.64(7)		167.97(8)
Ru···C			2.670(3) 2.757(3)	
Ru−Ru−C			164.93(8) 165.16(8)	

metal bond. The Ru−Ru distance in **1** is 2.2679(5) Å at 100 K and 2.2627(5) Å at 243 K (Table 1). Thus, the metal−metal distance in the "unligated" $[Ru_2(O_2CCF_3)_4]$ complex is slightly shorter than those in the structurally characterized bis-adducts $[Ru_2(O_2CCF_3)_4L_2]$: 2.276(3) (L = THF),[7b] 2.293(1) (L = Tempo),[14] 2.2920(3) (L = diethyl ether),[18] and 2.2866(6) Å (L = acetone).[19] It is even shorter than the Ru−Ru distance of 2.278(1) Å in $[Ru_2(O_2CCF_3)_5]$ that has a Ru_2^{5+} core with one less electron in the metal−metal antibonding orbital.[20] For comparison, the shortest Ru−Ru bond of 2.238(1) Å was found in $[Ru_2(mph)_4]$ (Hmph = 6-methyl-2-hydroxypyridine), but that was attributed to the discreet nature of the complex having no axial interactions as well as to electronic and steric effects of the mph ligands that encourage metal−metal bond formation.[21]

A comparison of major distances and angles in the structure of **1** at different temperatures shows very subtle changes in the geometry of the dimetal $[Ru_2(O_2CCF_3)_4]$ complexes (Table 1 and Supporting Information). These changes in characteristic parameters within the dimetal units as well as some intermolecular distances and angles for the 1D chain are statistically insignificant and cannot be responsible for the observed thermal compressibility effect. For the latter, the overall packing of the polymeric chains themselves is a major factor. From variable-temperature X-ray measurements, it is clear that the orientational motion of the CF_3 groups of trifluoroacetates is more hindered at low temperatures and becomes essentially free at temperatures above 173 K (CF_3 groups are heavily disordered at this and higher temperatures). The "freeze" of the CF_3 rotation at low temperatures is an important factor that allows chains to come closer to each other along the *c* axis (Figure 3). The estimated change in interchain spacing is ca. 0.4 Å, which is calculated as the difference between the two closest middle points of the Ru−Ru bond in neighboring chains at 100 versus 295 K. This thermal compressibility may significantly affect the interchain open void space and micropore volumes of the 1D polymeric materials and, therefore, should be accounted for, for example, when gas occlusion properties of ruthenium carboxylates are studied at variable temperatures.[5b]

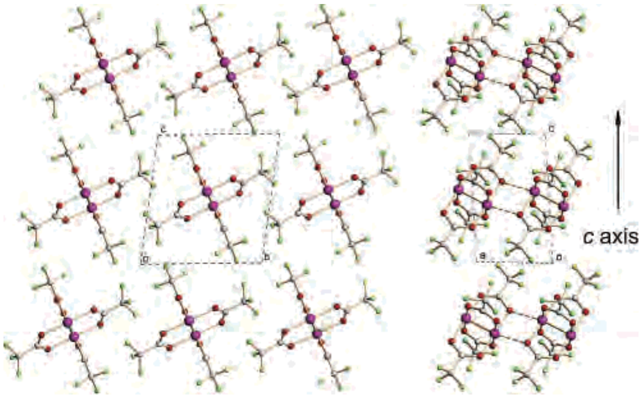

Figure 3. Solid-state packing of $[Ru_2(O_2CCF_3)_4]_\infty$ chains along the *c* axis.

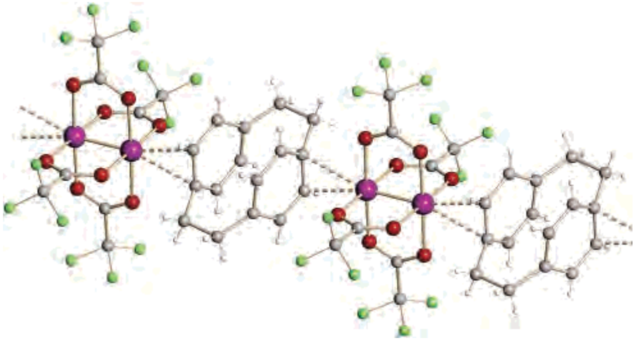

Figure 4. Fragment of the 1D polymeric chain in $[Ru_2(O_2CCF_3)_4 \cdot C_{16}H_{16}]_\infty$ (**2**). Ru purple, O red, F green, C dark gray, H light gray (the same color scheme is used in Figure 5).

