

Studies of Dirhodium Tetra(trifluoroacetate). 3. Solid State Isomers of the Compound $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$ Prepared by Sublimation

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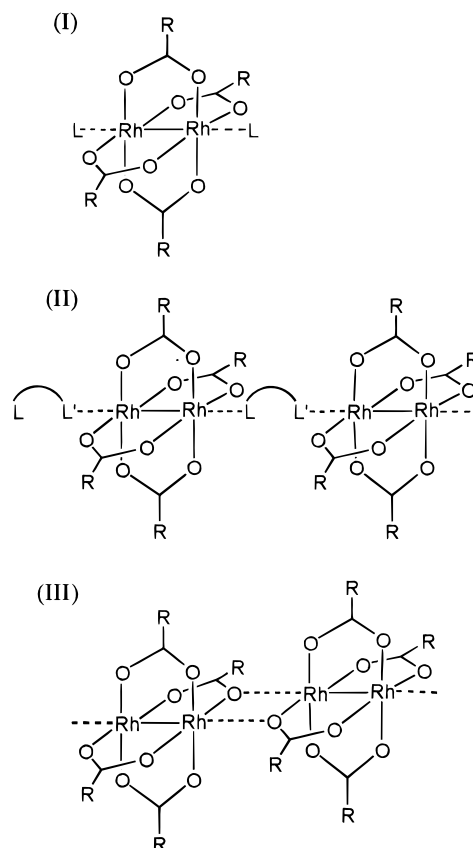
The monoadduct of dirhodium tetra(trifluoroacetate) with THF has been obtained by deposition from the vapor phase. The compound $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$ crystallizes in two isomeric forms, **1** and **2**, whose structures have been determined by X-ray crystallography. The crystallographic parameters are as follows: for **1**, triclinic space group $P\bar{1}$ with $a = 9.557(2)$ Å, $b = 10.126(2)$ Å, $c = 11.840(4)$ Å, $\alpha = 95.97(2)^\circ$, $\beta = 90.40(2)^\circ$, $\gamma = 115.58(1)^\circ$, and $Z = 2$; for **2**, triclinic space group $P\bar{1}$ with $a = 8.6347(3)$ Å, $b = 9.678(1)$ Å, $c = 13.773(4)$ Å, $\alpha = 73.182(5)^\circ$, $\beta = 74.622(5)^\circ$, $\gamma = 89.76(1)^\circ$, and $Z = 2$. Compound **1** is unique as the only extended structure where dirhodium carboxylate molecules are bridged by a single exogenous atom. The oxygen atom of the THF ligand coordinates to the axial positions of two Rh₂ units so that a one-dimensional zigzag chain is formed. The bridging is slightly asymmetric with Rh–O(THF) distances of 2.363(6) and 2.407(6) Å, and the Rh–O(THF)–Rh angle is 111.8(3)°. The crystal structure of **2** is not polymeric. Pairs of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$ units are associated through O atoms of carboxylate groups to produce a dimer of dimers. The lengths of the terminal Rh–O(THF) and axial bridging Rh···O(Ac) interactions are 2.214(7) and 2.406(6) Å, respectively.

Introduction

The ability of dirhodium(II) carboxylates to form $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_n$ ($n = 1$ or 2) complexes with axial ligands is well established.¹ By far the largest class of compounds known comprises diadducts having the discrete structure **I** (Chart 1), where axial ligands L are of a seemingly infinite variety and the known ones include almost all common donors.

Another group of compounds comprises 1:1 adducts that are polymeric arrays, such as the linear one, **II**. In all of these complexes² the axial ligands have at least two binding sites. There are two examples of complexes where the L ligand uses four binding sites. They both have composition $[\text{Rh}_2(\text{O}_2\text{CR})_4]_2\text{L}$, where $\text{R} = \text{CF}_3$ and L is TCNE^{3a} or $\text{R} = \text{Me}$ and L is $\text{Co}(\text{CN})_6^{3-}$.^{3b} However, there is no example so far of a single donor atom serving as a bridge in this type of structure.

