

Synthesis and Crystal Structure of a Rhodium(II) Formamidinate Dimer with Axial Water and Methanol Molecules

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The title compound of a lantern-type rhodium(II) dimer, $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})(\text{MeOH})]$ (4-Et-pf⁻ = *N,N'*-bis(4-ethylphenyl)formamidinate anion), was isolated and the crystal structure was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.866(2)\text{\AA}$, $b = 13.435(3)\text{\AA}$, $c = 14.834(4)\text{\AA}$, $\alpha = 85.764(3)^\circ$, $\beta = 75.546(3)^\circ$, $\gamma = 83.729(3)^\circ$, $V = 2082.0(7)\text{\AA}^3$, $D_x = 1.571\text{ g/cm}^3$, and $Z = 2$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0449 and 0.1222, respectively, for all 12360 independent reflections. The *cis*-(2:2) arrangement of the 4-Et-pf and trifluoroacetato ligands within the dimer was confirmed, the methanol and water molecules coordinating to each axial site of the dimer, respectively. The Rh-Rh distance is 2.4487(7) \AA and the axial Rh-O distances are 2.321(3) (for Rh-O (MeOH)) and 2.454(5) \AA (for Rh-O (H₂O)), respectively.

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Much interest has been devoted to lantern-type dimer complexes with a direct metal-metal bond, due to their unique properties based on the metal-metal bond.¹ Recently, lantern-type dimers have been used as building blocks in combination with axial linker ligands to produce assembled complexes with extended 1 - 3 dimensional structures.¹ Rhodium(II) formamidinate dimers, $[\text{Rh}_2(4\text{-R-pf})_4]$ (4-R-pf⁻ = *N,N'*-bis(4-alkylphenyl)formamidinate anion), were reported to work as building blocks, although rhodium(II) carboxylate dimers ($[\text{Rh}_2(\text{O}_2\text{CR})_4]$) are still more common as building blocks.¹⁻³ 1,4-Diisocyanobenzene (1,4-dib) coordinates to the rhodium(II) atoms through the crowded axial sites with four aryl groups of $[\text{Rh}_2(4\text{-R-pf})_4]$, because 1,4-dib has long and narrow coordinating isocyno

arms.^{2,3} We have reported crystal structures of 1-dimensional polymer complexes, $[\text{Rh}_2(4\text{-Me-pf})_4(1,4\text{-dib})]_n \cdot 2n(\text{C}_6\text{H}_6)$ and $[\text{Rh}_2(4\text{-Me-pf})_4(1,4\text{-dib})]_n \cdot 2n(\text{toluene})$, and a hexanuclear complex, $[\{\text{Rh}_2(4\text{-Me-pf})_4\}_3(1,4\text{-dib})_2] \cdot 6\text{H}_2\text{O}$.^{2,3} Although our attempts to obtain the assembled complexes using axial linkers

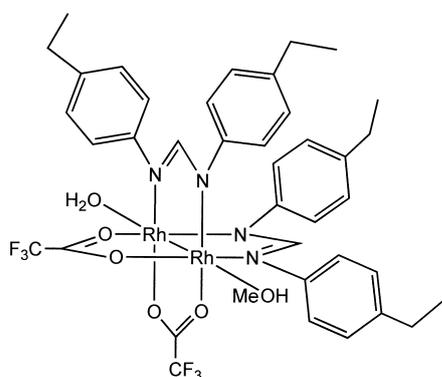


Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

| | |
|---|--|
| Chemical formula: $\text{C}_{39}\text{H}_{44}\text{F}_6\text{N}_4\text{O}_6\text{Rh}_2$ | |
| Formula weight = 984.60 | |
| $T = 90\text{ K}$ | |
| Crystal system: triclinic | Space group: $P\bar{1}$ |
| $a = 10.866(2)\text{\AA}$ | $\alpha = 85.764(3)^\circ$ |
| $b = 13.435(3)\text{\AA}$ | $\beta = 75.546(3)^\circ$ |
| $c = 14.834(4)\text{\AA}$ | $\gamma = 83.729(3)^\circ$ |
| $V = 2082.0(7)\text{\AA}^3$ | $Z = 2$ |
| $D_x = 1.571\text{ g/cm}^3$ | |
| Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$) | |
| $\mu(\text{Mo } K\alpha) = 0.868\text{ mm}^{-1}$ | $F(0\ 0\ 0) = 996$ |
| Crystal size = $0.20 \times 0.15 \times 0.07\text{ mm}^3$ | |
| No. of reflections collected = 12360 | |
| No. of independent reflections = 8954 | |
| θ range for data collection: 1.42 to 28.31° | |
| Data/Restraints/Parameters = 8954/7/542 | |
| Goodness-of-fit on $F^2 = 1.008$ | |
| R indices [$I > 2\sigma(I)$]: $R1 = 0.0449$, $wR2 = 0.1134$ | |
| R indices (all data): $R1 = 0.0750$, $wR2 = 0.1222$ | |
| $(\Delta/\sigma)_{\text{max}} = 0.001$ | |
| $(\Delta\rho)_{\text{max}} = 2.138\text{ e}\text{\AA}^{-3}$ | $(\Delta\rho)_{\text{min}} = -1.264\text{ e}\text{\AA}^{-3}$ |
| Measurement: Bruker Smart APEX CCD diffractometer | |
| Program system: SHELXTL | |
| Structure determination: Direct methods (SHELXS-97) | |
| Refinement: full matrix least-squares (SHELXL-97) | |
| CCDC deposition number: 851766 | |

other than 1,4-dib were unsuccessful,⁴ we found that the reaction of $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2]$ with pyrazine (pyz) in toluene gave a polymer complex, $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{pyz})]_n \cdot n(\text{toluene})$, of which the crystal structure was reported along with that of its parent dimer $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{MeOH})_2]$ (**1**).⁵ In order to develop the chemistry of the assembled complexes of rhodium(II) formamidinate dimers, it is important to investigate the dimers, themselves. Here, we report on $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{MeOH})(\text{H}_2\text{O})]$ (**2**), the structure of which is depicted in Fig. 1.