To show the coordinatively unsaturated nature of diruthenum(II,II) trifluoroacetate, we have tested the reactivity of the "unligated" $[Ru_2(O_2CCF_3)_4]$ units toward a weak aromatic donor. Cosublimation of the volatile electrophilic diruthenium(II,II) complex in the presence of [2.2]paracyclophane produced the corresponding donor−acceptor adduct in crystalline form in moderate yield. In contrast to extremely hydroscopic starting material **1**, the new complex is only slightly moisture sensitive. The IR spectra showed the presence of both aromatic and carboxylate functions. The composition of this product was confirmed to be $[Ru_2(O_2CCF_3)_4]-(C_{16}H_{16})$ = 1:1 by elemental analysis, and its molecular structure was determined by X-ray diffraction.

The new complex consists of the alternating diruthenium(II,II) units and [2.2]paracyclophane ligands (Figure 4) that assemble 1D polymeric chains $[Ru_2(O_2CCF_3)_4 \cdot (\mu_2\text{-}C_{16}H_{16})]_\infty$ (**2**). The organometallic network is built on interactions between the Ru(II) centers and the carbon atoms of aromatic rings. Each ruthenium atom has the two closest Ru−C contacts with [2.2]paracyclophane at 2.682(4) and 2.764(4) Å, resulting in an η^2-type coordination of $C_{16}H_{16}$ in respect to each metal center. Interestingly, the internal (bridgehead) carbon atoms are involved in metal binding. Although complexes of [2.2]paracyclophane are known to exhibit a variety of coordination modes,[22] **2** represents a rare example of the transition-metal complex having both aromatic rings of [2.2]paracyclophane involved in coordination. Such complexes, in which $C_{16}H_{16}$ acts in the bridging μ_2-η^2:η^2-mode, have been previously known only in the case of silver(I).[23] We have recently reported the diruthenium(I,I) complex

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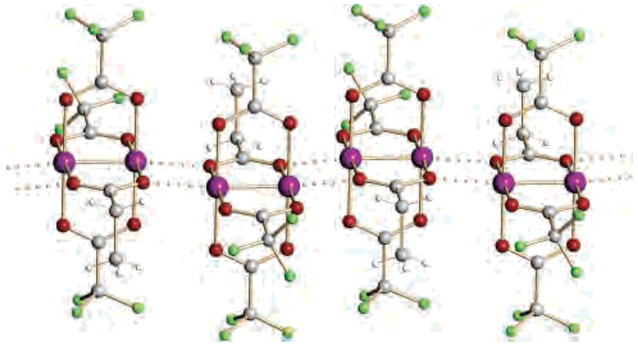

Figure 5. Fragment of the 1D polymeric chain in $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**).

$[Ru_2(O_2CCF_3)_2(CO)_4{\cdot}C_{16}H_{16}]_\infty$,[24] that has a similar 1D chain structure build on the μ_2-η^2:η^2-coordination of [2.2]paracyclophane.

We have also attempted to prepare diruthenium(II,II) tetra(trifluoroacetate) by the ligand-exchange reactions from the corresponding propionate, $[Ru_2(O_2CC_2H_5)_4]$. From that reaction, we have isolated crystals of the new carboxylate complex **3** in low yield along with the major product **1**. The IR spectrum of the new complex **3** shows the presence of both carboxylate groups: the intense bands at 1634 and 1540 cm^{-1} are due to $\nu_{asym}(CO_2)$ in $O_2CCF_3^-$ and $O_2CC_2H_5^-$, and the weaker bands at 1467 and 1430 cm^{-1} are due to $\nu_{sym}(CO_2)$ in $O_2CCF_3^-$ and $O_2CC_2H_5^-$, respectively. The X-ray diffraction study has revealed the composition, $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$, and the crystal structure of the new mixed-carboxylate diruthenium(II,II) complex that also bears no exogenous ligands (Figure 5).