Chart 1



- (1) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, 1993. (b) Cotton, F. A.; Kim, Y. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 525.
- (2) (a) IMME = 2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazolyl-1-oxy 3-oxide. Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1989**, *111*, 3230. (b) AAMP = 4-amino-5-(aminomethyl)-2-methylpyrimidine. Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1984**, *106*, 3691. (c) DDA = 2,3,5,6-tetramethyl-p-phenylenediamine; PHZ = phenazine. Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 600. (d) amp = 2-(aminomethyl)pyridine. Crawford, C. A.; Day, E. F.; Streib, W. E.; Huffman, J. C.; Christou, G. *Polyhedron* **1994**, *13*, 2933. (e) TCNE = tetracyanoethylene. Cotton, F. A.; Kim, Y.; Lu, J. *Inorg. Chim. Acta* **1994**, *221*, 1. (f) 1,4-bq = 1,4-benzoquinone; 1,4-nq = 1,4-naphthoquinone. Handa, M.; Nakao, T.; Mikuriya, M.; Kotera, T.; Nukada, R.; Kasuga, K. *Inorg. Chem.* **1998**, *37*, 149. (g) Handa, M.; Takata, A.; Nakao, T.; Kasuga, K.; Mikuriya, M.; Kotera, T. *Chem. Lett.* **1992**, 2085. (h) 2,3-Me₂-1,4-bq = 2,3-dimethyl-1,4-benzoquinone. Handa, M.; Mikuriya, M.; Sato, Y.; Kotera, T.; Nukada, R.; Yoshioka, D.; Kasuga, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3483.
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Several years ago we began to examine the behavior of dirhodium(II) tetra(trifluoroacetate), more systematically than had been done before. In our first contribution,⁴ which we shall regard as Part 1 of this series, it was established that, in the

absence of exogenous donors, $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ forms a structure in which there are infinite chains of molecules bound end to end (**III**), in a manner well-known for many other $\text{M}_2(\text{O}_2\text{CR})_4$ compounds.^{1a,4,5} More recently (Part 2⁶) it was shown that the compound $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{C}_6\text{Me}_6$ crystallizes as a one-dimensional copolymer in which bridging hexamethylbenzene molecules alternate with dirhodium units by making π -donor bonds. However, even this unusual 1:1 complex is not different in principle from those of group **II** since the bridging hexamethylbenzene ligands employ two bonding sites.

In this report we describe two solutions that Nature has found to the problem of what structures can arise when the stoichiometry is $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{L}$, and L is the commonly monodentate ligand, tetrahydrofuran, i.e., a ligand with only one donor atom.

Experimental Section

Synthesis of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$. All of the experimental manipulations involving the synthesis of the starting materials were carried out under dry, oxygen-free nitrogen by employing Schlenk techniques. The anhydrous form of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and the bis-adduct $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ were prepared using literature procedures.^{1b,4}

A small portion (~0.1 g) of a mixture of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ as a green powder and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ as blue crystals was sealed in an evacuated (10^{-2} atm) 11×60 mm Pyrex tube. The composition of the initial mixture was varied from molar ratio 5:1 to 1:1 in different experiments. The sublimations were carried out in a muffle furnace with the sample at 100 °C. The condensation of products in the "cold" zone of the ampule (90°–95 °C) was first observed after 1 day, but usually a period of several days was required to allow good crystal growth. In each experiment two types of crystals were visually recognized: small emerald-green needles (**1**) and large dark-green blocks (**2**). A similar procedure was also carried out with $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ alone. The crystalline sublimate consisted entirely of the starting material.

