Crystal Structure of a Lantern-Type Dirhodium(II) Complex with a *cis*-(2:2) Arrangement of Two Formamidinato and Two Trifluoroacetato Bridges

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The title compound of a lantern-type rhodium(II) dinuclear complex, *cis*-[Rh₂(3,5-Me₂-pf)₂(O₂CCF₃)₂(H₂O)₂]-0.5C₆H₁₄ (3,5-Me₂-pf = *N,N'*-bis(3,5-dimethylphenyl)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* = 11.4725(16) Å, *b* = 12.4679(17) Å, *c* = 16.113(2) Å, α = 77.391(2)°, β = 75.265(2)°, γ = 85.548(2)°, *V* = 2174.6(5) Å³, *D_x* = 1.548 g/cm³, and *Z* = 2. The *R*1 [*I* > 2σ(*I*)] and *wR*2 (all data) values are 0.0275 and 0.0625, respectively, for all 9465 independent reflections. The *cis*-(2:2) arrangement of the 3,5-Me₂-pf and trifluoroacetato ligands within the dinuclear core was confirmed, the axial sites of the dimer being occupied by the water molecules. The Rh-Rh distance is 2.4538(4) Å and the axial Rh-O (H₂O) distances are 2.3309(16) and 2.3196(16) Å.

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There has been much interest directed to lantern-type dinuclear metal complexes with direct metal-metal bonds due to their unique properties based on their metal-metal bonds.^{1,2} Formamidinate ions as well as carboxylate ions are known to work as a dinuclear bridging ligand to give a lantern-type dinuclear structure.^{1,2} Dinuclear complexes with the mixing of carboxylato and formamidinato bridges are intriguing, because the chemistry would be newly developed based on the different bridging groups within the dinuclear core. We have reported on the crystal structure rhodium(II) dinuclear complexes with two formamidinato and two carboxylato bridging ligands in a *cis*-(2:2) arrangement around the dinuclear core, *cis*-[Rh₂(4-Et-pf)₂(O₂CCF₃)₂(H₂O)(MeOH)] (1) and *cis*-[Rh₂(4-Et-pf)₂(O₂CCF₃)₂(MeOH)₂] (2), where 4-Et-pf = *N,N'*-bis(4-ethylphenyl)formamidinate anion.^{3,4} They have the same dinuclear structure with similar dimensions other than the

difference in the axial ligand between H₂O and MeOH (Rh-Rh = 2.4487(7) Å, Rh-N(4-Et-pf) = 2.008(4) - 2.012(3) Å, Rh-O(O₂CCF₃) = 2.078(3) - 2.100(3) Å, Rh-O(H₂O) = 2.453(5) Å, and Rh-O(MeOH) = 2.321(3) Å for 1; Rh-Rh = 2.4484(6) Å, Rh-N(4-Et-pf) = 2.005(3) - 2.016(3) Å, Rh-O(O₂CCF₃) = 2.079(2) - 2.115(2) Å, and Rh-O(MeOH) = 2.314(2) and

Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

Chemical formula: C ₄₁ H ₄₉ F ₆ N ₄ O ₆ Rh ₂	
Formula weight = 1013.66	
<i>T</i> = 90 K	
Crystal system: triclinic	Space group: <i>P</i> $\bar{1}$
<i>a</i> = 11.4725(16) Å	α = 77.391(2)°
<i>b</i> = 12.4679(17) Å	β = 75.265(2)°
<i>c</i> = 16.113(2) Å	γ = 85.548(2)°
<i>V</i> = 2174.6(5) Å ³	<i>Z</i> = 2
<i>D_x</i> = 1.548 g/cm ³	
Radiation: Mo <i>K</i> α (λ = 0.71073 Å)	
μ (Mo <i>K</i> α) = 0.834 mm ⁻¹	<i>F</i> (0 0 0) = 1030
Crystal size = 0.28 × 0.20 × 0.10 mm ³	
No. of reflections collected = 13170	
No. of independent reflections = 9465	
θ range for data collection: 1.67 to 28.36°	
Data/Restraints/Parameters = 9465/0/540	
Goodness-of-fit on <i>F</i> ² = 0.920	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> 1 = 0.0275, <i>wR</i> 2 = 0.0610	
<i>R</i> indices (all data): <i>R</i> 1 = 0.0376, <i>wR</i> 2 = 0.0625	
(Δ/ σ) _{max} = 0.003	
(Δρ) _{max} = 0.941 eÅ ⁻³	(Δρ) _{min} = -0.465 eÅ ⁻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: 1062091	

Table 2 Structural comparison of *cis*-[Rh₂(formamidinate)₂(trifluoroacetate)₂(L^{ax})₂] cores

