possesses two free pyridine rings which could be used to modify the rates of electron transfer using the free nitrogen atoms to interact with a suitable quencher. For the series of bis(bipyridine) complexes of ligands **3**–**5**, the complex ions become progressively poorer excited-state reductants but more potent excited-state oxidants. The excited-state redox potentials of $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ indicate the complexes are poorer reductants in the excited state than $[Ru(bpy)_3]^{2+}$ but more potent excited-state oxidants.

Conclusion

We report the preparation of a series of ruthenium complexes based on the quaterpyridyl ligand **3**. The complex $[Ru(bpy)_2qpy]^{2+}$ is strongly luminescent, has excited-state properties similar to those of $[Ru(bpy)_3]^{2+}$, and is an excellent candidate for use in energy conversion schemes. The complexes $[Ru(bpy)_2qpyme]^{3+}$ and $[Ru(bpy)_2(qpyme_2)]^{4+}$ demonstrate how simple modifications of the ground-state structure, quaternization on the remote pyridine nitrogens of $[Ru(bpy)_2qpy]^{2+}$, can have a large effect on excited-state properties.

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Contribution from the Department of Chemistry, Faculty of Science,
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Preparation, Structure, and Properties of the Bis(μ-acetato)(μ-oxo)Ruthenium(III) Dimers $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$

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Two ruthenium(III) dimers with a core structure similar to the methemerythrin active center have been prepared: $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ (**1**) and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ (**2**) (py = pyridine, bpy = 2,2'-bipyridine). $[Ru_2(CH_3COO)_2(O)(py)_6](PF_6)_2$ crystallizes in the monoclinic space group $C2/c$ with $a = 42.229$ (6) Å, $b = 10.726$ (1) Å, $c = 20.470$ (3) Å, $\beta = 112.45$ (1)°, $V = 8568$ (2) Å^3, and $Z = 8$. The Ru–Ru distance is 3.251 (2) Å, and the direct metal–metal bond is absent. ^1H NMR spectra of **1** in organic solvents are consistent with the solid-state structure. Those of **2** indicate that chelating bpy occupies the positions trans to the two acetate bridges. The complexes exhibit strong visible absorption bands at 581 nm ($\epsilon = 10\,000$ M^{-1} cm^{-1}) and 599 nm ($\epsilon = 19\,200$) in CH_3CN for **1** and **2**, respectively. Cyclic voltammograms of both complexes in CH_3CN show one reversible oxidation process and one irreversible reduction process in the range from −1 to +1 V vs $Ag/AgClO_4$. The substitution reaction of py-d_5 for the coordinated py in **1** shows that the position trans to the oxide bridge is at least 10 times more labile than the cis positions. The first-order rate constants in the presence of excess py-d_5 (0.125 mol dm^{-3}) are 2.2×10^{-4} and 5.5×10^{-5} s^{-1} for **1** and **2**, respectively, at 50 °C in CD_3CN.

Introduction

Dinuclear complexes with the $M_2(\mu\text{-}RCOO)_2(\mu\text{-}O)$ core[2] are now known for various first-row transition-metal ions, Ti(III),[3] V(III),[4] Mn(III),[5] and Fe(III)[6] and appear to be common to tervalent and also to some quadrivalent[7,8] metal ions as well as to the mixed-valence (III,IV) state.[5a,9] Mixed-metal dinuclear complexes with this core have also been reported.[10,11] These complexes are interesting not only from a purely chemical but also from a biochemical point of view, since the core is found in some iron and manganese enzymes.[5a,6a] Terdentate ligands such as 1,4,7-triazacyclononane and hydrotris(pyrazolyl)borate have been used in most cases to block the facial position of a metal ion to make favorable situation for the preparation of the face-shared dinuclear complexes.[5a,6a]

Studies of the trinuclear ruthenium complexes $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ ($L = H_2O$, pyridine (py)) and their derivatives showed that the Ru–Ru interaction through the central oxide ion is more significant than the metal–metal interactions in the similar trinuclear complexes of the first-transition-metal ions.[12–14] Electronic transitions, redox, and magnetic properties of the ru-

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thenium complexes are thus quite unique among the trinuclear complexes.[15] These facts indicate that the chemistry of the oxo–carboxylato-bridged di- and polynuclear complexes of the second- and the third-transition elements may be notably different from those of the first-transition-metal ions. Such expectations have been realized by the preparation of the dinuclear complexes of Mo(III)[16] and Ru(III)[17-21] with the bis(μ-carboxylato)(μ-oxo) core.

Ruthenium(III) complexes with bis(μ-acetate)(μ-oxo) core were first reported by Mitchell et al.[22] They described the structure $Ru_2(\mu\text{-}RCOO)_2(\mu\text{-}O)(RCOO)_2(PPh_3)_2$ (R = CH_3, C_2H_5, C_3H_7, C_6H_5), with some uncertainties as to the existence of the bridging carboxylates.[22] The proposed structure was recently confirmed by the X-ray structural determination of $[Ru_2(\mu\text{-}p\text{-}OMeC_6H_4COO)_2(\mu\text{-}O)(p\text{-}OMeC_6H_4COO)_2(PPh_3)_2]$ ($p\text{-}OMeC_6H_4COO$ = p-methoxybenzoate(1−)).[21] We have prepared and carried out a crystal structure determination of the pyridine derivative, $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ (**1**) (py = pyridine), which was published as a preliminary account.[18] Since then several complexes with the $Ru_2(\mu\text{-}RCOO)_2(\mu\text{-}O)$ core have been reported.[17,19-21] These are $[Ru_2(\mu\text{-}RCOO)_2(\mu\text{-}O)(Me_3tacn)_2]^{2+}$ (R = CH_3, CF_3, H, C_6H_5, CCl_3, CH_2Cl; Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[19] $[Ru_2(\mu\text{-}R'OO)_2(\mu\text{-}O)(tpm)_2]$ (R'OO = (OH)OPOO, OCOO, CH_3COO; tpm = tris(pyrazolyl)methane),[20] $[Ru_2(\mu\text{-}C_6H_5COO)_2(\mu\text{-}O)(PPh_3)_2(CH_3CN)_4]^{2+}$, and the above-mentioned $[Ru_2(\mu\text{-}p\text{-}OMeC_6H_4COO)_2(\mu\text{-}O)(p\text{-}OMeC_6H_4COO)_2(PPh_3)_2]$.[21] We wish to report here full details on the results of our investigations of the pyridine complex and the newly prepared $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ (**2**) (bpy = 2,2'-bipyridine). Substitution properties of nonbridging ligands are also reported for the first time for the dinuclear complexes with the bis(μ-carboxylato)(μ-oxo) core.

