

Variation of hydrogen-bonded networks in hexafluorophosphate salts of amidate-bridged dirhodium(II,III) complexes with axial aqua ligands

Masahiro Ebihara* and Yasuhiro Fuma

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

Correspondence e-mail: ebihara@apchem.gifu-u.ac.jp

Received 5 April 2006

Accepted 18 May 2006

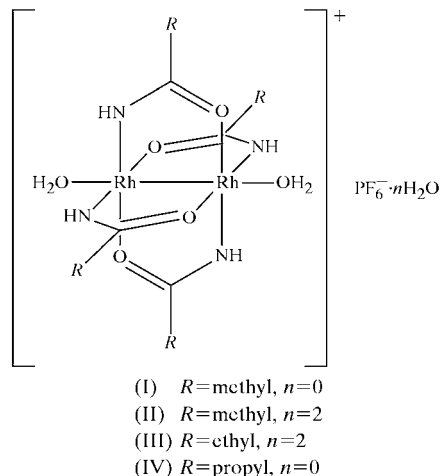
Online 15 June 2006

In diaquatetra- μ -acetamidato- $\kappa^4N:O;\kappa^4O:N$ -dirhodium(II,III) hexafluorophosphate, $[\text{Rh}_2(\text{C}_2\text{H}_4\text{NO})_4(\text{H}_2\text{O})_2]\text{PF}_6$, and diaquatetra- μ -acetamidato- $\kappa^4N:O;\kappa^4O:N$ -dirhodium(II,III)hexafluorophosphate dihydrate, $[\text{Rh}_2(\text{C}_2\text{H}_4\text{NO})_4(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2\text{H}_2\text{O}$, the cations and anions lie on inversion centers. Diaquatetra- μ -propionamidato- $\kappa^4N:O;\kappa^4O:N$ -dirhodium(II,III) hexafluorophosphate dihydrate, $[\text{Rh}_2(\text{C}_3\text{H}_6\text{NO})_4(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2\text{H}_2\text{O}$, and diaquatetra- μ -butyramidato- $\kappa^4N:O;\kappa^4O:N$ -dirhodium(II,III) hexafluorophosphate, $[\text{Rh}_2(\text{C}_4\text{H}_8\text{NO})_4(\text{H}_2\text{O})_2]\text{PF}_6$, crystallize with two crystallographically independent complexes that lie on inversion centers. In all of the structures, the dirhodium units are hydrogen bonded to one another. The hydrogen-bonded networks vary with the alkyl substituents.

Comment

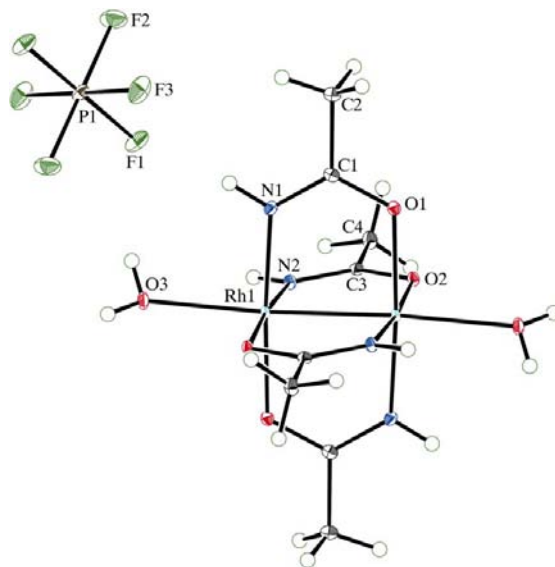
Amidate-bridged paddlewheel complexes are useful modules in building assembled structures because they have hydrogen-donating NH groups and hydrogen-accepting O-atom sites in addition to the axial coordination sites. We have studied assembled complexes of acetamidate-bridged paddlewheel dirhodium complexes with halide linkers, namely one-dimensional chain structures of $[\text{Rh}_2(\text{acam})_4(\mu\text{-}X)] \cdot n\text{H}_2\text{O}$ (Hacam is acetamide; $X = \text{Cl}, \text{Br}$ and I ; $n = 0, 2, 3$ and 7 ; Yang *et al.*, 2000, 2001), a two-dimensional honeycomb structure of $[\{\text{Rh}_2(\text{acam})_4\}_3(\mu_3\text{-Cl})_2] \cdot 4\text{H}_2\text{O}$ (Takazaki *et al.*, 2003) and a three-dimensional diamondoid structure of $[\{\text{Rh}_2(\text{acam})_4\}_2(\mu_4\text{-I})] \cdot 6\text{H}_2\text{O}$ (Fuma *et al.*, 2004). In all these structures, direct hydrogen bonds between the NH groups and O atoms of the amidate ligands play an important role. In the hydrates, hydrogen bonds between the amidate ligands and water molecules affect the physical properties (Fuma *et al.*, 2004). We have also reported anionic chain structures of the dirhodium complexes with tetrachloroplatinate and tetrachloropalladate linkers, *viz.* $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2][\text{Rh}_2(\text{acam})_4(\mu\text{-MCl}_4)] \cdot 2\text{H}_2\text{O}$ ($M = \text{Pd}$ and Pt ; Yang *et al.*, 2006). In these

