Selected Paper

Synthesis and Characterization of Polynuclear Chain and Tetranuclear Complexes of Mixed-Valent Ruthenium(II,III) Pivalate with *N*,*N*′-Didentate Ligands

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Polymeric chain complexes, $[Ru_2(piv)_4(pyz)]_n(BF_4)_n \cdot 3nH_2O$ (**1**), $[Ru_2(piv)_4(4,4'\text{-bpy})]_n(BF_4)_n \cdot nH_2O$ (**2**), $[Ru_2(piv)_4(dabco)]_n(BF_4)_n \cdot 2nH_2O$ (**3**), $[Ru_2(piv)_4(phz)]_n(BF_4)_n$ (**4**), and $[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n \cdot nCH_2Cl_2$ (**6**), (Hpiv = pivalic acid, pyz = pyrazine, 4,4′-bpy = 4,4′-bipyridine, dabco = 1,4-diazabicyclo[2.2.2]octane, phz = phenazine, and tmpyz = tetramethylpyrazine), were synthesized and characterized by elementary analyses, infrared and electronic spectroscopies, and variable-temperature magnetic susceptibilities (4.5–300 K). A tetranuclear complex, $[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**), was also synthesized, and a "dimer of dimers" structure was confirmed by an X-ray structure analysis. The crystal structure of **6** shows that $[Ru_2(piv)_4(H_2O)_2]^+$ units are linked by hydrogen bonds with tmpyz molecules, giving zigzag chains with Ru1–O5···N1 angle of 108.1(2)°. A red-shift of the $\delta^*/\pi^*(Ru_2) \rightarrow \sigma^*(Ru\text{–}O)$, and $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transition bands of the $Ru^{II,III}{}_2$ core was observed in polymeric chain adducts **1**–**4**. All of the present complexes show a very weak antiferromagnetic interaction between the dinuclear units with a considerable zero-field splitting parameter.

The chemistry of dinuclear metal carboxylates of the type $M_2(O_2CR)_4$ has attracted much attention over the past three decades, because of their unique properties imparted by the metal–metal interactions within the molecules.[1–6] We have been engaged in the chemistry of adducts of metal carboxylates with linkage ligands.[7–10] Our interest in their potential application as building blocks for supramolecular assembly has resulted in the formation of one-dimensional chain compounds of metal carboxylates with *N*,*N*′-didentate ligands, $[M_2(O_2CR)_4L]_n$ ($M = Mo^{II}$, Rh^{II}, Cu^{II}, and Ru^{II}; L = pyrazine, 4,4′-bipyridine, and 1,4-diazabicyclo[2.2.2]octane). In these systems, the $Mo^{II}{}_2$ and $Rh^{II}{}_2$ complexes are diamagnetic, whereas the $Cu^{II}{}_2$ and $Ru^{II}{}_2$ complexes are paramagnetic. In this context, the mixed-valent $Ru^{II,III}$ carboxylates are unique, showing a relatively higher spin state of three unpaired electrons ($S = 3/2$) due to an accidental near degeneracy of the π^* and δ^* orbitals.[11] This quartet ground state can be exploited in the design of molecular magnetic materials.[4] Therefore, several one-dimensional chain complexes of the dinuclear ruthenium(II,III) carboxylate have appeared in the literature,[12–15] and some extended systems based on the dinuclear ruthenium cores have been reported recently.[16,17] However, data concerning the relationship between the magnetic properties and the structures are still scant, and more knowledge is considered to be necessary as a basis for thoroughly understanding the magnetic properties of these systems. In this study, we chose ruthenium(II,III) pivalate with bulky groups on the carboxylate groups as dinuclear building blocks, and synthesized the adducts by using *N*,*N*′-didentate ligands, pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), 1,4-diazabicyclo[2.2.2]-octane (dabco), phenazine (phz), and tetramethylpyrazine (tmpyz). The isolated compounds were characterized based on the spectral and magnetic properties as well as the X-ray crystal structures of the phz and tmpyz complexes.

Experimental

Synthesis of Complexes. Unless otherwise specified, commercial chemicals were used as supplied. Benzene and dichloromethane were dried and distilled using standard laboratory techniques. All of the solvents used were distilled over suitable drying reagents. The tetrafluoroborate salt of ruthenium(II,III) pivalate, $[Ru_2(piv)_4(H_2O)_2]BF_4$ (Hpiv = pivalic acid) was synthesized by applying a method described in the literature.[12,13]

$[Ru_2(piv)_4(pyz)]_n(BF_4)_n \cdot 3nH_2O$ (1): To a solution of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) in benzene (10 cm^3) was added a slight excess of pyz (4 mg, 0.050 mmol) with stirring. The reaction mixture was stirred for 1 h at room temperature, giving a brown precipitate. The precipitate was filtered, washed with benzene, and dried in vacuo. Yield, 26 mg (77%). Found: C, 34.89; H, 5.24; N, 3.52%. Calcd for $C_{24}H_{46}BF_4N_2O_{11}Ru_2$: C, 34.82; H, 5.60; N, 3.38%. IR (KBr, cm^{-1}): ν_{asym}(COO) 1488, ν_{sym}(COO) 1422, $\nu(BF_4^-)$ 1057, ν(CH, pz) 817. Diffuse reflectance spectrum λ_{max}/nm 259, 430, 623sh, 1006. $\mu_{eff}(300\ K)/\mu_B$ 4.46.