Complex $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**) exhibits a chain polymeric structure built on axial Ru$\cdots$O interactions of 2.347(3) Å. The Ru−Ru distance of 2.2613(7) Å is slightly shorter than that in diruthenium(II,II) tetra(trifluoroacetate). The axial interdimer interaction of the dimetal units bridged by three electron-withdrawing trifluoroacetates and by one propionate is based on the contacts of the Ru(II) centers with the O-atoms of the propionate only. This is consistent with the greater electron-donating properties of the propionate groups. The Ru−O equatorial bond distance to the propionate ligand (2.084(3) Å) is notably longer than those to the CF_3COO^- ligands (average is 2.057(3) Å). Such axial binding results in the unique 1D chain motif (Scheme 1c). Similar selectivity in axial binding has previously been observed in the mixed-carboxylate rhodium tetramers, $\{[Rh_2(O_2CCF_3)_2(O_2CC_6H_2(2,4,6\text{-}^iPr_3))_2]L\}_2$, in which interdimer interactions occurred between the Rh centers and the O-atoms of 2,4,6-triisopropylbenzoates but not with the electron-withdrawing trifluoroacetate groups.[25]

The isolation of $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**) is consistent with the idea that the carboxylate substitution is a stepwise process and also reminds us that care should be taken to drive such reactions to completion. Our attempts to optimize the yield of this mixed-ligand $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ complex, which should be the last intermediate step to the fully substituted tetra(trifluoroacetate), were unsuccessful. Nevertheless, **3** represents the first mixed carboxylate of diruthenium(II,II) and the second example of the “unligated” Ru_2^{4+} core that also shows an interesting structural pattern and, therefore, is worth mentioning. Several mixed-valent diruthenium(II,III) complexes having various mixed-carboxylate bridges have been prepared,[26] but none was crystallographically characterized. The only other structurally confirmed example includes the diruthenium(II,III) carboxylate−carbonate complex $[Ru_2(O_2CC_{10}H_{15})_3(CO_3)(CH_3OH)_2]$.[8b] All the above mixed-carboxylate complexes were also isolated as intermediates in the ligand exchange processes. In general, the target formation of mixed-carboxylate complexes is a very challenging task, with major problems being the control over carboxylate substitution and stereochemistry,[27] the possibility of the mixed-ligand positions,[28] low product yields, and the need for efficient separation techniques.[29] Some successful synthetic approaches have recently been developed for the dirhodium core complexes having a pair of cis sites blocked off with chelating dicarboxylate ligands.[30]

Magnetic Susceptibility Studies. (1) $[Ru_2(O_2CR)_4]$. The Ru_2^{4+} core complexes attract special attention due to their interesting magnetic properties. For the triplet ground state, different electronic configurations are known, and they can be affected by various ligand environments at the Ru_2^{4+} core and also by temperature. First, room-temperature magnetic measurements have been carried out on a series of diruthenium(II,II) tetracarboxylates, such as acetate, propionate, benzoate, as well as trifluoroacetate.[7b] Then, a series of unligated diruthenium(II,II) long-chain tetracarboxylates that form liquid-crystalline phases has also been studied, but no correlation with crystallographic data was available then.[4c,d]

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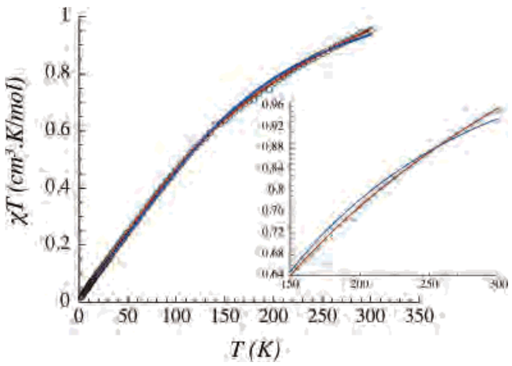

Figure 6. Temperature dependence of the χT product of **1**. The solid lines represent the theoretical fits with $g = 2.0$ (fixed), $D/k_B = 467(4)$ K (322(3) cm^{-1}), $\chi_{TIP} = 2.3(5) \times 10^{-4}$ cm^3 mol^{-1}, and $\rho = 0.7(1)\%$ (blue line) and $g = 2.0(1)$, $D/k_B = 320(11)$ K (220(8) cm^{-1}), $zJ = -70(24)$ K (49(17) cm^{-1}), $\chi_{TIP} = 7 \times 10^{-4}$ cm^3 mol^{-1}, and $\rho = 0.7\%$ (red line).