structures, the cationic $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2]^+$ complex participates in hydrogen-bonded networks using the bridging



amidate and axial aqua ligands. In this paper, we report a variation of hydrogen-bonded networks in the hexafluorophosphate salts of amidate-bridged dirhodium complexes, $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2]\text{PF}_6$, (I), $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2\text{H}_2\text{O}$, (II), $[\text{Rh}_2(\text{pram})_4(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2\text{H}_2\text{O}$ (Hpram is propionamide), (III), and $[\text{Rh}_2(\text{buam})_4(\text{H}_2\text{O})_2]\text{PF}_6$ (Hbuam is butyramide), (IV).

The structure of (I) is shown in Fig. 1. Compound (I) is isostructural with $[\text{Rh}_2(\text{acam})_4(\text{H}_2\text{O})_2]\text{ClO}_4$ (Baranovskii *et al.*, 1986). The dirhodium complex lies around an inversion center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The hexafluorophosphate ion lies on another inversion center at $(\frac{1}{2}, 0, 0)$. The complex is the so-called (2,2)-*cis* isomer, in which each Rh atom is coordinated by two *cis* N and two *cis* O atoms (Table 1). The complexes form a hydrogen-bonded chain along the *b* axis, with the axial aqua ligand (O3) donating a H atom to one of the amidate O atoms


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

[O2ⁱⁱ; symmetry code: (ii) $x, y - 1, z$] (Table 2 and Fig. 2). The complexes also form hydrogen bonds between amidate atom N2 and amidate atom O1ⁱⁱⁱ [symmetry code: (iii) $x + 1, y, z$]. These hydrogen bonds connect the complexes two-dimensionally in the *ab* plane. The hexafluorophosphate ion is also hydrogen bonded *via* the amidate (N1) and axial aqua ligands, and these connect the hydrogen-bonded sheets three-dimensionally. In this structure, all the N and O atoms are included in the hydrogen-bonded network.

In the structure of (II) (Fig. 3 and Table 3), there is one independent complex on an inversion center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ that has an equivalent site $(\frac{1}{2}, 0, 0)$. The hexafluorophosphate ion lies on another inversion center at $(0, \frac{1}{2}, 0)$ that has an equivalent site $(0, 0, \frac{1}{2})$. The water molecule lies on a general position. The crystal structure is shown in Fig. 4. In compound (II), two aqua ligands, two amidate N atoms and four amidate O atoms are used for direct hydrogen bonding between the complexes (Table 4), as also seen in (I), but the network structure is

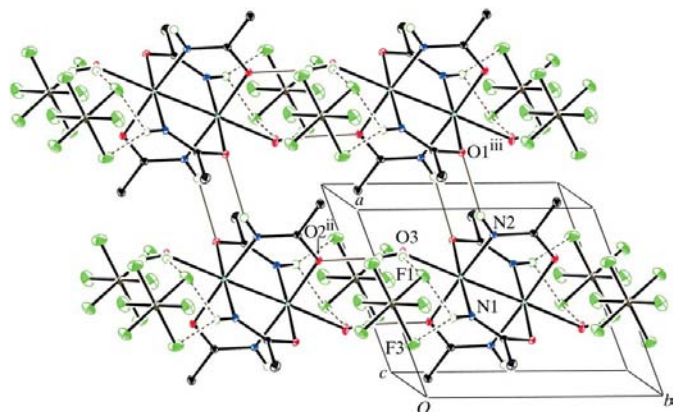


Figure 2

The crystal structure of (I). For clarity, H atoms of methyl groups have been omitted. Hydrogen bonds between the rhodium complexes are drawn as thin lines and the other hydrogen bonds are drawn as dashed lines. [Symmetry codes: (ii) $x, y - 1, z$; (iii) $x + 1, y, z$.]