Experimental Section

1. Preparations of the Complexes. a. Bis(μ-acetato)(μ-oxo)bis(tris(pyridine)ruthenium(III)) Hexafluorophosphate, $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$ ([1]$(PF_6)_2$). A 0.5-g sample of $RuCl_3\cdot nH_2O$ was dissolved in a mixed solvent of H_2O (60 cm^3)–CH_3COOH (40 cm^3)–C_2H_5OH (20 cm^3), and the solution was kept at 70 °C for 10 min, during which time the color changed from brown to red. After the addition of pyridine (3 cm^3), the solution was refluxed for ca. 1 h. After the deep blue solution was cooled to room temperature, 2 g of NH_4PF_6 was added. Blue precipitates appeared when the solution was evaporated to ca. 20 cm^3 on a rotatory evaporator. Water (20 cm^3) was added to the mixture, which was then kept in a refrigerator. The resulting blue crystalline powder was collected and washed with water several times. The solid was dissolved in a small amount of CH_3CN containing a few drops of pyridine. The solution was kept at 80 °C for 20 min and then kept in a refrigerator after the addition of an equal amount of water. The resulting blue fine crystals were collected and washed with water three times. Finally the crystals were recrystallized from hot CH_2Cl_2. Anal. Calcd for [1]$(PF_6)_2$: C, 37.10; H, 3.30; N, 7.63. Found: C, 36.55; H, 3.08; N, 7.78.[23]

Table I. Crystallographic Data for $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$

$C_{34}H_{36}N_6O_5P_2F_{12}Ru_2$	fw = 1100.8
a = 42.229 (6) Å	space group: $C2/c$
b = 10.726 (1) Å	T = 13 °C
c = 20.470 (3) Å	λ = 1.5418 Å
β = 112.45 (1)°	ρ_{calcd} = 1.707 g cm^{-3}
V = 8568 (2) $Å^3$	μ = 89.15 cm^{-1}
Z = 8	$R(F_o)^a$ = 0.077
	$R_w(F_o^2)^b$ = 0.086

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

The complex is highly soluble in acetonitrile and dichloromethane, but is insoluble in water.

b. Bis(μ-acetato)(μ-oxo)bis((2,2'-bipyridine)(pyridine)ruthenium(III)) Hexafluorophosphate, $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2](PF_6)_2$ ([2]$(PF_6)_2$). A solution of $RuCl_3\cdot nH_2O$ (240 mg) in a mixed solvent of H_2O (20 cm^3)–CH_3COOH (15 cm^3)–C_2H_5OH (8 cm^3) was kept at 70 °C for 10 min. To the red solution was added 2,2'-bipyridine (0.4 g) in C_2H_5OH and the temperature was raised to 90 °C. After 15 min, pyridine (1 cm^3) was added and the solution was kept at 90 °C for a further 15 min. After the addition of NH_4PF_6 (2 g), the solution was evaporated to 40 cm^3 under reduced pressure and to this was added 40 cm^3 of water. A dark green precipitate was collected by filtration and washed with water. The solid was dissolved in CH_3CN and kept in a refrigerator after the addition of an equal amount of water. The crystalline solid was collected and washed with water. The solid was again dissolved in CH_3CN and passed through a cellulose column (SE-cellulose of Seikagakukogyo Co.) to leave a yellow imupurity on the column. Addition of an equal amount of water to the CH_3CN eluate followed by evaporation on a rotatory evaporator gave fine blue crystals. Yield: ca. 100 mg. Anal. Calcd for [2]$(PF_6)_2$: C, 37.24; H, 2.94; N, 7.66. Found: C, 38.02; H, 3.08; N, 7.90. The complex is highly soluble in CH_3CN, but is insoluble in water.

2. Other Materials. Acetonitrile was distilled over P_2O_5 and then over CaH_2. CD_3CN (99% deuterated, Aldrich) was also distilled once before use. C_5D_5N (100%, Aldrich) and all other reagents were used as received.

3. Measurements. Ultraviolet and visible absorption spectra were measured with a Hitachi 340 spectrophotometer. ^1H NMR spectra were obtained on a JEOL GSX-270 FT-NMR spectrometer at 270 MHz. Infrared absorption spectra were recorded on a Jasco IR-810 spectrophotometer. Electrochemical measurements were carried out by using a YANACO P-1100 polarographic analyzer with a glassy-carbon working electrode at room temperature. The potentials were recorded vs a Ag/Ag^+ (0.1 M $AgClO_4$) electrode (1 M = 1 mol dm^{-3}).