$[Ru_2(piv)_4(4,4'\text{-bpy})]_n(BF_4)_n \cdot nH_2O$ (2): This compound was prepared as a brown precipitate by the reaction of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) with 4,4′-bpy (8 mg, 0.051 mmol) in benzene using the same method as that of **1**. Yield, 21 mg (59%). Found: C, 41.62; H, 5.27; N, 3.45%. Calcd for $C_{30}H_{46}BF_4N_2O_9Ru_2$: C, 41.52; H, 5.34; N, 3.23%. IR (KBr,

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cm^{-1}): ν_{asym}(COO) 1487, ν_{sym}(COO) 1422, $\nu(BF_4^-)$ 1065, ν(CH, bpy) 820. Diffuse reflectance spectrum λ_{max}/nm 254, 422, 567, 1051. μ_{eff}(300 K)/μ_B 4.25.

$[Ru_2(piv)_4(dabco)]_n(BF_4)_n \cdot 2nH_2O$ (3): This compound was prepared as a yellowish-brown precipitate by the reaction of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) with dabco (5 mg, 0.045 mmol) in benzene using the same method as that of **1**. Yield, 26 mg (75%). Found: C, 36.90; H, 5.93; N, 3.53%. Calcd for $C_{26}H_{52}BF_4N_2O_{10}Ru_2$: C, 37.10; H, 6.23; N, 3.33%. IR (KBr, cm^{-1}): ν_{asym}(COO) 1488, ν_{sym}(COO) 1422, $\nu(BF_4^-)$ 1059. Diffuse reflectance spectrum λ_{max}/nm 256, 425, 681, 1010. μ_{eff}(300 K)/μ_B 4.39.

$[Ru_2(piv)_4(phz)]_n(BF_4)_n$ (4): To a solution of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) in benzene (10 cm^3) was added a slight excess of phz (9 mg, 0.050 mmol) with stirring. The reaction mixture was refluxed for 1 h, giving an orange precipitate. The precipitate was filtered, washed with benzene, and dried in vacuo. Yield, 27 mg (85%). Found: C, 44.73; H, 5.00; N, 3.17%. Calcd for $C_{32}H_{44}BF_4N_2O_8Ru_2$: C, 44.84; H, 5.12; N, 3.15%. IR (KBr, cm^{-1}): ν_{asym}(COO) 1488, ν_{sym}(COO) 1419, $\nu(BF_4^-)$ 1060. Diffuse reflectance spectrum λ_{max}/nm 247, 352, 450, 659sh, 1010. μ_{eff}(300 K)/μ_B 4.18.

$[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (5): To a solution of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) in benzene (10 cm^3) was added a slight excess of phz (9 mg, 0.050 mmol) with stirring. The reaction mixture was stirred at room temperature for 1 h, giving an orange precipitate, which was filtered, washed with benzene, and dried in vacuo. Yield, 17 mg (52%). Found: C, 39.21; H, 5.01; N, 1.65%. Calcd for $C_{52}H_{84}B_2F_8N_4O_{18}Ru_4$: C, 38.96; H, 5.28; N, 1.75%. IR (KBr, cm^{-1}): ν_{asym}(COO) 1488, ν_{sym}(COO) 1419, $\nu(BF_4^-)$ 1061. Diffuse reflectance spectrum λ_{max}/nm 247, 361, 381, 437, 531sh, 1003. μ_{eff}(300 K)/μ_B 4.37.

$[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n \cdot nCH_2Cl_2$ (6): To a solution of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (30 mg, 0.041 mmol) in dichloromethane (10 cm^3) was added an excess of tmpyz (12 mg, 0.088 mmol) with stirring. The reaction mixture was stirred at room temperature for 1 h. Onto the reacted solution was added hexane, giving a reddish-brown precipitate, which was filtered, washed with hexane, and dried in vacuo. Yield, 21 mg (54%). Found: C, 35.98; H, 5.76; N, 2.62%. Calcd for $C_{29}H_{54}BCl_2F_4N_2O_{10}Ru_2$: C, 35.95; H, 5.83; N, 2.89%. IR (KBr, cm^{-1}): ν_{asym}(COO) 1487, ν_{sym}(COO) 1420, $\nu(BF_4^-)$ 1059. Diffuse reflectance spectrum λ_{max}/nm 273, 430, 540sh, 992. μ_{eff}(300 K)/μ_B 4.26.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region. The electronic spectra were measured with a Shimadzu UV–vis–NIR Recording Spectrophotometer Model UV-3100. The temperature dependence of the magnetic susceptibilities was measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T over a temperature range of 4.5–300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[18] The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi T}$, where χ is the magnetic susceptibility per mole of $Ru^{II,III}_2$ dinuclear unit.