The obtained values of χT at room temperature varied from 1.08 to 1.24 cm^3 K mol^{-1}, depending on the length of the alkyl chain (from decanyl to dodecanyl), and were consistent with a triplet state $S = 1$. The overall shape of the χ vs T plot strongly deviated from a paramagnetic $S = 1$ system and was interpreted as arising from a strong zero-field splitting (ZFS) with the following parameters: $g_{\|}$ from 1.92 to 2.07, $g_{\perp}$ from 2.11 to 2.22, χ_{TIP} from 5×10^{-4} to 7×10^{-4} cm^3 mol^{-1}, and D from 388 K (270 cm^{-1}) to 452 K (314 cm^{-1}). No intermolecular interactions were detected, and the main reason for that was assigned to the nature of the ground state. We expected that the presence of the four highly electrophilic trifluoroacetate groups bridging the Ru_2^{4+} core in **1** should enhance the interdimer interactions along the 1D chain compared with those of the above diruthenium(II,II) alkylcarboxylates.

The temperature dependence of the χT product for **1**, measured between 1.8 and 300 K, is shown in Figure 6. **1** exhibits a continuous decrease of the χT product with a lowering of the temperature from 0.95 cm^3 K mol^{-1} at 300 K to 0.018 cm^3 K mol^{-1} at 1.8 K. The overall magnetic behavior is very similar to that of the other $[Ru^{II}_2(O_2CR)_4]$ compounds that possess an $^3A_{2g}$ ground state and, therefore, exhibit an important ZFS contribution.[2b,4a−b,8a,14] For these compounds, the magnetic susceptibility has been modeled using the expression given by eq 1 for an isolated $S = 1$ center with a ZFS contribution.

$$\chi_{Ru_2^{II}} = \frac{2Ng^2\mu_B^2}{3k_BT}\left[\frac{\{\exp(-D/k_BT) + (2k_BT/D)(1 - \exp(-D/k_BT))\}}{1 + 2\exp(-D/k_BT)}\right] \quad (1)$$

At low temperatures, the χT product of **1** (Figure 6) is not extrapolating well to zero for $T = 0$ K. Therefore, as shown by eq 2, an extrinsic Curie-type paramagnetic contribution was taken into account in addition to the recurrent temperature-independent paramagnetism (TIP) that is always present for the Ru_2^{4+} dimers:

$$\chi = (1 - \rho)\chi_{Ru_2^{II}} + \rho C_{imp}/T + \chi_{TIP} \quad (2)$$

where C_{imp} is the Curie constant for the extrinsic paramagnetic impurity. As a first approach, the susceptibility given by eq 2 was used to model the experimental results obtained for **1**. The fitting procedure led to unphysical g values, and a qualitatively good fit was obtained only when g was fixed to 2.0. In this case, the best set of parameters obtained is $D/k_B = 467(4)$ K (322 cm^{-1}), $\chi_{TIP} = 2.3(5) \times 10^{-4}$ cm^3 mol^{-1}, and $\rho = 0.7(1)\%$ (blue line, Figure 6). To qualitatively improve this fitting to account for close contacts between the Ru_2^{4+} dimers along the 1D chain (vide supra), magnetic interactions have been introduced in the frame of the mean field approximation (eq 3):

$$\chi = (1 - \rho)\frac{\chi_{Ru_2^{II}}}{1 - \frac{2zJ}{Ng^2\mu_B^2}\chi_{Ru_2^{II}}} + \rho C_{imp}/T + \chi_{TIP} \quad (3)$$