4. Crystal Structure Determination. A crystal of [1]$(PF_6)_2$ with dimensions 0.1 × 0.2 × 0.3 mm was attached to a glass fiber and mounted on a Rigaku AFC-5R four circle diffractometer equipped with a rotating Cu anode (40 kV, 200 mA). The unit cell parameters were obtained by a least-squares refinement of the angular settings of 25 high-angle (39.5° ≤ 2θ ≤ 53.1°) reflections. Crystallographic data are given in Table I. Intensity data in the range 4° ≤ 2θ ≤ 126° were collected in the ω-scan mode at room temperature with Cu Kα (λ = 1.5418 Å) radiation and were corrected for Lorentz and polarization factors. No absorption correction was applied.

The positions of ruthenium atoms were determined from the Patterson map and all other non-hydrogen atoms were subsequently located by an alternative series of difference Fourier syntheses and block-diagonal least-squares refinements. The refinement was carried out with anisotropic temperature factors, and the final R value was 0.077 for 4981 independent reflections ($F_o \geq 3\sigma(F_o)$) and 569 parameters.

All the calculations were performed with the Universal Crystallographic Computer Program System UNICS III[24] on an ACOS-1000 computer at the Computer Center of Tohoku University.

Atomic positional parameters are given in Table II. Tables of the structure factors and thermal parameters of $[Ru_2(CH_3COO)_2(O)(py)_6](PF_6)_2$ are available as supplementary material.

Results and Discussion

1. Preparation of the Complexes. The most common approach to obtain the bis(μ-carboxylato)(μ-oxo) complexes is to hydrolyze the complexes with a facial-blocking terdentate ligand $LM^{III}X_3$ (L = 1,4,7-triazacyclononane, hydrotris(pyrazolyl)borate, tris-

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(23) To obtain the perchlorate salt, $NaClO_4$ was added to the deep blue solution in place of NH_4PF_6. The solution was evaporated to near dryness. (*Caution!* complete dryness should be avoided, since perchlorate may cause an explosion.) After the filtration, the solid was washed with water until the washings became blue from green. The residue was then dissolved in CH_3CN containing few drops of pyridine, and treated similarly as the preparation of the PF_6^- salt. Anal. Calcd for [1]$(ClO_4)_2\cdot 4H_2O$: C, 37.75; H, 4.10; N, 7.77. Found: C, 37.95; H, 3.93; N, 8.08.

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Table II. Atomic Positional and Equivalent Thermal Parameters for $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$

atom	*x*	*y*	*z*	B_{eqv},[a] Å^2
Ru(1)	0.39942 (3)	0.16874 (9)	0.41971 (5)	3.2
Ru(2)	0.34194 (3)	0.29655 (9)	0.46787 (5)	3.2
P(1)	0.3708 (1)	0.6541 (4)	0.2763 (2)	6.1
P(2)	0.2500	0.2500	0.0000	4.5
P(3)	0.5000	0.1505 (7)	0.2500	6.1
F(33)	0.5000	0.0013 (14)	0.2500	7.9
F(34)	0.5000	0.2957 (15)	0.2500	12.8
F(21)	0.2876 (2)	0.2935 (9)	0.0086 (5)	6.6
F(22)	0.2583 (3)	0.2862 (9)	0.0794 (5)	7.2
F(23)	0.2359 (3)	0.3875 (8)	−0.0240 (5)	6.9
F(31)	0.5115 (3)	0.1511 (13)	0.3322 (5)	9.7
F(32)	0.4617 (3)	0.1493 (12)	0.2442 (6)	9.0
F(11)	0.3794 (6)	0.5568 (13)	0.3337 (7)	16.0
F(12)	0.3627 (5)	0.7401 (14)	0.2131 (9)	15.4
F(13)	0.3483 (5)	0.5600 (13)	0.2215 (8)	15.2
F(14)	0.4019 (5)	0.6028 (21)	0.2606 (9)	16.7
F(15)	0.3397 (4)	0.7048 (25)	0.2852 (10)	20.2
F(16)	0.3913 (6)	0.7459 (14)	0.3296 (10)	19.5
N(1)	0.4330 (3)	0.3066 (10)	0.4125 (5)	3.6
N(2)	0.3758 (3)	0.1535 (10)	0.3107 (6)	4.0
N(3)	0.4358 (3)	0.0164 (10)	0.4271 (6)	3.6
N(4)	0.3652 (3)	0.4621 (10)	0.5174 (6)	3.9
N(5)	0.3058 (3)	0.3913 (9)	0.3824 (5)	3.4
N(6)	0.3099 (3)	0.2931 (10)	0.5289 (5)	3.5
O(1)	0.4229 (2)	0.1787 (9)	0.5297 (5)	4.4
O(2)	0.3752 (2)	0.1985 (9)	0.5539 (5)	4.2
O(3)	0.3671 (2)	0.0279 (8)	0.4280 (5)	3.8
O(4)	0.3200 (2)	0.1278 (8)	0.4218 (5)	4.0
O(5)	0.3692 (2)	0.2986 (8)	0.4158 (4)	3.7
CA(1)	0.4067 (4)	0.1753 (14)	0.5709 (7)	4.4
CA(2)	0.3369 (3)	0.0321 (12)	0.4208 (7)	3.6
CM(1)	0.4282 (6)	0.1385 (23)	0.6486 (9)	8.9
CM(2)	0.3174 (4)	−0.0926 (14)	0.4072 (9)	5.7
CP(11)	0.4458 (4)	0.3113 (14)	0.3618 (9)	5.3
CP(12)	0.4664 (5)	0.4081 (16)	0.3553 (10)	6.3
CP(13)	0.4715 (5)	0.5094 (17)	0.4011 (11)	7.2
CP(14)	0.4575 (4)	0.5066 (14)	0.4520 (10)	6.0
CP(15)	0.4384 (4)	0.4044 (13)	0.4579 (8)	5.1
CP(21)	0.3653 (4)	0.2600 (12)	0.2705 (7)	4.2
CP(22)	0.3473 (4)	0.2544 (15)	0.1972 (8)	5.4
CP(23)	0.3406 (5)	0.1383 (19)	0.1621 (8)	6.5
CP(24)	0.3507 (5)	0.0324 (15)	0.2045 (8)	6.2
CP(25)	0.3685 (4)	0.0424 (12)	0.2777 (8)	4.3
CP(31)	0.4462 (4)	−0.0567 (13)	0.4869 (8)	5.0
CP(32)	0.4720 (4)	−0.1440 (14)	0.4988 (9)	5.6
CP(33)	0.4870 (4)	−0.1636 (13)	0.4505 (9)	5.2
CP(34)	0.4754 (4)	−0.0923 (13)	0.3891 (9)	5.3
CP(35)	0.4497 (4)	−0.0047 (13)	0.3786 (9)	4.9
CP(41)	0.3704 (4)	0.5545 (14)	0.4770 (8)	4.7
CP(42)	0.3897 (4)	0.6604 (15)	0.5077 (9)	5.9
CP(43)	0.4052 (5)	0.6695 (17)	0.5822 (10)	7.1
CP(44)	0.3985 (5)	0.5746 (17)	0.6223 (9)	6.6
CP(45)	0.3780 (4)	0.4706 (15)	0.5885 (7)	4.6
CP(51)	0.2985 (4)	0.3410 (13)	0.3169 (7)	4.4
CP(52)	0.2749 (4)	0.3992 (15)	0.2571 (8)	5.5
CP(53)	0.2578 (4)	0.5073 (16)	0.2629 (9)	5.9
CP(54)	0.2667 (4)	0.5574 (15)	0.3305 (8)	5.6
CP(55)	0.2902 (4)	0.5002 (13)	0.3897 (8)	4.6
CP(61)	0.3020 (4)	0.1804 (14)	0.5486 (7)	4.3
CP(62)	0.2816 (4)	0.1676 (15)	0.5877 (8)	5.1
CP(63)	0.2703 (4)	0.2717 (16)	0.6122 (8)	5.7
CP(64)	0.2792 (4)	0.3890 (15)	0.5938 (8)	5.2
CP(65)	0.2995 (4)	0.3952 (14)	0.5535 (7)	4.2