X-Ray Crystal Structure Analyses. A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo Kα radiation at 20 ± 1 °C. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers (CCDC 249911 and 249912).

Table 1. Crystal Data and Data Collection Details

Complex	$[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**)	$[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n \cdot nCH_2Cl_2$ (**6**)
Formula	$C_{26}H_{42}BF_4NO_9Ru_2$	$C_{29}H_{54}BCl_2F_4N_2O_{10}Ru_2$
Formula weight	801.56	950.59
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2$
a/Å	9.4081(17)	13.352(3)
b/Å	12.648(2)	19.046(4)
c/Å	14.571(3)	9.928(2)
α/°	84.118(3)	90
β/°	85.728(3)	119.887(3)
γ/°	88.743(4)	90
V/Å^3	1719.7(5)	2189.0(8)
Z	2	2
D_c/g cm^{-3}	1.55	1.44
D_m/g cm^{-3}	1.56	1.45
μ(Mo Kα)/mm^{-1}	0.945	0.875
Crystal size/mm^3	0.35 × 0.30 × 0.15	0.40 × 0.20 × 0.10
Theta range for data collection/°	1.62 to 23.26	2.06 to 23.26
Reflections collected	7404	4669
Independent reflections	4903 [R(int) = 0.0215]	2963 [R(int) = 0.0167]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0375$, $wR2 = 0.0882$	$R1 = 0.0286$, $wR2 = 0.0703$
R indices (all data)	$R1 = 0.0560$, $wR2 = 0.0937$	$R1 = 0.0351$, $wR2 = 0.0730$

Table 2. Selected Bond Distances (Å) and Angles (°) with Their Estimated Standard Deviations in Parentheses

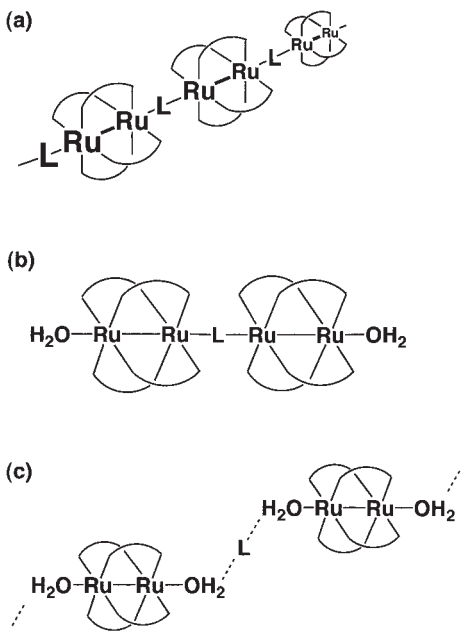
$[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**)[a]			
Ru1–Ru2	2.278(1)	Ru2–O8	2.022(3)
Ru1–O1	2.011(3)	Ru1–O9	2.253(3)
Ru1–O3	2.030(3)	Ru2–N1	2.533(4)
Ru1–O5	2.018(3)	O9···F3	2.745(7)
Ru1–O7	2.016(3)	O9···F4″	2.862(7)
Ru2–O2	2.026(3)	Ru2–Ru1–O9	176.54(9)
Ru2–O4	2.024(3)	Ru1–Ru2–N1	177.04(9)
Ru2–O6	2.032(3)	Ru2–N1···N1′	173.0(2)
$[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n \cdot nCH_2Cl_2$ (**6**)[b]			
Ru1–Ru1′	2.267(1)	Ru1–O5	2.261(2)
Ru1–O1	2.014(12)	O5···N1	2.808(7)
Ru1–O2	2.022(12)	Ru1′–Ru1–O5	177.2(2)
Ru1–O3	2.018(2)	Ru1–O5···N1	108.1(2)
Ru1–O4	2.021(2)	O5···N1···N1″	167.9(4)

a) Prime refers to the equivalent position $(-x+1, -y+2, -z)$. Double prime refers to the equivalent position $(-x, -y+1, -z+1)$. b) Prime refers to the equivalent position $(-x+1, y, -z+2)$. Double prime refers to the equivalent position $(-x, y, -z+1)$.