X-ray Crystallographic Procedures. Single crystals of compounds **1** and **2** were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo K α radiation. Details concerning data collection have been fully described elsewhere.⁴ Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (–60 °C) of a low-temperature controller. Fifty reflections were used in cell indexing and about 240 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.⁷ Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.⁸

All calculations were done on a DEC Alpha running VMS. The coordinates of rhodium and oxygen atoms for the structures were found in direct-method *E* maps using the structure solution program SHELXTL.⁹ The positions of the remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps. The fluorine atoms of all CF_3 groups were found to be disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine atoms. Hydrogen atoms of the THF ligands were

Table 1. Crystallographic Data for $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_\infty$ (**1**) and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2]$ (**2**)

	1	2
formula	$\text{Rh}_2\text{O}_9\text{F}_{12}\text{C}_{12}\text{H}_8$	$\text{Rh}_2\text{O}_9\text{F}_{12}\text{C}_{12}\text{H}_8$
fw	730.00	730.00
space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> , Å	9.557(2)	8.6347(3)
<i>b</i> , Å	10.126(2)	9.678(1)
<i>c</i> , Å	11.840(4)	13.773(4)
α , deg	95.97(2)	73.182(5)
β , deg	90.40(2)	74.622(5)
γ , deg	115.58(1)	89.76(1)
<i>V</i> , Å ³	1026.2(5)	1059.0(3)
<i>Z</i>	2	2
ρ_{calcd} , g cm ^{–3}	2.363	2.289
μ , mm ^{–1}	1.761	1.706
radiation (λ , Å)	Mo K α (0.710 73)	Mo K α (0.710 73)
temp, °C	–60	–60
$R1$, ^a $wR2$ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0496, 0.1102	0.0556, 0.1283
$R1$, ^a $wR2$ ^b (all data)	0.0612, 0.1195	0.0689, 0.1441

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

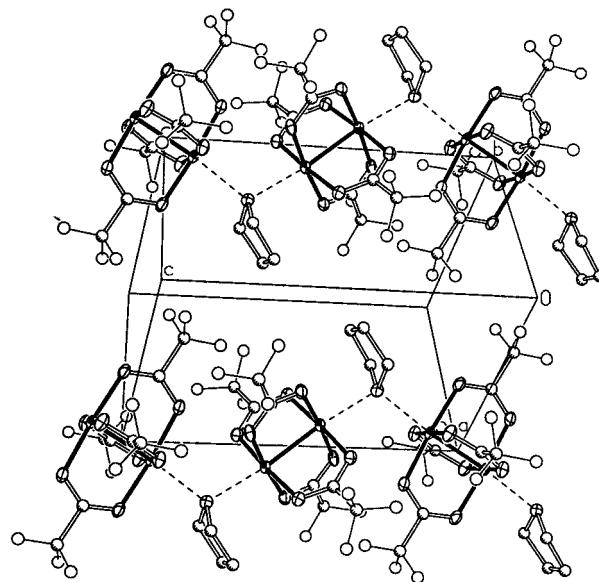


Figure 1. Packing diagram of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_\infty$ (**1**). The view is almost down the [110] direction of the unit cell. Hydrogen atoms of THF groups are omitted for clarity. The Rh–O(THF) bridges are shown by dashed lines.

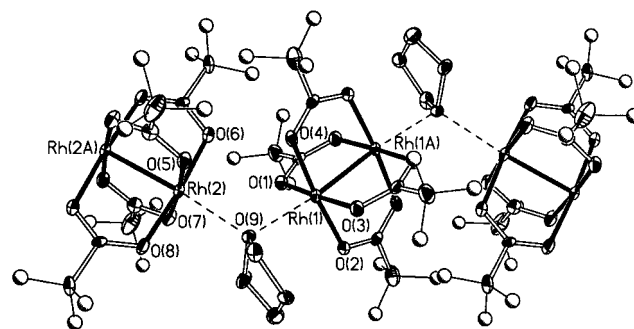


Figure 2. A fragment showing the arrangement of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and THF units in the chain structure of **1**. Fluorine atoms are shown as spheres of arbitrary radius, with only one orientation of each CF_3 group depicted. Hydrogen atoms of THF groups are omitted.