[a] The equivalent isotropic thermal parameter, B_{eqv}, is calculated as $(4/3)\sum_j\sum_i\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

(pyrazolyl)methane, etc.; X = Cl, Br) in the presence of carboxylate.[5a,6a] In contrast, the present complexes are formed directly from $RuCl_3 \cdot nH_2O$ in acetate media without using a facial-blocking terdentate ligand and thus are considered as a typical example of true self-assembly to form a bis(μ-acetato)(μ-oxo) complex. Our result as well as Wilkinson's earlier one[22] indicates the facile formation of the $Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)$ core. In that sense, it is rather surprising that the chemistry of the ruthenium compounds with this core has not been developed until recently, while tetrakis(acetato)diruthenium or trinuclear (μ_3-oxo)hexakis(μ-acetato) complexes which require more severe reaction conditions have been known for over 2 decades.[12,25] It is possible that the $Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)$ core would be a precursor to these well-known complexes.

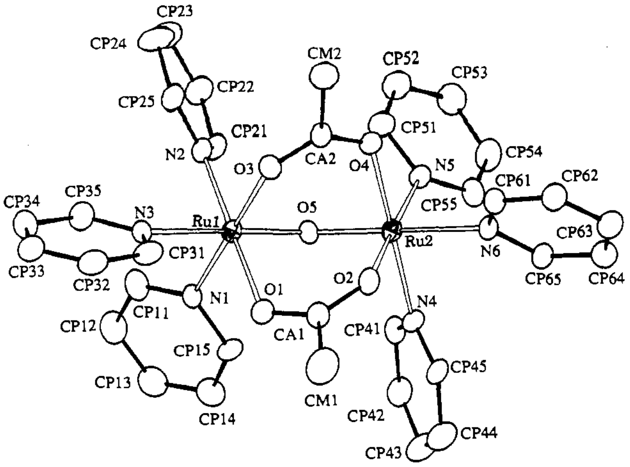

Figure 1. Structure of $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ showing 20% probability thermal ellipsoids and atomic-labeling scheme.

The most critical point of the preparation is the initial reaction time and temperature. When the solution of $RuCl_3 \cdot nH_2O$ in $CH_3COOH\text{–}C_2H_5OH\text{–}H_2O$ is kept at 70 °C for 10 min, a red solution is obtained. This solution should contain a precursor species to the isolated dinuclear complexes, and the basic dinuclear unit, $Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)$, is very likely formed at this stage. Prolonged heating at 70 °C or higher temperature gives a brown solution, from which the dinuclear complex, **1**, is not separated on addition of pyridine. It is interesting to note that the red solution is useful for the preparation of the mixed-metal trinuclear complexes of the type, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^{n+}$.[26,27] Facile formation of the red dinuclear species would explain why only $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ and not the $RuRh_2$ analogue was obtained from the reaction mixture of Ru(III) and Rh(III) salts in acetic acid media.[13] Similarly, only the Ru_2Cr complex was obtained from the mixture of Ru(III) and Cr(III) salts in acetate media.[26] Further efforts to prepare Ru_2M (M = Zn(II), Ni(II), etc.) type mixed-metal complexes are underway in this laboratory.[27]

2. Descriptions of the Structure of $[Ru_2(CH_3COO)_2(O)(py)_6](PF_6)_2$. An ORTEP drawing of the complex cation, 1, is shown in Figure 1, and the selected bond distances and angles are given in Table III. Complete data tables are given as supplementary material. The complex possesses the bis(μ-acetato)(μ-oxo) structure, which is now rather common in a wide variety of tervalent metal ions. The two distorted octahedra are twisted around the Ru–Ru axis with torsion angles of 22.7 and 21.3° for O(1)–Ru(1)–Ru(2)–O(2) and O(3)–Ru(1)–Ru(2)–O(4), respectively. The compound is thus asymmetric and exists as a pair of enantiomers in the crystal.