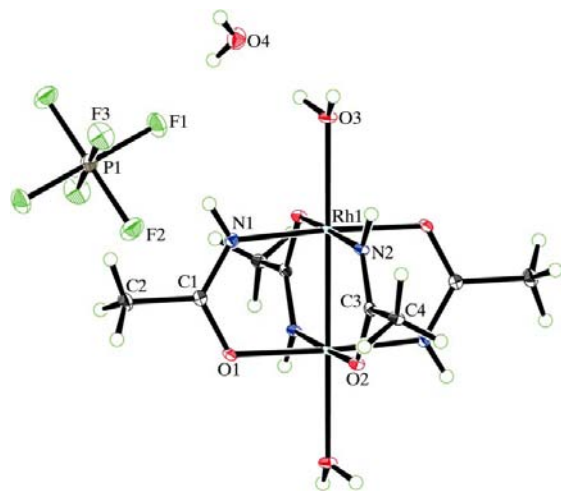


Figure 3

The molecular structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

different from that in (I). The complex donates a H atom of the axial aqua ligand (O3) to amidate atom O2ⁱⁱ [symmetry code: (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$]. The complex also donates the

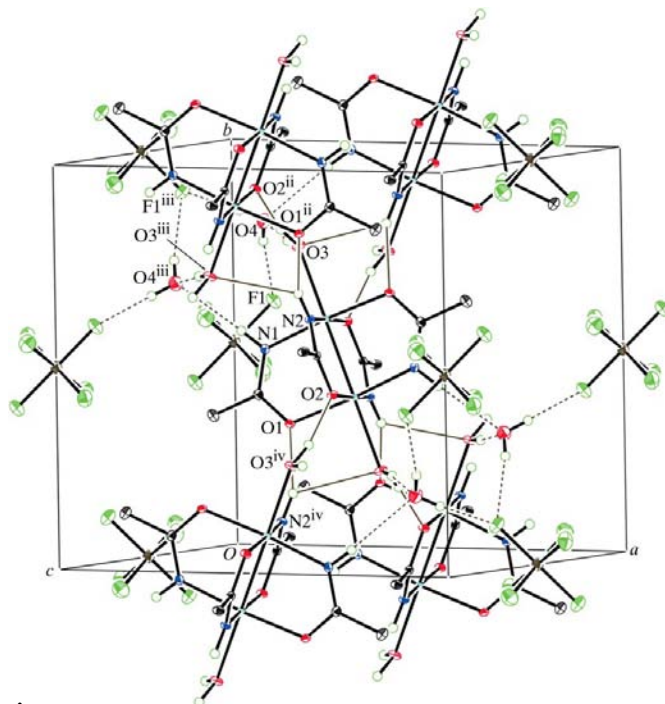


Figure 4

The crystal structure of (II). For clarity, methyl H atoms have been omitted. Hydrogen bonds between the rhodium complexes are drawn as thin lines and the other hydrogen bonds are drawn as dashed lines. [Symmetry codes: (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.]

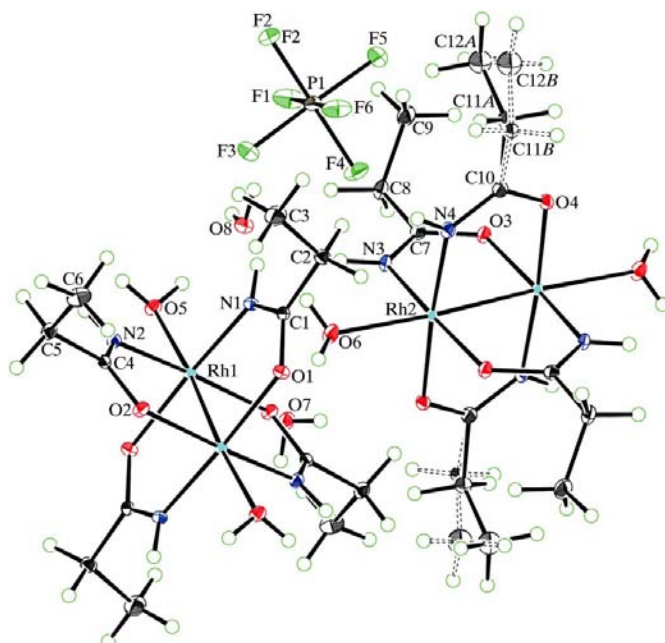


Figure 5

The molecular structure of (III), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor disorder components are shown with dashed lines.

amine H atom of atom N2 to amidate atom O1ⁱⁱ. The resulting two-dimensional sheet structure is extended in the *bc* plane. The aqua ligand (O3) and amide atom N1 also hydrogen bond to water molecules [O4 and O4ⁱⁱⁱ; symmetry code: (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$]. Water molecule O4 donates H atoms to atoms F1 and F1ⁱⁱⁱ of the hexafluorophosphate ions. The water molecule and the hexafluorophosphate ion then connect the hydrogen-bonded sheets.