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 (5) Baxter, D. V.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Putilina, E. F.; Tagg, S.; Wesemann, J. L.; Zwanziger, J. W.; Darrington, F. D. *J. Am. Chem. Soc.* **1994**, 116, 4551.
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 (7) Pflugrath, J.; Messerschmitt, A. MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, 20, 306.
 (8) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, 21, 67; (b) **1988**, 21, 916.
 (9) SHELXTL V.5; Siemens Industrial Automation Inc.: Madison, WI, 1994.

included in the structure factor calculations at idealized positions. Relevant crystallographic data for complexes **1** and **2** are summarized in Table 1.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_{\infty}^1$ (**1**) and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_2$ (**2**)

	1		2	
Rh–Rh	Rh(1)–Rh(1A)	2.408(2)	Rh(1)–Rh(2)	2.391(1)
	Rh(2)–Rh(2A)	2.406(2)		
Rh–O _{eq}	Rh(1)–O(1)	2.031(6)		2.029(7)
	Rh(1)–O(2)	2.037(6)		2.016(7)
	Rh(1)–O(3)	2.032(6)		2.032(6)
	Rh(1)–O(4)	2.024(6)		2.034(7)
	Rh(2)–O(5)	2.030(6)		2.032(6)
	Rh(2)–O(6)	2.029(7)		2.026(7)
	Rh(2)–O(7)	2.035(6)		2.015(6)
	Rh(2)–O(8)	2.024(7)		2.067(7)
Rh–O _{ax}	Rh(1)–O(9)	2.363(6)	Rh(1)–O(9)	2.214(7)
	Rh(2)–O(9)	2.407(6)	Rh(2)–O(8A)	2.406(6)
O _{eq} –Rh–O _{eq}	O(1)–Rh(1)–O(2)	86.6(2)		88.3(3)
	O(1)–Rh(1)–O(3)	175.6(3)		176.0(3)
	O(1)–Rh(1)–O(4)	95.1(2)		91.3(3)
	O(2)–Rh(1)–O(3)	91.5(3)		91.9(3)
	O(2)–Rh(1)–O(4)	175.2(2)		176.7(3)
	O(3)–Rh(1)–O(4)	86.5(3)		88.2(3)
	O(5)–Rh(2)–O(6)	91.0(3)		89.0(3)
	O(5)–Rh(2)–O(7)	176.1(2)		177.0(3)
	O(5)–Rh(2)–O(8)	89.5(3)		91.2(2)
	O(6)–Rh(2)–O(7)	89.6(3)		91.1(3)
	O(6)–Rh(2)–O(8)	175.4(2)		175.6(3)
	O(7)–Rh(2)–O(8)	89.6(3)		88.5(3)
Rh–Rh–O _{eq}	Rh(1A)–Rh(1)–O(1)	87.9(2)	Rh(2)–Rh(1)–O(1)	87.8(2)
	Rh(1A)–Rh(1)–O(2)	87.9(2)	Rh(2)–Rh(1)–O(2)	89.0(2)
	Rh(1A)–Rh(1)–O(3)	88.0(2)	Rh(2)–Rh(1)–O(3)	88.2(2)
	Rh(1A)–Rh(1)–O(4)	87.6(2)	Rh(2)–Rh(1)–O(4)	87.8(2)
	Rh(2A)–Rh(2)–O(5)	88.0(2)	Rh(1)–Rh(2)–O(5)	88.7(2)
	Rh(2A)–Rh(2)–O(6)	86.0(2)	Rh(1)–Rh(2)–O(6)	87.5(2)
	Rh(2A)–Rh(2)–O(7)	88.2(2)	Rh(1)–Rh(2)–O(7)	88.3(2)
	Rh(2A)–Rh(2)–O(8)	89.4(2)	Rh(1)–Rh(2)–O(8)	88.2(2)
O _{eq} –Rh–O _{ax}	O(1)–Rh(1)–O(9)	87.8(2)	O(1)–Rh(1)–O(9)	92.7(3)
	O(2)–Rh(1)–O(9)	96.6(2)	O(2)–Rh(1)–O(9)	90.5(3)
	O(3)–Rh(1)–O(9)	96.4(2)	O(3)–Rh(1)–O(9)	91.3(3)
	O(4)–Rh(1)–O(9)	88.0(2)	O(4)–Rh(1)–O(9)	92.8(3)
	O(5)–Rh(2)–O(9)	91.1(2)	O(5)–Rh(2)–O(8A)	93.1(2)
	O(6)–Rh(2)–O(9)	99.3(2)	O(6)–Rh(2)–O(8A)	103.5(3)
	O(7)–Rh(2)–O(9)	92.6(2)	O(7)–Rh(2)–O(8A)	89.9(3)
	O(8)–Rh(2)–O(9)	85.3(2)	O(8)–Rh(2)–O(8A)	80.9(2)
Rh–Rh–O _{ax}	Rh(1A)–Rh(1)–O(9)	173.6(2)	Rh(2)–Rh(1)–O(9)	179.3(2)
	Rh(2A)–Rh(2)–O(9)	174.7(2)	Rh(1)–Rh(2)–O(8A)	169.0(2)
Rh–O _{ax} –Rh	Rh(1)–O(9)–Rh(2)	111.8(3)	Rh(2)–O(8)–Rh(2A)	99.1(2)