where J is the magnitude of the interdimer interaction, which is assumed to be an intrachain magnetic interaction between the $S = 1$ centers. To minimize the usual problems of refining several parameters (g, D, zJ, χ_{TIP}, and ρ), the least-squares calculations were performed step by step. First, ρ was evaluated by fitting the χ vs T plot below 20 K. Using this value as a starting point, the fitting of the whole χT vs T data was performed with g fixed at 2.0. Finally, the fitting procedure was made with all free parameters. The best set of parameters obtained was $g = 2.0(1)$, $D/k_B = 320(11)$ K (220 cm^{-1}), $zJ = -70(24)$ K, $\chi_{TIP} = 7.0(5) \times 10^{-4}$ cm^3 mol^{-1}, and $\rho = 0.7(1)\%$ (red line, Figure 6). The obtained values of D, g, and χ_{TIP} are close to the values previously obtained for the Ru_2^{4+} $S = 1$ dimers (vide supra).[2] Although the accounting of interaction between the diruthenium(II,II) dimers in the model clearly improves the quality of the fitting, the determination of the corresponding parameters is not very accurate, as seen by the error values. Fitting of the χ or $1/\chi$ vs T plots led to the same problem. Unfortunately, the magnetic data and their fit do not allow for an accurate estimation of the magnetic interaction between the Ru_2^{4+} $S = 1$ dimers in **1**, and zJ must be taken with great caution. Moreover, the structural changes detected for **1** between 100 and 295 K (and highlighted in Figure 1 and Table 1) may also influence the magnetic parameters, such as D and zJ, complicating the fitting procedure.

(2) $[Ru_2(O_2CCF_3)_4\cdot(C_{16}H_{16})]$. The [2.2]paracyclophane ligand was long considered to be an interesting bridge for connecting the paramagnetic metal centers to form extended organometallic polymeric networks.[22,23] The unusual structure of $C_{16}H_{16}$, with the close proximity of two aromatic rings resulting in the nonplanarity of the benzene moieties,[31] was

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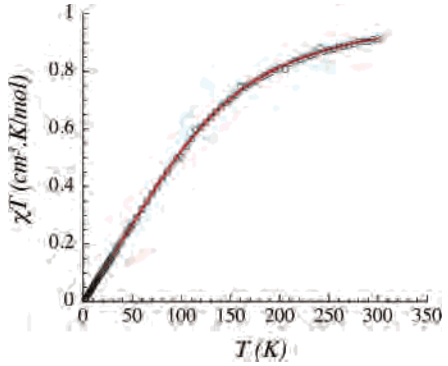

Figure 7. Temperature dependence of the χT product of **2**. The solid line represents the theoretical fit with $g = 2.00(1)$, $D/k_B = 375(3)$ K (261 cm^{-1}), and $\chi_{TIP} = 8.0(5) \times 10^{-4}$ cm^3 mol^{-1} (red line).

expected to facilitate magnetic interactions along the chain in the above paramagnetic complexes. The 1D polymeric complex **2**, in which [2.2]paracyclophane acts as a bridge between two paramagnetic ruthenium(II) centers, allowed the performance of the magnetic measurements to support or refute the above assumption for the first time.

The temperature dependence of the χT product measured between 1.8 and 300 K is shown for **2** in Figure 7. The overall magnetic behavior is very similar to that of the parent [$Ru_2(O_2CCF_3)_4$] complex (**1**). **2** also exhibits a continuous decrease of the χT product with lowering the temperature, from 0.92 cm^3 K mol^{-1} at 300 K to 0.01 cm^3 K mol^{-1} at 1.8 K. Again, the magnetic susceptibility for **2** has been modeled using the expression given by eq 1 for an isolated $S = 1$ center with a ZFS contribution.

The best set of parameters obtained is $D/k_B = 375(3)$ K (261(2) cm^{-1}), $\chi_{TIP} = 8.0(5) \times 10^{-4}$ cm^3 mol^{-1}, and $g = 2.00(1)$ (red line, Figure 7). The obtained values of D, g, and χ_{TIP} are close to the values previously obtained for the Ru_2^{4+} core $S = 1$ dimers.[2b,4a−b,8a,14] No interdimer interaction is detected in this case, confirming that the Ru−π−arene bonding is weak and the [2.2]paracyclophane ligand does not facilitate magnetic interactions along the 1D chain in **2**.