Results and Discussion

Polynuclear chain compounds, formulated as $[Ru_2(piv)_4L]_n(BF_4)_n$ (L = pyz (**1**), 4,4′-bpy (**2**), and dabco (**3**)), were successfully prepared by reacting $[Ru_2(piv)_4(H_2O)_2]BF_4$ with a slight excess of *N*,*N*′-didentate ligand at room temperature in satisfactory yields. In the case of a reaction with phenazine at room temperature, a tetranuclear complex with a "dimer of dimers" structure, $[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**), was obtained. When the same reaction was carried out in benzene heated to reflux, a polynuclear chain complex, $[Ru_2(piv)_4(phz)]_n(BF_4)_n$ (**4**), was obtained in a good yield. Heating is necessary to obtain chain compound of **4**, possibly because of the weak bridging property of phenazine. A trend to decrease the interaction by phenazine was observed for $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$, compared with that of pyrazine complex.[14] A reaction with 2 equiv of tetramethylpyrazine afforded a polynuclear chain complex, $[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n \cdot nCH_2Cl_2$ (**6**).

The IR spectra of all of the present complexes show the O–C–O vibrations as a set of distinctive two bands in a similar energy region to those of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (ν_{asym}(COO) 1486 cm^{-1} and ν_{sym}(COO) 1425 cm^{-1}). This fact suggests that the dinuclear skeleton is preserved upon a reaction with the *N*,*N*′-didentate ligand to form chain and tetranuclear complexes.[12,13] The stretching bands of the tetrafluoroborate ion appear around 1060 cm^{-1}. No coordination of tetrafluoroborate ion to metal centers could be deduced, due to the small splitting of this band. The out-of-plane CH bending mode is shifted from 790 cm^{-1} for free pyrazine to 817 cm^{-1} for the pyrazine complex **1**.[19a,c] The centrosymmetric stretching at 1580 cm^{-1}, the in-plane C–H bending at 1230 cm^{-1}, and the ring deformation at 695 cm^{-1} of monodentate pyrazine were not observed in the IR spectra of **1**, indicative of the bridging mode of pyrazine.[19b,c] A similar shift to higher energy of the out-of-plane C–H bending, and a disappearance of the in-plane C–H bending at 1215 cm^{-1} and the ring vibration at 1585 cm^{-1} were observed in the 4,4′-bpy complex **2**, indicative of bridging 4,4′-bipyridine.[19b]



Scheme 1. (a) Chain structure, (b) tetranuclear structure of "dimer of dimers", (c) chain structure with hydrogen bonds.

For **1**–**4**, a chain structure with an alternated arrangement of the $Ru_2(piv)_4$ dinuclear units and *N*,*N*′-didentate ligands can be proposed based on the analytical data, IR spectra, and bridging nature of the *N*,*N*′-didentate ligands (Scheme 1). Diffuse reflectance spectra of these complexes are shown in Figs. 1 and 2. The spectra show a comparatively distinctive band at 422–450 nm with a shoulder at 567–681 nm and a broad band at 1006–1051 nm, which correspond to a distinctive band at 427 nm with a shoulder at 545 nm and a band at 990 nm

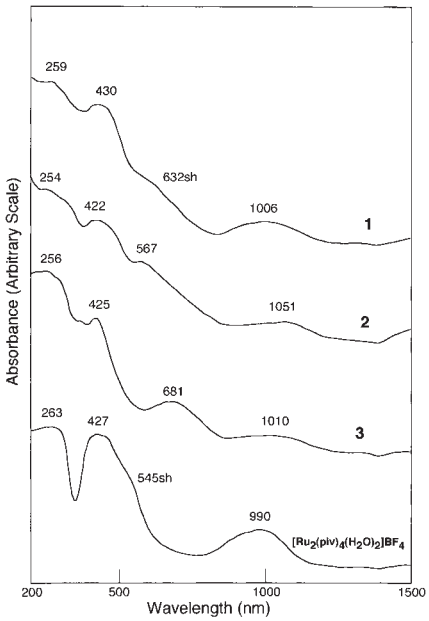


Fig. 1. Diffuse reflectance spectra of **1**, **2**, and **3**.

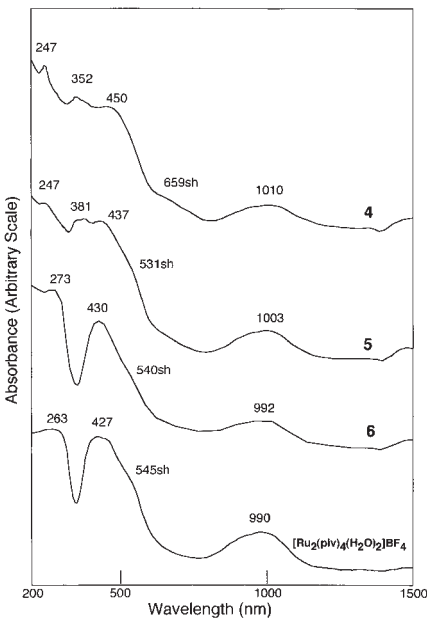


Fig. 2. Diffuse reflectance spectra of **4**, **5**, and **6**.