The bond distances and angles within the $Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)$ core are similar to those of other complexes with this core.[17,19–21] The Ru–N(pyridine) distances trans to the oxide bridge (2.21 and 2.16 Å) are about 0.1 Å longer than those trans to the acetate bridge as a consequence of the trans effect of the oxide bridge. The effect may be reflected in the difference in substitution lability of the pyridines (vide infra).

3. Spectroscopic Properties. Figure 2 shows the UV–visible absorption spectra of the two new complexes. The spectra are characterized by strong visible absorption bands at 581 nm (ϵ =

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(25) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285–2291. (b) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388–391.

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Table III. Selected Interatomic Distances and Angles for $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$

	Bond Distances (Å)		
Ru(1)–Ru(2)	3.251 (2)	Ru(1)–N(1)	2.091 (11)
Ru(1)–O(1)	2.087 (9)	Ru(1)–N(2)	2.072 (10)
Ru(2)–O(2)	2.071 (8)	Ru(1)–N(3)	2.208 (11)
Ru(1)–O(3)	2.085 (9)	Ru(2)–N(4)	2.092 (10)
Ru(2)–O(4)	2.087 (8)	Ru(2)–N(5)	2.093 (9)
Ru(1)–O(5)	1.869 (9)	Ru(2)–N(6)	2.162 (13)
Ru(2)–O(5)	1.845 (10)	O(1)–C(A1)	1.275 (20)
O(2)–C(A1)	1.267 (17)	O(3)–C(A2)	1.229 (17)
O(4)–C(A2)	1.257 (16)	C(A1)–C(M1)	1.555 (21)
C(A2)–C(M2)	1.537 (20)		
	Bond Angles (deg)		
Ru(1)–O(5)–Ru(2)	122.2 (5)	O(1)–Ru(1)–O(3)	90.4 (4)
O(1)–Ru(1)–O(5)	92.4 (4)	O(3)–Ru(1)–O(5)	95.0 (4)
O(5)–Ru(1)–N(1)	86.6 (4)	O(5)–Ru(1)–N(2)	88.5 (4)
O(5)–Ru(1)–N(3)	178.6 (4)	O(1)–Ru(1)–N(1)	89.1 (4)
O(1)–Ru(1)–N(2)	178.4 (4)	O(1)–Ru(1)–N(3)	86.2 (4)
O(3)–Ru(1)–N(1)	178.4 (4)	O(3)–Ru(1)–N(2)	88.2 (4)
O(3)–Ru(1)–N(3)	85.3 (4)	N(1)–Ru(1)–N(2)	92.3 (4)
N(1)–Ru(1)–N(3)	93.1 (4)	N(2)–Ru(1)–N(3)	92.9 (4)
O(2)–Ru(2)–O(4)	89.1 (3)	O(2)–Ru(2)–O(5)	97.3 (4)
O(4)–Ru(2)–O(5)	91.0 (4)	O(5)–Ru(2)–N(4)	89.4 (5)
O(5)–Ru(2)–N(5)	85.9 (4)	O(5)–Ru(2)–N(6)	179.7 (4)
O(2)–Ru(2)–N(4)	88.8 (4)	O(2)–Ru(2)–N(5)	176.4 (4)
O(2)–Ru(2)–N(6)	82.6 (4)	O(4)–Ru(2)–N(4)	177.9 (3)
O(4)–Ru(2)–N(5)	89.2 (3)	O(4)–Ru(2)–N(6)	88.7 (4)
N(4)–Ru(2)–N(5)	92.9 (4)	N(4)–Ru(2)–N(6)	90.9 (5)
N(5)–Ru(2)–N(6)	94.3 (4)	Ru(1)–O(1)–C(A1)	124.1 (7)
Ru(1)–O(3)–C(A2)	130.3 (8)	Ru(2)–O(2)–C(A1)	129.4 (10)
Ru(2)–O(4)–C(A2)	124.1 (8)		

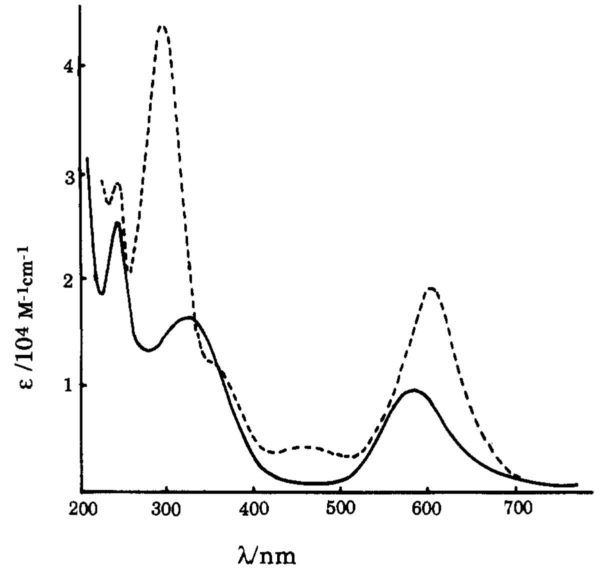

Figure 2. Electronic absorption spectra of $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$ (—) and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2](PF_6)_2$ (- -) in acetonitrile at room temperature.