In conclusion, herein we presented the first structural characterization of the diruthenium(II,II) tetracarboxylate complex, [$Ru_2(O_2CCF_3)_4$] (**1**), that bears no exogenous ligands. The variable-temperature X-ray structural studies revealed a noticeable thermal compressibility effect due to a change in the packing of the 1D polymeric chains. The magnetic measurements performed on **1** confirmed the $S = 1$ ground state of the Ru_2^{4+} dimer with a large ZFS ($D/k_B = 320(11)$ K). The presence of interdimer antiferromagnetic interactions along the chain is strongly suggested by the fitting procedure, but they have been only roughly evaluated at −35 ± 12 K (taking into account the 1D nature of **1** and $z = 2$). Lewis acidity of the electrophilic ruthenium(II) centers in trifluoroacetate was confirmed by reaction of **1** with an aromatic ligand, [2.2]paracyclophane. As a result, an interesting organometallic polymer, [$Ru_2(O_2CCF_3)_4 \cdot C_{16}H_{16}]_\infty$ (**2**), built on the bridging μ_2-η^2:η^2-coordination of [2.2]paracyclophane, has been isolated and structurally characterized. The magnetic measurements performed on **2** confirmed the $S = 1$ ground state with a large ZFS ($D/k_B = 375(3)$ K) but did not indicate any interdimer interactions along the organometallic chain. A new complex of the diruthenium(II,II) core, [$Ru_2(O_2CCF_3)_3(O_2CC_2H_5)$] (**3**), has been isolated as an intermediate in the carboxylate-exchange reactions. It shows an interesting 1D structure and represents the first recorded example of diruthenium(II,II) carboxylate with mixed bridges.

Experimental Section

General Procedures. All manipulations were carried out in a dry, oxygen-free, dinitrogen (HP 99.998) atmosphere by employing standard Schlenk techniques. Elemental analysis was performed by Chemisar Laboratories Inc., Ontario, Canada. IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using KBr pellets. NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz for proton and at 282 MHz for fluorine. Chemical shifts for ^{19}F are reported relative to internal standard $CFCl_3$ $\delta = 0.0$ ppm. [$Ru_2(O_2CCH_3)_4$] was prepared according to the literature procedure.[7a]

[$Ru_2(O_2CCF_3)_4$] (1). Freshly prepared [$Ru_2(O_2CCH_3)_4$] (0.5 g) was heated under reflux in degassed trifluoroacetic acid−trifluoroacetic anhydride (9:1, 30 mL) containing CF_3CO_2Na (1.0 g) for 4 days. The deep-red solution was then evaporated to dryness. The residue was extracted into ether, which was then removed to leave a dark-brown residue. The solid was recrystallized from acetone/hexanes to afford red-brown crystals of [$Ru_2(O_2CCF_3)_4 \cdot (C_3H_6O)_2$], which were dried at ambient temperature. Yield: 0.53 g (60%, calculated for the bis-acetone adduct).

Thus obtained [$Ru_2(O_2CCF_3)_4 \cdot (C_3H_6O)_2$] (0.25 g) was first heated at 120 °C for 3 days under reduced pressure. Then the product was sealed in an ampule under vacuum and heated at 140 °C for 24 h to give a few crystals of the more volatile acetone adduct in the cold zone and leaving the less volatile unligated [$Ru_2(O_2CCF_3)_4$] product in the hot end of the tube. These sublimation−separation procedures were repeated 2−3 times at 140−160 °C to finally give an orange-brown powder of the title complex. Yield: 0.17 g (70%).

Crystals of [$Ru_2(O_2CCF_3)_4$], suitable for X-ray diffraction study, were obtained by sublimation under vacuum at 170−175 °C to give thin orange-brown needles deposited in a cold zone of the ampule. Decomposition of [$Ru_2(O_2CCF_3)$] with a formation of the “Ru mirror” was observed when the product was heated in a sealed ampule at 210−220 °C for 1−2 days. IR (KBr, cm^{-1}): 1634 s, 1467 m, 1262 sh, 1194 s, 1166 s, 862 m, 777 w, 736 m, 535 w, 518 w, 492 w, 454 w. ^{19}F NMR (22 °C, $CDCl_3$) δ: −74.3. Anal. Calcd for $C_8F_{12}O_8Ru_2$: C, 14.69; H, 0.00; O, 19.57; F, 34.85; Ru, 30.90. Found: C, 14.22; H, 0.00; O, 19.78; F, 34.27; Ru, 30.52.