of $[Ru_2(piv)_4(H_2O)_2]BF_4$. These bands can be assigned to the transitions $\pi(\text{Ru–O, Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$, $\delta^*/\pi^*(\text{Ru}_2) \rightarrow \sigma^*(\text{Ru–O})$, and $\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$, respectively.[20] Although the former distinctive band appears at almost the same region, both of the latter two bands show a slight red shift upon coordination of the *N*,*N*′-didentate ligands. The σ-donation of the nitrogen donor is generally stronger than that of the oxygen donor, such as an aqua ligand. Therefore, the axial coordination of the nitrogen donor of the *N*,*N*′-didentate ligand may weaken the metal–metal bonding of the $Ru^{II,III}{}_2$ core, and then cause a lowering of the $\sigma^*(\text{Ru–O})$ and $\delta^*(\text{Ru}_2)$ levels, resulting in a red shift of these bands. A similar red-shift of the $\delta \rightarrow \delta^*$ transition band has been observed in polymeric chain compounds of molybdenum(II) carboxylates with *N*,*N*′-didentate ligands.[7b,c]

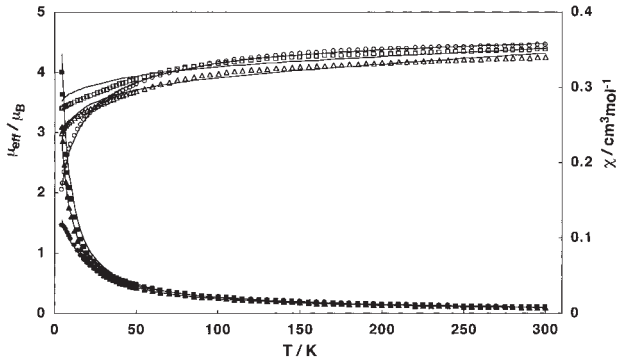


Fig. 3. Temperature dependence of magnetic susceptibilities (●, ▲, ■) and effective magnetic moments of (○, △, □) of **1**, **2**, and **3**. The solid lines show the best fit obtained (see text).

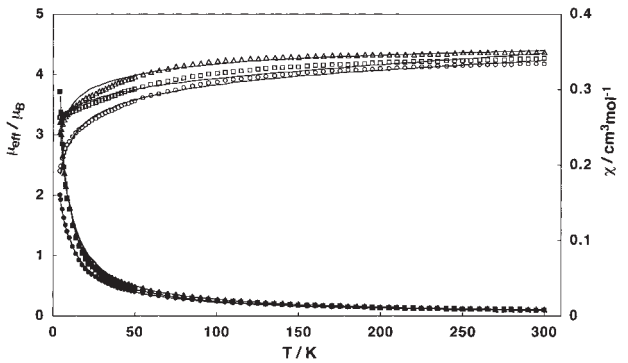


Fig. 4. Temperature dependence of magnetic susceptibilities (●, ▲, ■) and effective magnetic moments of (○, △, □) of **4**, **5**, and **6**. The solid lines show the best fit obtained (see text).

The temperature dependence of the effective magnetic moments for **1**–**4** are shown in Figs. 3 and 4. These complexes exhibit room-temperature magnetic moments at around 4 μ_B per mole of the dinuclear unit [4.46 (for **1**), 4.25 (for **2**), 4.39 (for **3**), and 4.18 μ_B (for **4**) at 300 K], consistent with three unpaired electrons per $Ru^{II,III}{}_2$ unit. The magnetic moments gradually decrease with lowering of the temperature in the range of 50–300 K, then begin to clearly decrease with lowering of the temperature below 50 K, and reach the minimum values [2.05 (for **1**), 2.99 (for **2**), 3.39 (for **3**), and 2.34 μ_B (for **4**) at 4.5 K]. The drop in the magnetic moments at low temperature reflect the zero-field splitting of the $Ru^{II,III}{}_2$ core.[12,13] Moreover, the magnetic moments of some compounds are slightly lower than that for the parent dinuclear complex, $[Ru_2(piv)_4(H_2O)_2]BF_4$ (4.31 μ_B at 300 K), over the whole range, indicative of an antiferromagnetic interaction between the dinuclear units. Therefore, we adopted a molecular field approximation described by Telser and Drago,[15a]

$$\chi' = \chi/(1 - (2zJ/Ng^2{\mu_B}^2)\chi), \quad (1)$$

where, zJ is the exchange energy multiplied by the number of interacting neighbors, and χ is the magnetic susceptibility of