10000 M^{-1} cm^{-1}) and 599 nm (ϵ = 19200) for **1** and **2**, respectively. Similar strong absorption bands are reported for all the complexes with the bis(μ-carboxylato (or phosphato))(μ-oxo)-diruthenium moiety.[17,19–22]

Meyer and co-workers discussed on the electronic structure of their tpm (tris(pyrazolyl)methane) complexes in terms of Ru d π–O(μ) p π interactions.[20] Two sets, one perpendicular to the Ru–O(μ)–Ru plane and the other within it, of the interactions are important, each set giving rise to one bonding, one nonbonding (or slightly antibonding), and one antibonding orbitals. Electrons available for these molecular orbitals are 10 altogether (three from each Ru and four from oxygen). With a Ru–O–Ru angle of ca. 120°, the antibonding orbital of the in-plane set ($\pi_1{}^*$) is considerably lower in energy than that from the set perpendicular to the plane ($\pi_2{}^*$), leaving the filled $\pi_1{}^*$ and the empty $\pi_2{}^*$ orbitals in the ground state.

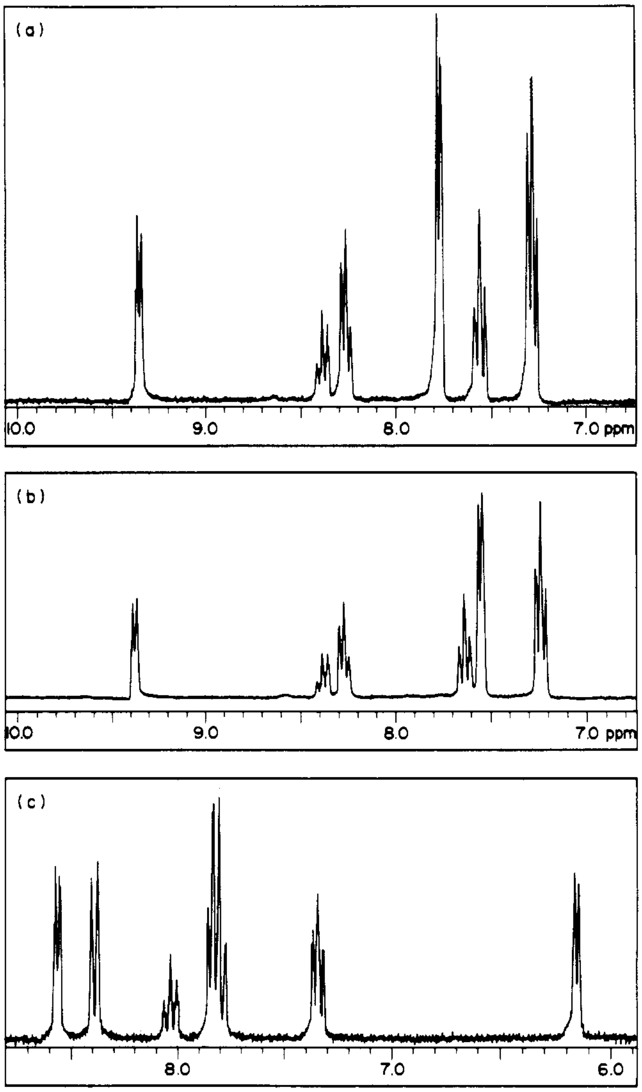

Figure 3. ^1H NMR spectra of aromatic ring hydrogens of $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ in CD_2Cl_2 (a) and CD_3CN (b) and of $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ in CD_2Cl_2 (c).

The strong transitions are assigned to that from the lower occupied orbitals to $\pi_2{}^*$. The complexes with nonbridging ligands which have empty π^* orbitals (such as py, bpy, tpm, and CH_3CN) tend to show the visible peaks at lower energy with larger intensity. It is possible that the interaction of ligand π^* orbital with $\pi_2{}^*$ causes the lowering of the latter in energy and the transition has more charge-transfer character. In addition to the strong band at around 600 nm, **2** shows a peak at 459 nm which is absent in **1**. This absorption band should be of charge-transfer origin (possibly $\pi_1{}^*$ to π^*(bpy)), since the coordinating atoms around ruthenium ions are very similar to **1** and the absorption of ligand field origin is unlikely to be the subject of significant shift in energy.

Resonance Raman (RR) spectra of **1** were measured in CH_2Cl_2 solution. The strongly enhanced band in the RR spectrum with 568.2-nm excitation was observed at 590.0 cm^{-1}, which was assigned to ν_s(Ru–O–Ru). A weak overtone was also observed at 1172.1 cm^{-1}. On excitation at 488 and 325 nm, the 590-cm^{-1} band was not at all observed. An attempt to prepare the μ-^{18}O-enriched Ru dimer in order to confirm the assignment was unsuccessful. Enhancement of ν_s(Fe–O–Fe) with excitation at the charge-transfer band between μ-O and Fe was reported.[28,29]

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Table IV. ^{1}H NMR Chemical Shift Data (ppm) for $[Ru_2(\mu\text{-}CH_3COO)_6(\mu\text{-}O)(py)_6]^{2+}$ (**1**) and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ (**2**) in Various Solvents

	1					**2**		
	chem shift				pattern (intens)	chem shift		pattern (intens)
assignt	CD_3CN	CD_2Cl_2	acetone-d_6	DMSO-d_6		CD_3CN	CD_2Cl_2	
CH_3 acetate	1.58	1.62	1.68	1.62	s (6 H)	2.09	2.16	s (6 H)
C–H py (trans to μ-O)								
2,6	9.38	9.36	9.68	9.45	d (4 H)	8.57	8.66	d (4 H)
3,5	8.29	8.28	8.43	8.40	t (4 H)	7.8^a	7.8^a	
4	8.38	8.4	8.55	8.49	t (2 H)	8.13	8.04	t (2 H)
C–H py (cis to μ-O)								
2,6	7.55	7.8	7.90	7.58	d (8 H)			
3,5	7.23	7.3	7.43	7.37	t (8 H)			
4	7.63	7.57	7.78	7.74	t (4 H)			
C–H bpy								
3,3′						8.54	8.40	d (4 H)
4,4′						7.8^{a,b}	7.8^{a,b}	
5,5′						7.23^b	7.35^b	t (4 H)
6,6′						6.08	6.15	d (4 H)

^{a} py 2,6-H and bpy C-3 H proton signals are overlapped. Overall intensity corresponds to 8 H. ^{b} Assignments of these two signals were made by the irradiation experiment of the 3,3′-hydrogens. The signals at around 7.8 ppm were significantly affected, while those at 7.2–7.3 ppm were not.