The structure of (III) is shown in Fig. 5 and selected bond lengths are given in Table 5. In the unit cell there are two independent dirhodium complexes that lie around inversion centers at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$. Two independent water molecules are also included. The hydrogen-bonded network in (III) is shown in Fig. 6. There is only one hydrogen bond that directly connects the complexes in (III); aqua ligand O6 hydrogen bonds to amidate atom O2ⁱ [symmetry code: (i) $-x, -y + 1, -z$]. The resulting one-dimensional hydrogen-bonded chain extends in the [111] direction. The water molecules connect the chains two-dimensionally. One water molecule (O7) acts as a hydrogen-bond donor to atom O4ⁱⁱ [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$] and accepts hydrogen bonds from N2ⁱⁱⁱ and O5ⁱⁱⁱ [symmetry code: (iii) $-x + 1, -y + 1, -z$]. The other water molecule (O8) acts as a donor to atom O1^v [symmetry code: (v) $x + 1, y, z$] and an acceptor from atoms O5 and O6. Hydrogen bonds also exist to the F atoms of the hexafluorophosphate ion (Table 6).

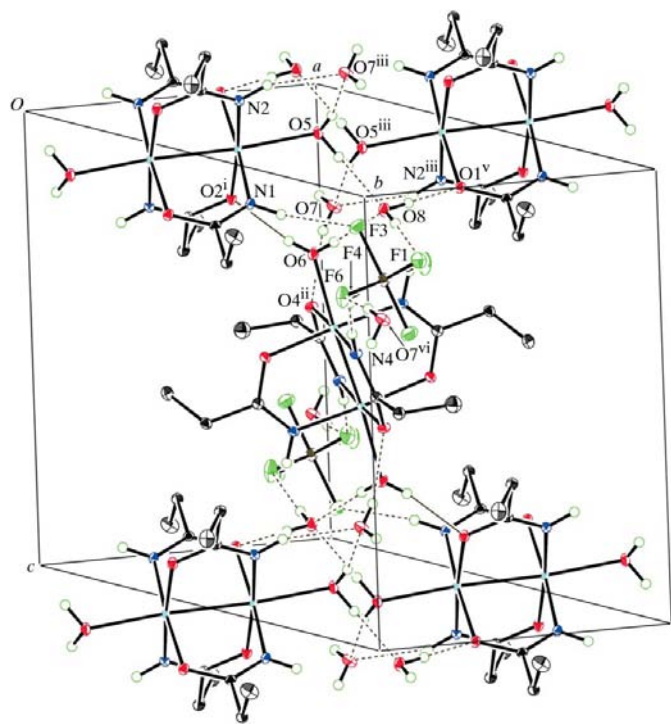


Figure 6
The crystal structure of (III). For clarity, the minor components of the disordered atoms and ethyl H atoms have been omitted. Hydrogen bonds between the rhodium complexes are drawn as thin lines and the other hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (v) $x + 1, y, z$; (vi) $x - 1, y + 1, z$.]

The structure of (IV) is shown in Fig. 7 and selected bond lengths are given in Table 7. Compound (IV) also has two independent dirhodium complexes in the unit cell. One

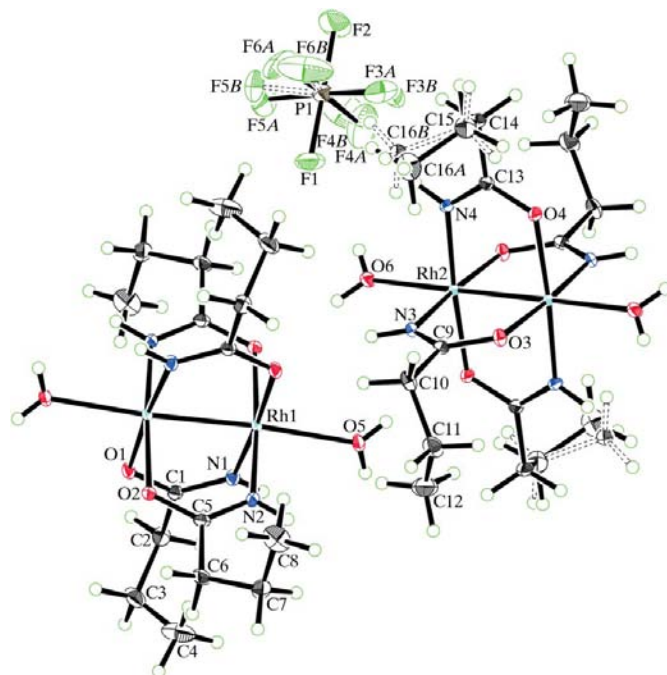


Figure 7
The molecular structure of (IV), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The minor disorder components are shown with dashed lines.