Table 3. Magnetic Parameters of Complexes

Complex	D/cm^{-1}	g	zJ/cm^{-1}	$tip/\mathrm{cm}^3\,\mathrm{mol}^{-1}$	p
1	68	2.40	−1.49	4.40×10^{-4}	0
2	45	2.13	−0.28	1.87×10^{-3}	0.021
3	50	2.09	−0.03	2.26×10^{-3}	0
4	70	2.17	−0.76	1.39×10^{-3}	0.0066
5	80	2.37	−0.42	5.00×10^{-4}	0.045
6	50	2.07	−0.10	1.95×10^{-3}	0.0017

an isolated molecule,

$$\chi = (1-p)[(\chi_{\parallel} + 2\chi_{\perp})/3 + tip] + pN\mu_B{}^2 g_{\mathrm{mono}}{}^2/4kT. \quad (2)$$

Here, $\chi_{\parallel}$ and $\chi_{\perp}$ are magnetic susceptibility terms defined as follows:

$$\chi_{\parallel} = (Ng^2\mu_B{}^2/kT)[1 + 9\exp(-2D/kT)] /[4\{1 + \exp(-2D/kT)\}], \quad (3)$$

$$\chi_{\perp} = (Ng^2\mu_B{}^2/kT)[4 + (3kT/D)\{1 - \exp(-2D/kT)\}] /[4\{1 + \exp(-2D/kT)\}], \quad (4)$$

where D is the zero-field splitting parameter. Equation 2 includes correction terms for temperature-independent paramgnetism (*tip*) and a small amount (p) of paramagnetic impurity (usually a mononuclear Ru^{III} species ($S = 1/2$) with a g factor, noted as g_{mono}).

An analysis using Eq. 1 for the magnetic data of all four complexes with the composition $[Ru_2(piv)_4L]BF_4$, where L is pyz (**1**), 4,4′-bipy (**2**), dabco (**3**), or phz (**4**), indicates an antiferromagnetic coupling; the four complexes have zJ values of −1.49, −0.28, −0.03, and −0.76 cm^{-1}, respectively, although the theoretical fitting of the data is rather poor in the low-temperature region for some compounds. The g and D values obtained for the present complexes are similar to those reported previously for noninteracting mixed-valent diruthenium carboxylates (Table 3).[12d,15] The antiferromagnetic interaction for the pyrazine-bridged complex **1** is significantly greater than those observed for the other three compounds. For the 4,4′-bpy complex **2**, the large separation between the two Ru_2 units is most probably the main reason for the attenuation of any magnetic interaction. In the case of the phz complex **4**, it is reasonable to assume a similar situation to the 4,4′-bpy complex, because of the rather weak coordination of the phz molecule.[14] It is clear that the dabco complex **3** exhibits the least interaction among the present complexes. The dabco molecule does not have a viable superexchange pathway, because it has only a σ framework, and lacks a π-system. It seems reasonable to conclude that pyrazine mediates an antiferromagnetic interaction most efficiently by using the π system.

Single crystals of the phenazine complex, $[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**), can be isolated from the reaction at room temperature. An ORTEP drawing of the tetranuclear cation with the atom numbering scheme is depicted in Fig. 5. Selected bond distances and angles are given in Table 2. The cation consists of two μ-tetrakis(pivalato)aquadiruthenium(II,III) units with a Ru1–Ru2 distance of 2.278(1) Å and one axially bridging phenazine molecule. A crystallographic inversion center is located at the midpoint of the bridging phz molecule. The axial Ru2–N1 distance (2.533(4) Å) is rather long. In a similar tetranuclear complex with pyrazine $[\{Ru_2(chp)_4\}_2(pyz)](BF_4)_2$ (chp = 6-chloro-2-hydroxypyridinato), the Ru–N distance is 2.275(5) Å.[21] This fact suggest that steric interactions with phz may cause the Ru–N distance to be longer than it would be with pyrazine.[19c] Similar long Ru–N distances are also found in an analogous phz adduct, but a polynuclear chain complex, $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$, which has axial Ru–N distances of 2.436(4) and 2.443(5) Å.[14] The Ru1–Ru2–N1 angle is essentially linear (177.04(9)°). The other axial site of the dimer unit is occupied by a water molecule with a Ru1–O9 distance of 2.253(3) Å. The Ru–Ru and axial Ru–O_{ax} distances and equatorial Ru–O_{eq} bond lengths [2.011(3)–2.032(3) Å] are nearly the same as those found in the $[Ru_2(piv)_4(H_2O)]^+$ cation [Ru–Ru = 2.256(1)–2.260(1) Å, Ru–O_{ax} = 2.247(4)–2.330(5) Å, and Ru–O_{eq} = 2.005(4)–2.026(3) Å].[12d,22] This kind of "dimer of dimers" complex is also found in an adduct of ruthenium(II,III) pivalate with 7,7,8,8-tetracyanoquinodimethane.[23] In the crystal, the tetranuclear units are loosely connected to be a chain molecule, described as $[\{\{Ru_2(piv)_4(H_2O)\}_2(phz)\}(BF_4)_2]_n$, using hydrogen bonds between the axial water molecules and two tetrafluoroborate ions [O9···F3 2.745(7) Å, O9···F4″ 2.862(7) Å] (Fig. 6).