Table 3. Average Key Distances (Å) and Angles (deg) for the Molecules $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_n$ ($n = 0,^a 1$ (**1** and **2**), and 2^b)

	$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_{\infty}^1$	$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_2$ (2)	$\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$	$[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_{\infty}^1$ (1)
Rh–Rh	2.3813(8)	2.391(1)	2.3969(9)	2.407(2)
Rh–O _{eq}	2.039(4)	2.031(7)	2.037(7)	2.030(6)
Rh–O _{ax} (Ac)	2.337(4)	2.406(6)		
Rh–O _{ax} (THF)		2.214(7)	2.210(8)	2.385(6)
O _{eq} –Rh–O _{eq}	90.0(2), 176.4(2)	89.9(3), 176.3(3)	90.0(3), 176.2(3)	89.9(3), 175.6(2)
Rh–Rh–O _{eq}	88.2(1)	88.2(2)	88.1(2)	87.9(2)
O _{eq} –Rh–O _{ax} (Ac)	81.1(1)–102.9(2)	80.9(2)–103.5(3)		
O _{eq} –Rh–O _{ax} (THF)		91.8(3)	91.9(3)	92.1(2)
Rh–Rh–O _{ax} (Ac)	169.3(1)	169.0(2)		
Rh–Rh–O _{ax} (THF)		179.3(2)	178.8(2)	174.2(2)
Rh–O _{ax} (Ac)–Rh	98.9(1)	99.1(2)		
Rh–O _{ax} (THF)–Rh				111.8(3)

^a Reference 4. ^b Reference 1b. ^c Ac = acetate; THF = tetrahydrofuran; ax = axial; eq = equatorial.

Results and Discussion

Molecular Structures. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent dirhodium tetrafluoroacetate cages each having an inversion center at the midpoint of the Rh–Rh bond. The oxygen atom of the THF ligand bridges the axial positions of two Rh₂ units thereby producing a one-dimensional zigzag chain structure $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})]_{\infty}^1$ extended along the [001] direction of the unit cell (Figure 1). The zigzag arrangement arises from

tetrahedral coordination of the tetrahydrofuran oxygen atom (Figure 2) where the Rh–O(THF)–Rh angle is 111.8(3)° (Table 2). The bridging is slightly asymmetric with Rh–O(THF) distances of 2.363(6) and 2.407(6) Å for Rh(1) and Rh(2) atoms, respectively. These bond lengths are much longer than those for the axially coordinated THF molecules in the diadduct of dirhodium(II) tetra(trifluoroacetate) (2.210(8) Å)^{1b} (Table 3) and also in the complex **2** (2.214(7) Å) (vide infra). On the other hand, they are similar to the bond lengths for axial coordination