The synthetic procedure is basically the same as those reported for the rhodium(II) dimers, $[\text{Rh}_2(4\text{-Me-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})_2]$ ⁶ and $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{MeOH})_2]$ (**1**),⁵ which have been synthesized by the reaction of $[\text{Rh}(\text{cod})(4\text{-R-pf})_2]$ (cod = cycloocta-1,5-diene; R = Me and Et)⁷ with silver(I) trifluoroacetate. The details are presented in the deposit material.

Crystals suitable for the X-ray structure analysis were deposited in a $\text{CH}_2\text{Cl}_2\text{-MeOH}$ reaction solution. Crystal data and details concerning data collection are given in Table 1. There are disorders at fluorine atoms (F4, F5, and F6) on the carboxylate ions, and hence they are divided into two positions (refinement resulted in 0.747:0.253 ratio), respectively. The hydrogen atoms, except for those with O6 (in the water molecule), were inserted at their calculated positions and fixed there.

The crystal structure of the title compound, $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})(\text{MeOH})]$ (**2**), is drawn by ORTEP in Fig. 2. Selected bond distances and angles are listed in Table S1. The (rhodium(II))₂ core has two bridging *N,N'*-bis(4-ethylphenyl)-formamidinate ions (4-Et-pf⁻) and two bridging trifluoroacetate ions (CF_3CO_2^-) with the *cis*-(2:2) arrangement. One of the two axial sites of the dimer is occupied by a methanol molecule with a Rh(1)-O(5) distance of 2.321(3) Å; the other axial site is occupied by the water molecule with a Rh(2)-O(6) distance of 2.454(5) Å. We recently reported on the crystal structures of a dimer complex, $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{MeOH})_2]$ (**1**), and a polymer complex, $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{pyz})]_n \cdot n(\text{toluene})$.⁵ The *cis*-(2:2) arrangement of the intra-dimer bridging ligands of the dimer core is preserved in the polymer having the axial linker pyz (pyrazine). The most important difference between $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{MeOH})_2]$ (**1**) and $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})(\text{MeOH})]$ (**2**) is that both axial sites of **1** are occupied by two methanol molecules, although those of **2** are with water and methanol molecules. The crystallization of **2** was made in a $\text{CH}_2\text{Cl}_2\text{-MeOH}$ mixed-solvent solution, although that for **1** was in a MeOH solution, which led to the different axial coordinating features between **1** and **2**. The residual water in the crystallization solvent after the synthetic reaction possibly participated in the axial coordination in the case of **2**, while the recrystallization in methanol allowed only axial coordination by methanol molecules in the case of **1**. The Rh(1)-Rh(2) distance for **2** is 2.4487(7) Å is almost the same as that for **1** (2.4484(6) Å), and longer than that (2.425(1) Å) for $[\text{Rh}_2(4\text{-Me-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})_2] \cdot 0.5\text{C}_6\text{H}_6$ (4-Me-pf⁻ = *N,N'*-di-*p*-tolyl-formamidinate anion),⁶ but shorter than that (2.4564(10) Å) for $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2(\text{pyz})]_n \cdot n(\text{toluene})$.⁵ This may be because pyrazine (pyz) strongly donates to the rhodium(II) dimer core compared with water and methanol, resulting in an enlargement of the Rh-Rh distance. A packing diagram of **2** is shown in Fig. S1. There is no noticeable interaction between the present dimer units in the crystal, like in the case of **1**, of

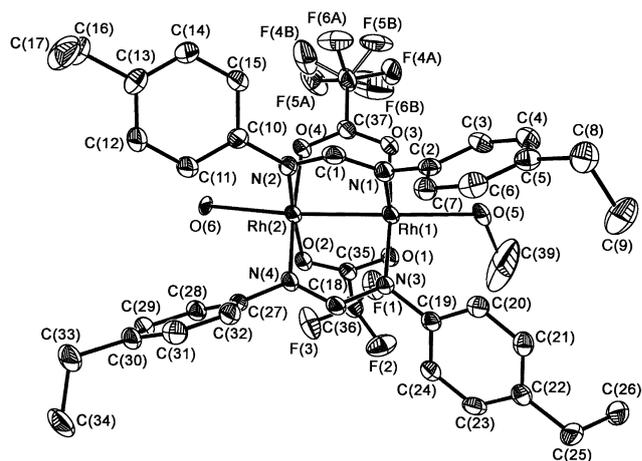


Fig. 2 ORTEP view of the title compound **2**. The thermal ellipsoids are shown at the 50% probability level.

which a diagram is given in Fig. S2.

In the ¹H and ¹³C NMR spectra of $[\text{Rh}_2(4\text{-Et-pf})_2(\text{O}_2\text{CCF}_3)_2]$ (Figs. S3 and S4), which were measured in CD_2Cl_2 solutions at room temperature, all signals observed were assigned as those for protons and carbons of the 4-Et-pf and trifluoroacetate ligands with the *cis*-(2:2) arrangement in the dimer, indicating that the dimer core structure is maintained in the CD_2Cl_2 solution.

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