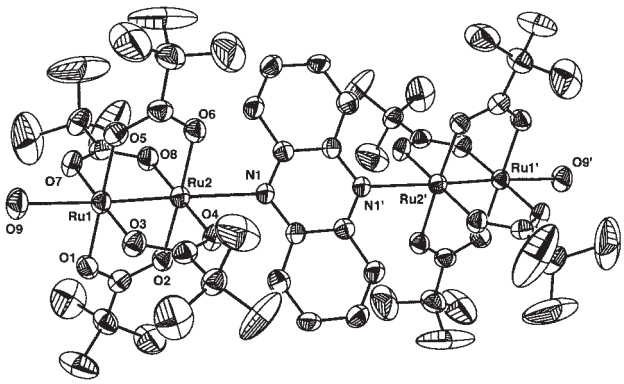


Fig. 5. ORTEP drawing of the structure of the $[\{Ru_2(piv)_4(H_2O)\}_2(phz)]^{2+}$ cation in **5** showing the 50% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

The tetramethylpyrazine complex $[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n$ (**6**), crystallizes as a polynuclear chain compound in the monoclinic space group $C2$. A perspective view of $[Ru_2(piv)_4(H_2O)_2(tmpyz)]^+$ is shown in Fig. 7. Selected bond distances and angles are listed in Table 2. The two ruthenium atoms are equatorially linked by the four bridging carboxylates, and the water molecules are axially coordinated. The Ru–Ru, axial Ru–O_{ax}, and equatorial Ru–O_{eq} distances [Ru1–

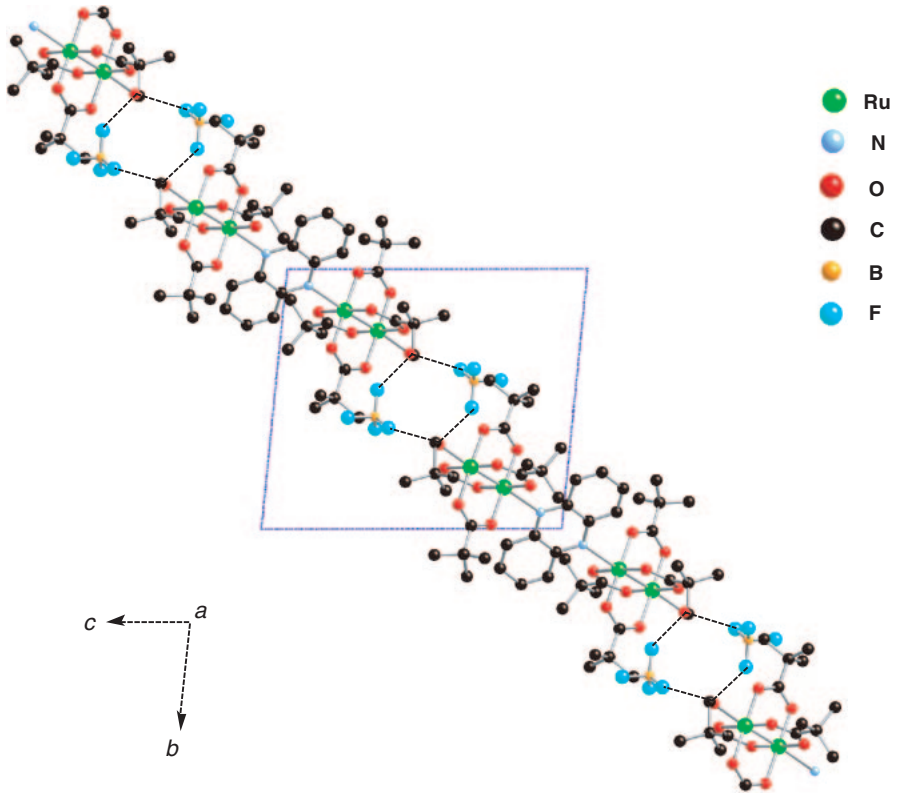


Fig. 6. Perspective view on *bc* plane of **5**. Only one chain structure is shown for clarity. Broken lines show hydrogen bonds.

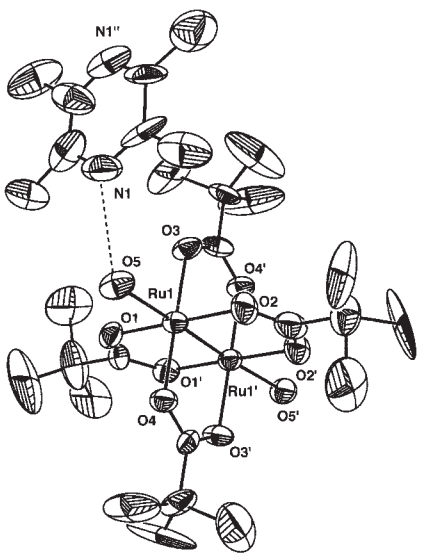


Fig. 7. ORTEP drawing of the structure of the $[Ru_2(piv)_4(H_2O)_2(tmpyz)]^+$ cation in **6** showing the 50% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