[$Ru_2(O_2CCF_3)_4 \cdot (C_{16}H_{16})$] (2). A mixture of **1** (0.030 g, 0.046 mmol) with [2.2]paracyclophane (0.010 g, 0.048 mmol) was sealed under vacuum in a small glass ampule that was placed in an electric furnace at 147 °C. In 5 days, brown, plate-shaped crystals were deposited in the “cold” end of the ampule, where the temperature was set ca. 140 °C. Yield: 35−40%. Anal. Calcd for $Ru_2C_{24}F_{12}O_8H_{16}$: C, 33.42; H, 1.87. Found: C, 33.75; H, 2.02. IR (KBr, cm^{-1}): 3035 w, 3015 w, 2953 w, 2929 m, 2889 w, 2852 w, 1894 w, 1684 sh, 1647 s, 1634 sh, 1594 sh, 1559 w, 1506 w, 1468 w, 1440 w, 1415 w, 1194 s, 1170 sh, 1088 w, 1020 w, 945 w, 937 w, 897 w, 862 m, 809 m, 779 m, 737 s, 720 m, 624 m. ^{1}H NMR (22 °C, acetone-d_6): δ 3.10 (s, 8H, CH_2), 6.54 (s, 8H, C−H_{arom}). ^{19}F NMR (22 °C, acetone-d_6): δ −74.3.

X-ray Crystallographic Procedures. X-ray data sets for **1**−**3** were collected on a Bruker APEX CCD X-ray diffractometer equipped with graphite-monochromated Mo Kα radiation (λ =

0.71073 Å). For **1**, the same crystal was studied at six temperatures in the range 100−295 K (Bruker KRYO-FLEX); the crystal was kept at the given temperature at least for 6 h prior an X-ray experiment. The frames were integrated with the Bruker SAINT software package,[32a] and the data were corrected for absorption using the program SADABS.[32b] The structures were solved and refined using the Bruker SHELXTL software (Version 6.1).[32c] Crystallographic data and X-ray experimental conditions for **1**, **2**, and **3** are listed in Table 2. Selected distances and angles for **1**−**3** are given in Table 1.

Magnetic Measurements. The magnetic susceptibility measurements on **1** (11.6 mg) and **2** (11.5 mg) were obtained on finely ground polycrystalline samples with the use of a Quantum Design SQUID magnetometer MPMS-XL. The dc measurements were collected from 1.8 to 300 K and from −70 to 70 kOe. Experimental data were corrected for the sample holder, and the diamagnetic contribution was calculated from Pascal's constants.[33]

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Supporting Information Available: X-ray crystallographic files in CIF format. Tables of crystallographic data and selected distances and angles at different temperatures, plots of temperature dependence of the unit cell parameters, cell volume, and density for $[Ru_2(O_2CCF_3)_4]$ (**1**), fully labeled ORTEP diagrams for structures of **1**, **2**, and **3** as well as for bis-adducts of **1** with diethyl ether and acetone. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 2. Crystallographic Data and Structural Refinement Parameters for $[Ru_2(O_2CCF_3)_4]$ (**1**), $[Ru_2(O_2CCF_3)_4{\cdot}C_{16}H_{16}]$ (**2**), and $[Ru_2(O_2CCF_3)_3(O_2CC_2H_5)]$ (**3**)

	1	**2**	**3**
formula	$C_8F_{12}O_8Ru_2$	$C_{24}H_{16}F_{12}O_8Ru_2$	$C_9H_5F_9O_8Ru_2$
fw	654.22	862.51	614.27
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/m$
a (Å)	5.2485(6)	8.9689(6)	8.6643(5)
b (Å)	8.6377(10)	9.1449(6)	9.0576(5)
c (Å)	8.9147(10)	10.8909(7)	11.1165(7)
α (deg)	83.493(2)	114.557(1)	90.00
β (deg)	83.698(2)	104.483(1)	100.779(1)
γ (deg)	86.921(2)	99.843(1)	90.00
V (Å^3)	398.77(8)	747.35(8)	857.01(9)
Z	1	1	2
T (K)	100(2)	213(2)	243(2)
λ (Å)	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	2.724	1.916	2.380
μ (mm^{-1})	2.069	1.130	1.893
data/restr/params	1743/0/136	3343/18/259	2122/0/157
R1^b, wR2^c [$I > 2\sigma(I)$]	0.0282, 0.0725	0.0389, 0.1030	0.0378, 0.0957
R1^b, wR2^c (all data)	0.0313, 0.0743	0.0414, 0.1054	0.0525, 0.1046
GOF^a on F^2	1.087	1.041	1.035

^{a} GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$. ^{b} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} wR2 = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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