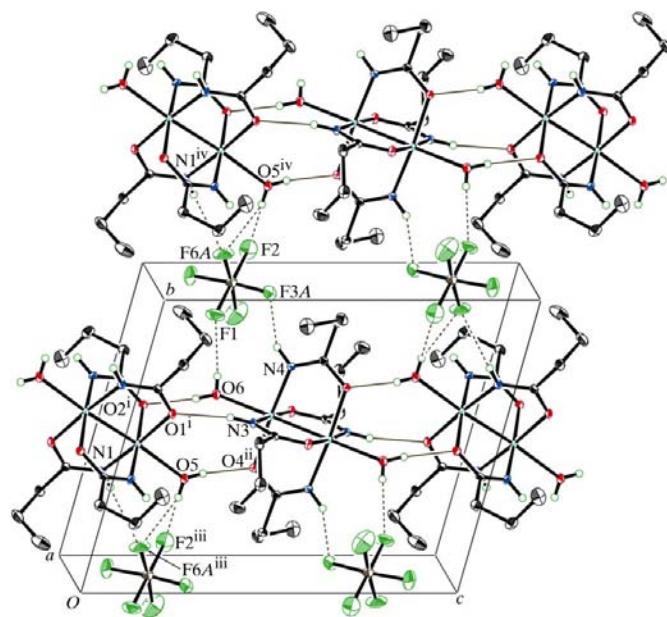


Figure 8
The crystal structure of (IV). For clarity, the minor components of the disordered atoms and propyl H atoms have been omitted. Hydrogen bonds between the rhodium complexes are drawn as thin lines and the other hydrogen bonds are drawn as dashed lines. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y - 1, z$; (iv) $x, y + 1, z$.]

complex lies on an inversion center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the other on another inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$. The two independent complexes are hydrogen bonded to each other (Table 8 and Fig. 8). Axial aqua ligands of both complexes act as donors to the O atoms of neighboring complexes [O5 to O4ⁱⁱ and O6 to O2ⁱ; symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$]. Amidate atom N3 acts as a donor to amidate atom O1ⁱ. These hydrogen bonds connect the complexes into a one-dimensional chain in the *c* direction. The hexafluorophosphate ion accepts hydrogen bonds from atoms N4 and O6 and from N1^{iv} and O5^{iv} [symmetry code: (iv) $x, y + 1, z$]. The anion thus connects the chains two-dimensionally.

Experimental

[Rh₂(acam)₄(H₂O)₂]-6H₂O was synthesized according to a published method (Doyle *et al.*, 1990). Compounds (I) and (II) were prepared by a modification of the method of Baranovskii *et al.* (1986) for preparing [Rh₂(acam)₄(H₂O)₂]ClO₄. To an aqueous solution (50 ml) of [Rh₂(acam)₄(H₂O)₂]-6H₂O (0.751 g, 1.29 mmol) at 353 K, Ag₂SO₄ (0.200 g, 0.64 mmol) was added and the mixture was stirred for 10 min. The solution was cooled to 273 K and the precipitate was filtered off. NH₄PF₆ (10.1 g, 62.1 mmol) was added to the brown filtrate and left for 20 h to give brown crystals of (II) (yield 0.612 g, 72%). The crystals gradually lost their water of crystallization. Crystals of (I) were obtained by slow evaporation of an aqueous solution of (II). Analysis calculated for C₈H₂₀F₆N₄O₆PRh₂: C 15.52, H 3.26, N 9.05%; found: C 15.42, H 3.12, N 8.74%. Compound (III) was prepared in a similar manner to (II). [Rh₂(CH₃CO₂)₄(CH₃OH)₂] (0.515 g, 1.02 mmol) was heated at 363 K for 1 h under reduced pressure. An excess of propionamide (3.60 g, 49.3 mmol) and toluene (76 ml) were added. The suspension was refluxed for 7 d under an argon atmosphere using a Soxhlet extractor in which the extraction thimble contained sodium carbonate and molecular sieves (3 Å). The resulting blue–purple solution was distilled to remove the solvent and amide. The residual amide was sublimed from the resulting blue–purple powder. An aqueous solution (60 ml) of Ag₂SO₄ (0.16 g, 0.51 mmol) was added and the mixture was stirred for 12 h at 323 K. The gray precipitate was filtered off and NH₄PF₆ (10.5 g, 64.5 mmol) was added. After the solution had been left to stand for several days, X-ray quality crystals of (III) were obtained (yield 0.318 g, 44%). Analysis calculated for C₁₂H₃₂F₆N₄O₈PRh₂: C 20.27, H 4.54, N 7.88%; found: C 20.05, H 4.25, N 7.77%. Compound (IV) was also prepared in a similar manner to (II). Starting from [Rh₂(CH₃CO₂)₄(CH₃OH)₂] (0.502 g, 0.992 mmol) and butyramide (3.35 g, 35.2 mmol), a brown powder of (IV) was obtained (0.291 g, 40%). X-ray quality crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution. Analysis calculated for C₁₆H₃₆F₆N₄O₆PRh₂: C 26.28, H 4.96, N 7.66%; found: C 26.51, H 4.89, N 8.06%.