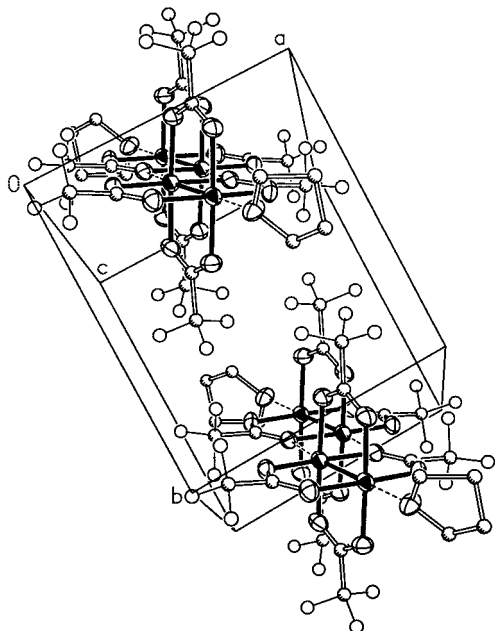


Figure 3. Packing diagram of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2]$ (**2**). The view is almost down the c axis of the unit cell. Hydrogen atoms of the THF group are omitted for clarity. Axial interactions to rhodium atoms are shown by dashed lines.

to a rhodium atom by the carboxylic oxygen atom of neighboring molecules in $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ ($2.337(4) \text{ \AA}$)⁴ and in **2** ($2.406(6) \text{ \AA}$). A bridging role for the THF ligand is extremely rare in the solid state. We can recall just two examples: $[\text{Co}(\text{acac})_2(\text{PhHgOHgPh})(\text{THF})_2]_{10}$ and $[(\text{C}_5\text{H}_4\text{Me})\text{TiF}_3]_2 \cdot \text{THF}$ ¹¹ with only the second one being fully described. Compound **1** is unique as the only extended structure where dirhodium carboxylate molecules are bridged by a single exogenous atom.

Compound **2**, having the same composition as **1**, also adopts the triclinic space group $P\bar{1}$ but crystallizes as discrete molecules (Figure 3). Two dirhodium(II) tetra(trifluoroacetate) units with a THF molecule in one of the axial coordination positions are associated through O atoms of carboxylate groups to form a centrosymmetric dimer of dimers $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2]$ (Figure 4). The Rh–Rh distance of $2.391(1) \text{ \AA}$ is typical for $\text{Rh}_2(\text{O}_2\text{CR})_4$ molecules, and the whole $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ core (Table 2) is in no way different from those in other dirhodium tetra(trifluoroacetate) compounds. The molecule of **2** can be described as a “hybrid” of two structures: the side portions (Rh(1) and Rh(1A)) are very similar to rhodium atoms in the bis-adduct complex $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$,^{1b} while the central part (Rh(2) and Rh(2A)) resembles the rhodium atoms in unligated $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ ⁴ (Table 3).

This type of structure is not new; it was reported a long time ago¹² for monoadducts of dirhodium acetate with phenylisocyanide and triphenylphosphine, but no details were made available. Quite recently the geometry of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4 \cdot \text{P}(o\text{-CH}_3\text{OC}_6\text{H}_4)_2]_2$ has been described¹³ and, apparently, is very similar to that of **2**. Finally, the similar structural fragment $[\text{Rh}_2(\text{O}_2\text{CBu}^t)_4(\text{O}_2\text{CMe})_2]$ is present in the complex anion $[\text{Rh}_8-$

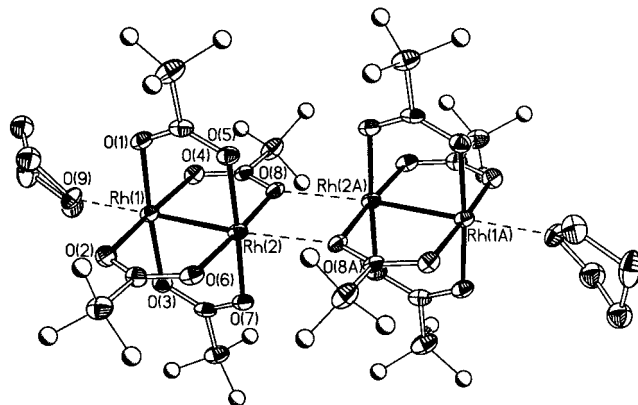


Figure 4. Perspective drawing of the $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2]$ molecule (**2**). Fluorine atoms are shown as spheres of arbitrary radius, with only one orientation of each CF_3 group depicted. Hydrogen atoms of THF groups are omitted. Axial interactions to dirhodium units are drawn by dashed lines.