Compound	Rh-Rh (Å)	Rh-L ^{ax} (Å)/donor atom	Ref.
<i>cis</i> -[Rh ₂ (4-Et-pf) ₂ (O ₂ CCF ₃) ₂ (H ₂ O)(MeOH)] (1)	2.4487(7)	2.321(3)/O _{MeOH} , 2.454(5)/O _{H₂O}	3
<i>cis</i> -[Rh ₂ (4-Et-pf) ₂ (O ₂ CCF ₃) ₂ (MeOH) ₂] (2)	2.4484(6)	2.314(2)/O, 2.328(2)/O	4
<i>cis</i> -[Rh ₂ (3,5-Me ₂ -pf) ₂ (O ₂ CCF ₃) ₂ (H ₂ O) ₂]-0.5C ₆ H ₁₄ (3)	2.4538(5)	2.3309(16)/O, 2.3196(16)/O	This work
<i>cis</i> -[Rh ₂ (4-Me-pf) ₂ (O ₂ CCF ₃) ₂ (H ₂ O) ₂]-0.5C ₆ H ₆	2.425(1)	2.311(3)/O, 2.319(3)/O	5
<i>cis</i> -[Rh ₂ (4-Me-pf) ₂ (O ₂ CCF ₃) ₂ (MeCN) ₂]	2.474(5)	2.267(5)/N, 2.265(5)/N	6
[Rh ₂ (4-Et-pf) ₂ (O ₂ CCF ₃) ₂ (pyz)] _n · <i>n</i> (toluene)	2.4564(10)	2.314(4)/N, 2.286(4)/N	4

2.328(2)Å for **2**).^{3,4} Compared with lantern-type Rh₂ dinuclear complexes with *N,N'*-bis(4-alkylphenyl)formamidinato bridging ligands,⁵⁻⁷ the dinuclear complexes of the formamidinato ligands with alkyl groups at the 3 and 5 positions of the phenyl rings are relatively limited in number.¹ Here, we report on the crystal structure of *cis*-[Rh₂(3,5-Me₂-pf)₂(O₂CCF₃)₂(H₂O)₂]-0.5C₆H₁₄ (3,5-Me₂-pf⁻ = *N,N'*-bis(3,5-dimethylphenyl)formamidinate anion, **3**), of which the chemical structure is depicted in Fig. 1.

The synthetic procedure of [Rh₂(3,5-Me₂-pf)₂(O₂CCF₃)₂] is basically the same as those for [Rh₂(4-Et-pf)₂(O₂CCF₃)₂]^{3,4} and [Rh₂(4-Me-pf)₂(O₂CCF₃)₂] (4-Me-pf⁻ = *N,N'*-di-*p*-tolylformamidinate anion).⁵⁻⁷ Crystals suitable for X-ray crystal structure analysis were obtained by recrystallization from a THF solution containing hexane.

One of the blackish single crystals obtained for **3** was mounted on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo-*K*_α radiation; a preliminary examination was made and data were collected. Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there.

The crystal structure, drawn by ORTEP, is shown for **3** in Fig. 2. The selected bond distances and angles are given in Table S1. It is clearly shown that bridging ligands, 3,5-Me₂-pf⁻ and CF₃CO₂⁻, adopt the *cis*-(2:2) arrangement around the Rh₂ lantern-type dinuclear core. The packing diagram (Fig. S1) shows that hexane molecules exist as the crystal solvent other than the Rh₂ dinuclear units with axial water molecules; there is no contact to be mentioned between the crystal solvent hexane and the Rh₂ dinuclear unit. The Rh(1)-Rh(2) distance is 2.4538(4)Å. This short distance is indicative of the existence of a direct Rh-Rh bond within the dinuclear core.¹ The axial water molecules coordinate to the dinuclear core with the distances of 2.3309(16) (for Rh(1)-O(5)) and 2.3196(16)Å (for Rh(2)-O(6)). The axial distances are similar to those of [Rh₂(4-Me-pf)₂(O₂CCF₃)₂(H₂O)₂]-0.5C₆H₆ (2.311(3) and 2.319(3)Å).⁵ The Rh-Rh and Rh-L^{ax} (L^{ax} = axial ligand) bond distances are summarized in Table 2 for the lantern-type rhodium(II) dinuclear cores with the *cis*-(2:2) arrangement of formamidinate and trifluoroacetate bridging anions. The Rh-Rh bond lengths, (2.474(5)Å for *cis*-[Rh₂(4-Me-pf)₂(O₂CCF₃)₂(MeCN)₂] and 2.4564(10) for [Rh₂(4-Et-pf)₂(O₂CCF₃)₂(pyz)]_n·*n*(toluene)), of the dinuclear complexes axially coordinated by nitrogen atoms are rather longer than those (2.4487(7)Å for **1**, 2.4484(6)Å for **2**, 2.4538(4)Å for **3**, and 2.425(1)Å for *cis*-[Rh₂(4-Me-pf)₂(O₂CCF₃)₂(H₂O)₂]-0.5C₆H₆) of the dinuclear cores axially coordinated by oxygen atoms. This could come from the stronger donating nature of nitrogen atoms (MeCN and pyz (pyrazine)) compared with that of oxygen atoms (MeOH and H₂O).³⁻⁶ There seems to be no important effect on the Rh-Rh bond length due to the difference in the substituted alkyl groups (Me and Et), their numbers, and positions on the phenyl rings of the formamidinate ligands.

Fig. 2 ORTEP view of the title compound, **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

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