Compound (I)

Crystal data

[Rh₂(C₂H₄NO)₄(H₂O)₂]PF₆
M_r = 619.07
 Triclinic, *P* $\bar{1}$
a = 6.631 (3) Å
b = 7.719 (4) Å
c = 9.645 (4) Å
 α = 92.014 (5)°
 β = 92.205 (5)°
 γ = 110.471 (7)°
V = 461.6 (4) Å³
Z = 1
D_x = 2.226 Mg m⁻³
 Mo *K*α radiation
 μ = 1.97 mm⁻¹
T = 118 (2) K
 Platelet, brown
 0.10 × 0.10 × 0.03 mm

Data collection

Rigaku/MSC Mercury CCD
 diffractometer
 ω scans
 Absorption correction: integration
 (NUMABS; Higashi, 1999)
T_{min} = 0.751, *T_{max}* = 0.940
 3818 measured reflections
 2096 independent reflections
 1903 reflections with *I* > 2σ(*I*)
R_{int} = 0.026
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.026
wR(*F*²) = 0.058
S = 1.04
 2096 reflections
 133 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 0.4628P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.64 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0080 (14)

Table 1

Selected bond lengths (Å) for (I).

Rh1–Rh1 ⁱ	2.4084 (10)	Rh1–O3	2.284 (2)
Rh1–O1 ⁱ	2.028 (2)	Rh1–N1	1.982 (3)
Rh1–O2 ⁱ	2.040 (2)	Rh1–N2	1.969 (3)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O3–H4...O2 ⁱⁱ	0.80 (4)	1.97 (4)	2.760 (3)	170 (4)
O3–H3...F1	0.75 (4)	2.20 (4)	2.922 (3)	162 (4)
N1–H1...F1	0.88	2.35	3.064 (3)	138
N1–H1...F3	0.88	2.44	3.284 (3)	162
N2–H2...O1 ⁱⁱⁱ	0.88	2.21	3.022 (3)	154

Symmetry codes: (ii) $x, y - 1, z$; (iii) $x + 1, y, z$.

Compound (II)

Crystal data

[Rh₂(C₂H₄NO)₄(H₂O)₂]PF₆·2H₂O
M_r = 655.10
 Monoclinic, *P*2₁/*c*
a = 11.6918 (17) Å
b = 11.5727 (13) Å
c = 7.9774 (13) Å
 β = 110.506 (6)°
V = 1011.0 (3) Å³
Z = 2
D_x = 2.152 Mg m⁻³
 Mo *K*α radiation
 μ = 1.81 mm⁻¹
T = 118 (2) K
 Block, brown
 0.30 × 0.30 × 0.15 mm

Data collection

Rigaku/MSC Mercury CCD
 diffractometer
 ω scans
 Absorption correction: integration
 (NUMABS; Higashi, 1999)
T_{min} = 0.712, *T_{max}* = 0.828
 7888 measured reflections
 2308 independent reflections
 2208 reflections with *I* > 2σ(*I*)
R_{int} = 0.026
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.027
wR(*F*²) = 0.056
S = 1.17
 2308 reflections
 151 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 1.4706P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.60 \text{ e } \text{Å}^{-3}$

Table 3
Selected bond lengths (Å) for (II).