Figure 3 shows the ^{1}H NMR spectra of **1** in CD_2Cl_2 and CD_3CN and **2** in CD_2Cl_2. The spectra clearly show that the complexes are diamagnetic, being consistent with the molecular orbital consideration as mentioned above. All of the signals were unambiguously assigned by the use of spin-decoupling experiments as well as the pyridine exchange reaction with py-d_5 (vide infra). The complete assignments are given in Table IV. The spectrum of **2** showed that the chemical environments of each half of the bipyridine are equivalent. Therefore the 2,2′-bipyridine should occupy the trans position to the bridging acetates and therefore pyridine is trans to the oxide bridge. This is in contrast to the fact that the known binuclear complexes with bpy, $[Mn_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(H_2O)_2]^{2+}$,[5c] $[Mn_2(\mu\text{-}C_6H_5COO)_2(\mu\text{-}O)(bpy)_2(N_3)_2]$,[5d] and $[Fe_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2Cl_2]$,[30] have the configuration with unidentate ligand trans to the acetate bridge. Although we note that the unidentate ligand of the ruthenium dimer **2** has π-accepting character, it is not appropriate to discuss further the geometrical isomerism of this type of complex on the basis of information from the limited number of complexes.

Several interesting features are seen in the ^{1}H NMR data in Table IV. The acetate methyl signal of **1** appeared at significantly higher magnetic field as compared with those (in the range, 1.96–2.42 ppm) of **2** and some "diamagnetic" trinuclear complexes, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3$.[12,13,31] This anomaly found in **1** may be due to the anisotropic influence from the neighboring pyridine trans to another acetate and cis to the oxide bridge. The pyridine trans to the oxide bridge appears to be less important, because it is at a greater distance from the acetate methyl group. The 2,2′-bipyridine ligand, with a fixed orientation of the aromatic ring, appears to be less influential.

Signals from the coordinated pyridine ligands trans to the oxide bridge appeared at a significantly lower magnetic field (ca. 1 ppm differences) than the corresponding signals of the pyridine ligand trans to the acetate bridges. Structural data show that the former pyridines coordinate considerably more weakly than the latter. If the chemical shifts can be taken as a measure of the strength of the Ru–N(py) bond, then the pyridines of **2** appear to coordinate more strongly than the trans-to-oxo pyridines of **1**.

The 2,6-protons of the pyridines cis to the oxide bridge showed significant solvent effect (Table IV). The signal appeared at lower field than the 3,5-protons' signal in CD_2Cl_2, but at higher field in CD_3CN. The signal from the bipyridine C-3 protons, which are in a chemical environment similar to that of the pyridine 2,6-protons, did not show such solvent dependence. The absorption spectra of **1** in these two solvents did not show significant difference (in CH_2Cl_2, 584 nm (ϵ = 10 800 cm^{-1} mol dm^{-3}), 322 nm (ϵ = 18 000), 242 nm (ϵ = 30 000)). It is possible that the rotation of the pyridine around the Ru–N axis causes the shielding of the 2,6-protons by neighboring pyridines to some extent, while such an effect is not possible for the bipyridine of **2**. Such a free rotation might be restricted by different solvents, to show the observed solvent effect. Additional measurements in acetone-d_6 and

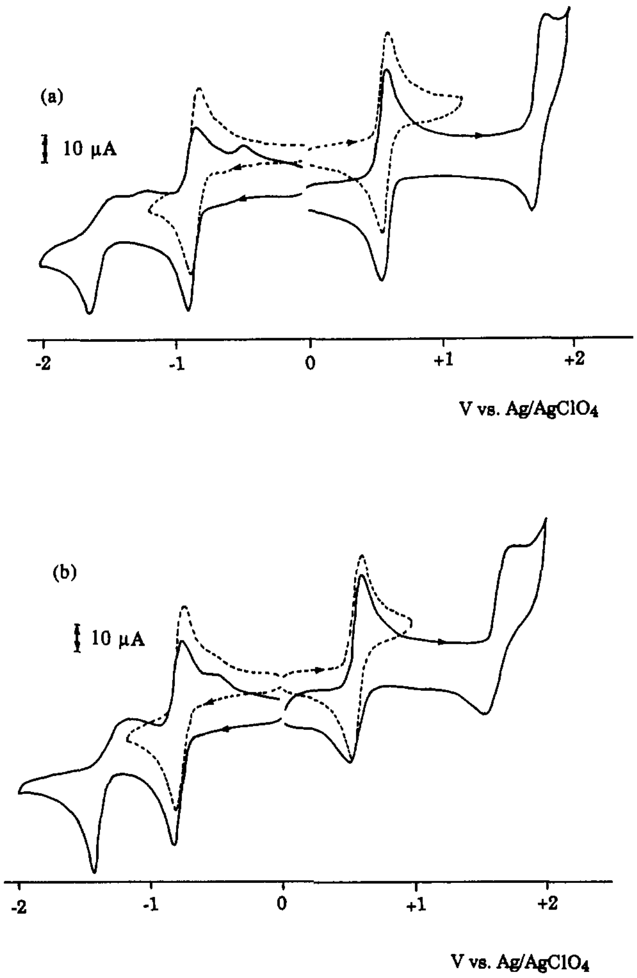

Figure 4. Cyclic voltammograms of (a) $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$ and (b) $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)_2(py)_2]^{2+}$ in 0.1 M $(n\text{-}Bu_4N)ClO_4$ in CH_3CN (V vs Ag/AgClO$_4$ electrode) at a scan rate of 50 mV/s at room temperature.