$(\text{O}_2\text{CBu}^t)_{16}(\mu\text{-}\eta^1, \eta^1\text{-O}_2\text{CMe})_2(\text{toluene})_2]^{2-}$ obtained by Chisholm et al.¹⁴ One interesting feature of this compound is that the linking of two Rh_2 units via the carboxylate oxygen atoms involves only a weak $\text{Rh}\cdots\text{O}$ interaction, $2.61(2) \text{ \AA}$. In the crystal structures of the phosphine adduct¹³ and **2** the distances are much shorter, $2.437(3)$ and $2.406(6) \text{ \AA}$, respectively, but they are still longer than those for polymeric carboxylates without exogenous ligands, $2.337(4)$ ⁴ and $2.34(1) \text{ \AA}$.¹⁵

It is worth noting that both structures, **1** and **2**, are close packed; the volume per non-hydrogen atom is about 15 \AA^3 . Still, the volume per $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$ unit is 16.5 \AA^3 smaller for isomer **1**, which is in accord with its polymeric organization.

One can imagine at least four ways in which Nature could have dealt with the problem of assembling a structure from $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and THF units in a 1:1 ratio. One way, obviously, is to allow only the formation of two separate compounds, namely, our starting materials. Under solution conditions this is what happens. It is also conceivable that a crystal might have been formed containing both $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_\infty$ chains and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ molecules. It is not surprising that the incommensurate nature of these two components does not appear to permit this. The remaining two structures, as they arise from the gas phase, are shown in Chart 2. The occurrence of one or the other of these structures might not be considered surprising, but the formation of both, simultaneously, is interesting and, certainly, unusual. Evidently, the two types of crystals nucleate with about equal probability under the conditions used, and then each type continues to grow by accretion.

Synthetic Aspects. Compounds **1** and **2** have been obtained by the unusual technique of crystallization from the vapor phase. In all experiments we observed the deposition of both emerald-green needles (**1**) and dark-green blocks (**2**) together in the same ampule. These complexes have the same stoichiometry but different crystal structures and can be considered as solid state isomers of the monoadduct $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$. Crystals of **1** and **2** are not air stable and quickly turn blue when exposed to air, which is a typical indication of the formation of diadducts, and which in this case might be $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})(\text{H}_2\text{O})$, $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{H}_2\text{O})_2$, or $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$.

The only complex of rhodium(II) tetra(trifluoroacetate) with tetrahydrofuran previously reported^{1b} was the bis-adduct

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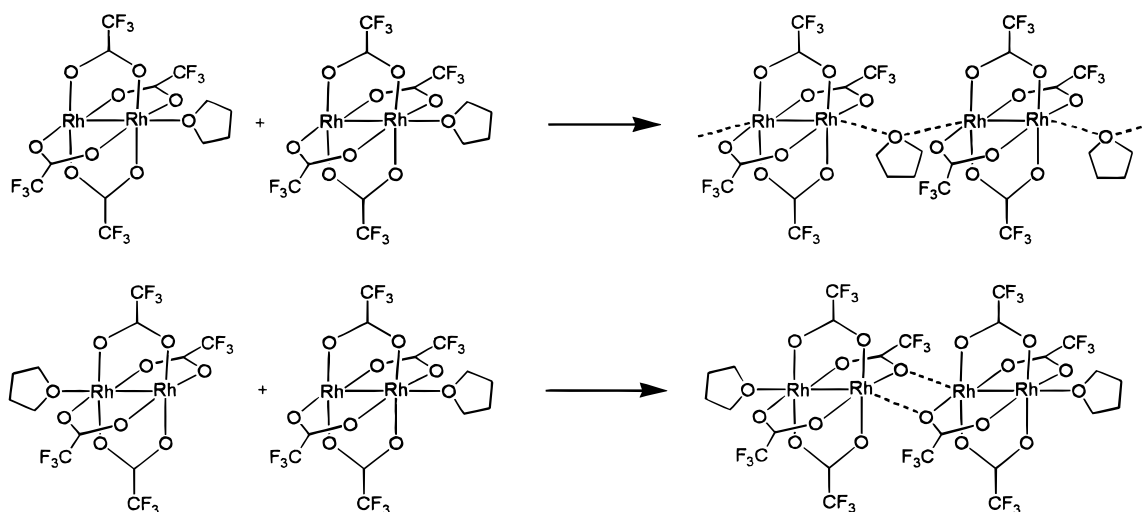
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Chart 2