Rh1—Rh1 ⁱ	2.4015 (4)	Rh1—O3	2.2407 (19)
Rh1—O1 ⁱ	2.0301 (17)	Rh1—N1	1.980 (2)
Rh1—O2 ⁱ	2.0419 (18)	Rh1—N2	1.973 (2)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3···O2 ⁱⁱ	0.93 (4)	1.86 (4)	2.775 (3)	168 (3)
O3—H4···O4	0.78 (4)	2.00 (4)	2.774 (3)	173 (4)
O4—H11···F1	0.72 (5)	2.22 (6)	2.938 (4)	170 (5)
O4—H12···F1 ⁱⁱⁱ	0.80 (6)	2.18 (6)	2.922 (3)	156 (5)
N1—H1···O4 ⁱⁱⁱ	0.88	2.44	3.213 (3)	146
N2—H2···O1 ⁱⁱ	0.88	2.27	3.073 (3)	152
N2—H2···O3 ⁱⁱⁱ	0.88	2.59	3.192 (3)	126

Symmetry codes: (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Compound (III)

Crystal data

[Rh₂(C₃H₆NO)₄(H₂O)₂]PF₆·2H₂O

M_r = 711.21
Triclinic, *P* $\bar{1}$
a = 8.980 (2) Å
b = 11.866 (3) Å
c = 12.682 (4) Å
 α = 87.696 (10)°
 β = 85.095 (8)°
 γ = 69.032 (6)°
V = 1257.2 (6) Å³

Z = 2
D_x = 1.879 Mg m⁻³
Mo *K*α radiation
 μ = 1.46 mm⁻¹
T = 118 (2) K
Prism, brown
0.30 × 0.10 × 0.10 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
 ω scans
Absorption correction: integration (NUMABS; Higashi, 1999)
*T*_{min} = 0.619, *T*_{max} = 0.773

10284 measured reflections
5685 independent reflections
5122 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.023
 θ _{max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.026
wR(*F*²) = 0.065
S = 1.06
5685 reflections
327 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.006P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
 $\Delta\rho$ _{max} = 0.66 e Å⁻³
 $\Delta\rho$ _{min} = -0.76 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0026 (5)

Table 5
Selected bond lengths (Å) for (III).

Rh1—Rh1 ⁱ	2.4105 (6)	Rh2—Rh2 ⁱⁱ	2.4095 (7)
Rh1—O1 ⁱ	2.0356 (17)	Rh2—O3 ⁱⁱ	2.0289 (18)
Rh1—O2 ⁱ	2.0469 (18)	Rh2—O4 ⁱⁱ	2.0318 (17)
Rh1—O5	2.2388 (19)	Rh2—O6	2.237 (2)
Rh1—N1	1.983 (2)	Rh2—N3	1.985 (2)
Rh1—N2	1.979 (2)	Rh2—N4	1.977 (2)

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 6
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H6···O7 ⁱⁱⁱ	0.82 (4)	1.91 (4)	2.706 (3)	164 (3)
O5—H5···O8	0.86 (4)	1.89 (4)	2.755 (3)	176 (3)
O6—H7···O2 ⁱ	0.76 (4)	2.04 (4)	2.789 (3)	168 (4)
O6—H8···O8	0.81 (4)	1.90 (4)	2.711 (3)	173 (4)
O7—H10···O4 ⁱⁱ	0.72 (4)	2.07 (4)	2.775 (3)	163 (4)
O7—H9···F6 ^{iv}	0.84 (4)	2.07 (4)	2.879 (3)	164 (3)
O8—H11···O1 ^v	0.77 (4)	1.97 (4)	2.729 (3)	168 (4)
O8—H12···F1	0.80 (4)	2.05 (4)	2.845 (3)	173 (3)
N1—H1···F3	0.88	2.28	3.123 (3)	161
N2—H2···O7 ⁱⁱⁱ	0.88	2.14	2.963 (3)	155
N4—H4···F4	0.88	2.26	3.120 (3)	168

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $x + 1, y - 1, z$; (v) $x + 1, y, z$.

Compound (IV)

Crystal data

[Rh₂(C₄H₈NO)₄(H₂O)₂]PF₆

M_r = 731.28
Triclinic, *P* $\bar{1}$
a = 9.1037 (4) Å
b = 11.0653 (1) Å
c = 14.0104 (5) Å
 α = 73.667 (10)°
 β = 82.143 (10)°
 γ = 79.486 (10)°
V = 1326.18 (11) Å³

Z = 2
D_x = 1.831 Mg m⁻³
Mo *K*α radiation
 μ = 1.38 mm⁻¹
T = 173 (2) K
Needle, brown
0.35 × 0.10 × 0.03 mm

Data collection

Rigaku/MSC Mercury CCD diffractometer
 ω scans
Absorption correction: integration (NUMABS; Higashi, 1999)
*T*_{min} = 0.643, *T*_{max} = 0.960

10813 measured reflections
6014 independent reflections
5456 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.028
 θ _{max} = 27.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.041
wR(*F*²) = 0.069
S = 1.17
6014 reflections
373 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + 2.8905P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.012
 $\Delta\rho$ _{max} = 0.75 e Å⁻³
 $\Delta\rho$ _{min} = -0.71 e Å⁻³

Table 7
Selected bond lengths (Å) for (IV).