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Table V. Electrochemical Data for the Dinuclear Complexes $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(N)_6]^{2+}$ in 0.1 M $(Bu_4N)ClO_4$ in CH_3CN at Room Temperature

	$E_{1/2}$,[a] V ($E_{ap} - E_{cp}$, mV)			
$(N)_6$	(II,II)/ (II,III)	(II,III)/ (III,III)	(III,III)/ (III,IV)	(III,IV)/ (IV,IV)
$(py)_6$	(−1.4)[b]	−0.85 (60)	+0.60 (60)	+1.71[c]
$(bpy)_2(py)_2$	−1.1[b]	−0.77 (60)	+0.56 (80)	+1.52[c]

[a] $E_{1/2}$ vs the Ag/Ag$^+$ (0.1 M $AgClO_4$) electrode. [b] E_{ap}. [c] E_{cp}.

DMSO-d_6 (Table IV) did not reveal any clear correlation between the chemical shifts and solvent parameters.

4. Redox Properties. The cyclic voltammograms of the two complexes are shown in Figure 4, and the data are summarized in Table V. Both complexes showed two reversible oxidation waves, which are assigned to the processes, $Ru^{III}Ru^{IV}/Ru^{III}_2$ and $Ru^{IV}_2/Ru^{III}Ru^{IV}$. In the negative region, two irreversible waves were observed. On the reoxidizing cycle, a small peak at ca. −0.5 V was observed, the intensity depending on the decrease in the main reoxidation signal, which was stronger if the reoxidation sweep was carried out after the second reduction process. Addition of pyridine did not improve the reversibility of the first reduction process. A comparison of the cyclic voltammograms of the present two complexes indicates that the Ru^{III}_2 state of **2** is more easily oxidized and also more easily reduced than **1**.

5. Ligand Substitution Reactions. The pyridine exchange reaction was examined in CD_3CN containing py-d_5 by following the change in the ^{1}H NMR spectra. The signals of **1** at 9.38, 8.38, and 8.28 ppm decreased with concomitant increase in the signal intensities of the free pyridine (8.50, 7.80, and 7.35 ppm). These decreasing signals are assigned to the pyridine trans to the oxide bridge. There is no significant change in the visible absorption spectrum during the ^{1}H NMR change. Thus the change should be exclusively due to a simple ligand-exchange process. Only the pyridine trans to the oxide bridge was exchanged during the time of the observation.

$$[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+} + 2py\text{-}d_5 \rightarrow [Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_4(py\text{-}d_5)_2]^{2+} + 2py$$

The first-order exchange rate constant (k_0) was evaluated from the time-dependence of the relative integrated intensities of the NMR signals at 9.38 ppm, using the following Mckay type equation.[32]

$$\ln \{(I_t - I_\infty)/(I_0 - I_\infty)\} = -\{(2m + n)/(2mn)\}Rt + \text{const} \qquad (1)$$

m and n are the initial concentrations of the complex and py-d_5, respectively. I is equal to $p/(p + q)$ (p and q are the relative integrated intensity of the coordinated and the free pyridine, respectively). The plot of the left-hand side of eq 1 against t gave a good straight line from the slope of which R ($=k_0/m$) was obtained. The first-order rate constant, k_0, was 2.2×10^{-4} s^{-1} at 50 °C under the conditions [complex] = 1.77×10^{-2} M and [py-d_5] = 0.125 M. The exchange of the pyridine cis to the oxide bridge must be much less than 2×10^{-5} s^{-1}. The k_0 value for $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(py)_2]^{2+}$ was similarly evaluated to be 5.5×10^{-5} s^{-1} at 50 °C under the conditions [complex] = 3.17×10^{-3} M and [py-d_5] = 0.125 M. No sign of bpy dissociation was observed. The difference in the rates between the complexes **1** and **2** is consistent with the conclusion from the NMR spectra that the pyridines in **2** coordinate more strongly than the trans-to-oxo pyridines in **1** (vide supra).

The regioselective pyridine exchange in **1** should be due to the trans effect of the oxide bridge. Under similar conditions, the trinuclear ruthenium(III) complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ underwent the py exchange reaction with a first-order rate constant of 3×10^{-5} s^{-1} at 55 °C.[31] This reaction was assigned to proceed by a dissociative mechanism due to the trans effect of the central oxide. In the present dinuclear complex, the oxide bridge is shared by only two Ru(III) ions and would cause a stronger trans effect. Two to ten times acceleration in the dimeric complex against the trimer is consistent with this expectation. The strong trans effect of the oxide bridge is also seen from the remarkable regioselectivity observed for **1**. X-ray structural data giving the Ru–N distances and ^{1}H NMR chemical shift data for pyridines in **1** are consistent with the observed regioselectivity.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 02245106) on the Priority Area of "Molecular Approaches to Non-equilibrium Processes in Solutions" and a Grant-in-Aid for Scientific Research (No. 01430009) from the Ministry of Education, Science, and Culture, Japan. We are grateful to Professor T. Kitagawa and Dr. S. Hashimoto (Institute for Molecular Science, Okazaki, Japan) for the measurements of the resonance Raman spectra.

Supplementary Material Available: Tables SI and SII, listing atomic and anisotropic thermal parameters and complete interatomic distances and bond angles for $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6](PF_6)_2$ (4 pages); Table SIII, listing observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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