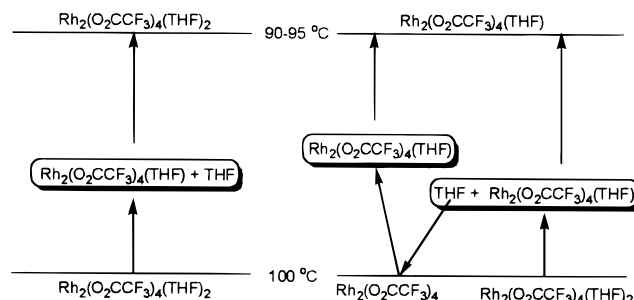


$\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$, which may be easily obtained from solution. Our synthetic strategy for preparation of the 1:1 complex was based on the idea that we need to put the dirhodium complex in conditions where the availability of exogenous ligands is limited. However, this approach does not work in solution chemistry because the much lower solubility of the diadduct compared to other species leads to its exclusive deposition. That is why we used the vaporization process to achieve our goal.

Several 1:1 adducts of dirhodium(II) carboxylates with donor ligands $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}$ have been obtained before. Most of them have L ligands with more than one coordination site: IMME (*N,O*), NITMe (*O,O*),^{2a} AAMP (*N,N*),^{2b} DDA (*N,N*), PHZ (*N,N*),^{2c} amp (*N,N*),^{2d} TCNE (*N,N*),^{2e} 1,4-bq (*O,C*^{2f,g} and *O,O*^{2h}), 1,4-nq (*O,C*^{2f} and *O,O*^{2h}), 2,3-Me₂-1,4-bq (*O,O*),^{2h} C₆Me₆ (*C,C*).⁶ They all have structures of type II, noted earlier. The synthetic procedure for the preparation of these complexes in solution (except C₆Me₆) is very similar to that for diadducts $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$.¹ At the same time there are few reports on isolation of $\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}$ compounds where L ligands are formally monodentate. A monohydrate $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})$ has been described¹⁶ as obtained from the reaction mixture containing small quantities of water, but its characterization is still not confirmed. The preparation of monoadducts of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{L}$ (L = DMSO, SEt₂) as bulk materials by thermal decomposition of corresponding bis-adducts has been reported,¹⁷ but structural characterization is lacking. Finally, the complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ with the P(*o*-CH₃OC₆H₄)Ph₂ ligand has been isolated and fully characterized.¹³ In the latter case the authors have managed to find specific conditions when the monoadduct exists in solution and crystallizes out in preference to the corresponding 1:2 compound. This approach, however, cannot be applied for dirhodium tetra(trifluoroacetate), which shows an exceptional ability for coordination of donor ligands to both axial positions whenever possible.

The results obtained here are more easily described than explained. We feel obliged to proffer some explanation, however, and offer the following qualitative suggestion. In addition to the reported results on the heating of a physical mixture of

Chart 3



$\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ we must take into account the results of attempting to sublime each of these components alone. As we have already⁴ reported, a temperature of at least 200 °C is necessary to achieve a reasonable rate of sublimation for $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$; at only 100 °C the rate is negligible. On the other hand, we have studied the behavior of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ and found that it can be sublimed efficiently at 100 °C to deposit as $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$, i.e., unchanged.

To explain the totality of our results at 100 °C we propose the schemes shown in Chart 3. We first postulate, as shown on the left, that $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ sublims by dissociation into $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$ and THF, with recombination occurring as they condense in the cooler region. For the mixture of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$, we then suppose that THF in the gas phase, which arises from heating $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})_2$ at 100 °C, reacts rapidly with the hot solid $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ to generate more molecules of gaseous $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$. All gaseous molecules of monoadduct, however created, then condense in the cooler region to give the two crystalline phases of composition $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{THF})$, **1** and **2**.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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