Rh1—Rh1 ⁱ	2.4026 (3)	Rh2—Rh2 ⁱⁱ	2.4064 (3)
Rh1—O1 ⁱ	2.0389 (10)	Rh2—O3 ⁱⁱ	2.0118 (11)
Rh1—O2 ⁱ	2.0314 (10)	Rh2—O4 ⁱⁱ	2.0268 (9)
Rh1—O5	2.2608 (10)	Rh2—O6	2.2844 (10)
Rh1—N1	1.9706 (12)	Rh2—N3	1.9843 (13)
Rh1—N2	1.9735 (13)	Rh2—N4	1.9845 (11)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$.

One ethyl group in (III) was disordered. Atoms C11 and C12 were refined with isotropic displacement parameters over two sites, with the occupancies of the two sets of atoms, *A* and *B*, taken as 0.50. In (IV), one methyl C atom, C16, was refined as disordered over two sites with occupancies of 0.75 and 0.25. Atoms F3, F4, F5 and F6 in (IV) were refined as disordered over two sites, with the occupancies of the two sets of atoms, *A* and *B*, taken as 0.60 and 0.40, respectively.

Table 8

Hydrogen-bond geometry (Å, °) for (IV).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O4 ⁱⁱ	0.75 (2)	2.02 (2)	2.7651 (15)	171.5 (16)
O5—H6 \cdots F6A ⁱⁱⁱ	0.766 (16)	2.277 (19)	2.970 (2)	151.2 (19)
O5—H6 \cdots F6B ⁱⁱⁱ	0.766 (16)	2.215 (19)	2.902 (4)	149.8 (19)
O5—H6 \cdots F2 ⁱⁱⁱ	0.766 (16)	2.540 (16)	3.2410 (17)	153.1 (19)
O6—H7 \cdots O2 ⁱ	0.801 (19)	2.044 (19)	2.8420 (15)	174.5 (15)
O6—H8 \cdots F1	0.664 (17)	2.273 (15)	2.8931 (13)	156 (2)
N1—H1 \cdots F6A ⁱⁱⁱ	0.88	2.47	3.071 (2)	126
N3—H3 \cdots O1 ⁱ	0.88	2.20	3.0706 (15)	170
N4—H4 \cdots F3A	0.88	2.30	3.077 (2)	148
N4—H4 \cdots F3B	0.88	2.37	3.095 (4)	140

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y - 1, z$.

H atoms on O atoms were refined freely. All other H atoms were placed in idealized positions and treated as riding atoms, with C—H distances in the range 0.98–0.99 Å and N—H distances of 0.88 Å.

For all compounds, data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Rigaku/MS, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *TEXSAN*.

This work was supported by the Research Foundation for Electrotechnology of Chubu.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3015). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Baranovskii, I. B., Golubnichaya, M. A., Dikareva, L. M., Rotov, A. V., Shchelokov, R. N. & Porai-Koshits, M. A. (1986). *Russ. J. Inorg. Chem.* **31**, 1652–1656.
- Doyle, M. P., Bagheri, V., Wandless, T. J., Harn, N. K., Brinker, D. A., Eagle, C. T. & Loh, K.-L. (1990). *J. Am. Chem. Soc.* **112**, 1906–1912.
- Fuma, Y., Ebihara, M., Kutsumizu, S. & Kawamura, T. (2004). *J. Am. Chem. Soc.* **126**, 12238–12239.
- Higashi, T. (1999). *NUMABS*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation & Rigaku (2001). *CrystalClear*. Version 1.3. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
- Rigaku/MS (2004). *TEXSAN*. Version 2.0. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Takazaki, Y., Yang, Z., Ebihara, M., Inoue, K. & Kawamura, T. (2003). *Chem. Lett.* **32**, 120–121.
- Yang, Z., Ebihara, M. & Kawamura, T. (2006). *Inorg. Chim. Acta*, **359**, 2465–2471.
- Yang, Z., Ebihara, M., Kawamura, T., Okubo, T. & Mitani, T. (2001). *Inorg. Chim. Acta*, **321**, 97–106.
- Yang, Z., Fujinami, T., Ebihara, M., Nakajima, K., Kitagawa, H. & Kawamura, T. (2000). *Chem. Lett.* pp. 1006–1007.