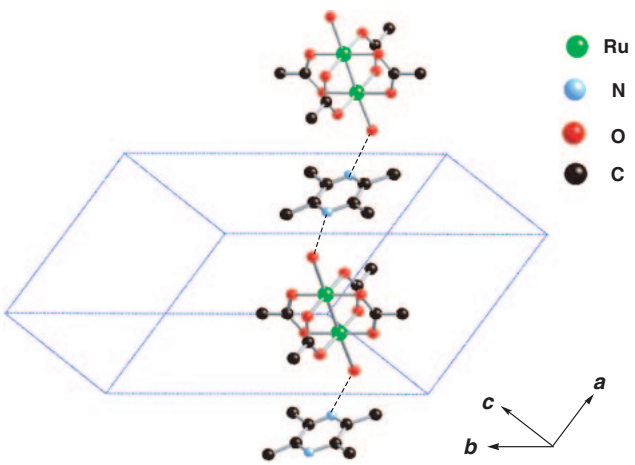


Fig. 8. Crystal structure of **6**. Only one chain structure is shown. Broken lines show hydrogen bonds. Methyl groups of pivalate groups, BF_4^-, and solvent molecules are omitted for clarity.

Ru1′ 2.267(1) Å, Ru1–O5 2.261(2) Å, Ru1–O_{eq} 2.014(12)–2.022(12) Å] agree with the values already published for all other mixed-valent diruthenium carboxylates.[1,4] In the crystal, the dinuclear units are bridged by the tmpyz molecules by the hydrogen bonds, giving infinite $[\cdots\{Ru_2(piv)_4(H_2O)_2\}\cdots tmpyz\cdots]_n$ zigzag chains packed along the *b* direction, the propagation direction of these chain being parallel, while alternating to the *c* and *a* axes (Fig. 8). In this case, the coordination ability of the tmpyz seems to be too weak to substitute for the axial water molecules, because of a steric crowding of the methyl groups attached to the pyrazine ring. Alternatively, the tmpyz molecules connect the $[Ru_2(piv)_4(H_2O)_2]$ units by the hydrogen bonds between the pyrazine nitrogen and the axial water molecules [O5···N1 2.808(7) Å, Ru1–O5···N1 108.1(2)°]. So far, we have found the hydrogen-bond-linked chain compounds in $[Ru_2(piv)_4(nitr)_2][Ru_2(piv)_4(H_2O)_2]_n(BF_4)_{2n}$ (nitr = nitronyl nitroxide radicals),[12c,g] where the $[Ru_2(piv)_4(nitr)_2]$ units are

connected by hydrogen bonds with the axial water molecules of the $[Ru_2(piv)_4(H_2O)_2]$ units.

The diffuse reflectance spectra of **5** and **6** are similar to those of $[Ru_2(piv)_4(H_2O)_2]BF_4$, exhibiting the $\delta^*/\pi^*(Ru_2) \rightarrow \sigma^*(Ru–O)$ and $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ bands at 531(sh) and 1003 nm and 540(sh) and 992 nm, respectively (Fig. 2), This feature is consistent with the occupation of a water molecule for one or both axial sites of the ruthenium pivalate core.

The temperature dependence of the effective magnetic moments for **5** and **6** is shown in Fig. 4. The magnetic behavior is similar to those of **1**–**4**. The magnetic data were analyzed by Eq. 1. The obtained parameters are $g = 2.37$, $zJ = -0.42$ cm^{-1}, $D = 80$ cm^{-1} for **5**, and $g = 2.07$, $zJ = -0.10$ cm^{-1}, $D = 50$ cm^{-1} for **6**, respectively. The zJ value of **5** is comparable to that of the phenazine complex **4**. In the case of **6**, the magnetic interaction between the $[Ru_2(piv)_4(H_2O)_2]$ units is expected to be very weak because of the long distances between these units; this can be confirmed by the zJ value of **6**.

Conclusion

In this study, we isolated and characterized polynuclear chain complexes, $[Ru_2(piv)_4L]_n(BF_4)_n$ (L = pyz (**1**), 4,4′-bpy (**2**), dabco (**3**), and phz (**4**)) and $[Ru_2(piv)_4(H_2O)_2(tmpyz)]_n(BF_4)_n$ (**6**), and a tetranuclear complex, $[\{Ru_2(piv)_4(H_2O)\}_2(phz)](BF_4)_2$ (**5**), showing that the *N*,*N*′-didentate ligands are useful to link ruthenium(II,III) pivalate as the building blocks for supramolecular assembly. The magnetic interaction via the *N*,*N*′-didentate ligands was found to be generally weak and antiferomagnetic, dependent on the nature of the bridging ligands.

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