Structure and Magnetic Properties of a Nitroxide Diruthenium(II,III) Complex, $[Ru_2(O_2CCMe_3)_4(tempo)_2]$ $[Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (tempo=2,2,6,6-Tetramethylpiperidine-1-oxyl)

Makoto Handa,* Yasuyoshi Sayama, Masahiro Mikuriya,*,† Ryoji Nukada,†
Ichiro Hiromitsu,†† and Kuninobu Kasuga

Department of Chemistry, Faculty of Science, Shimane University, Nishikawatsu, Matsue 690
†Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662
††Department of Physics, Faculty of Science, Shimane University, Nishikawatsu, Matsue 690

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A nitroxide complex, $[Ru_2(O_2CCMe_3)_4(tempo)_2][Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (tempo = 2, 2, 6, 6-tetramethylpiperidine-1-oxyl) has been prepared and characterized by elemental analysis, X-ray crystal structure analysis, and variable temperature magnetic susceptibility and ESR spectrum measurements. A fairly large antiferromagnetic interaction ($J=-130$ cm^{-1}) between the diruthenium core and the nitroxide radical has been observed.

Much interest has been devoted to the metal-cluster compounds; in these compounds, the tetra-μ-carboxylato-dimetal complex ($M_2(O_2CR)_4X_m$, $m=0$—2) is one of the most extensively studied systems.1) Tetra-μ-carboxylato-diruthenium complexes are known to exist both as homovalent Ru(II,II) and mixed-valent Ru(II,III) species.2,3) The Ru(II,III) oxidation state is thermodynamically preferred. The core of Ru(II,III) possesses three unpaired electrons, so some magnetic studies have been performed to investigate the electronic states.4) Recently, some chain complexes of the Ru(II,III) dimers linked by phenazine and pyrazine showing intrachain antiferromagnetisms have also been reported.5) In these complexes, however, the magnetic interactions between the diruthenium cores through the bridging ligands are weak; hence remarkable magnetic properties have not been observed. It is well known that, in the nitroxide complexes of tetra-μ-carboxylato-dirhodium(II), $[Rh_2(O_2CR)_4L_n]$ ($R=CF_3$, C_3F_7, C_6F_5, L=nitroxide radical, $n=1,2$), fairly strong antiferromagnetic interactions operate between the nitroxide radicals through the Rh–Rh bond.6) Based on this fact, we expected that the paramagnetic complexes of tetra-μ-carboxylato-diruthenium(II,II or II,III) coordinated by nitroxide radicals would exhibit the magnetic interactions between the diruthenium core and the radical, such study may give suggestions for producing chain complexes having the strong magnetic interactions between the diruthenium cores. From such a viewpoint, we started the study of the compounds formed by the combination of tetra-μ-carboxylato-diruthenium(II,II or II,III) complexes and nitroxide radicals. During the course of our study, bis adducts of tempo (2,2,6,6-tetramethylpiperidine-1-oxyl) with the Ru(II,II) species, $[Ru_2(O_2CCF_3)_4(tempo)_2]$ (**1**) and $[Ru_2(O_2CC_6F_5)_4(tempo)_2]$ (**2**) have been reported.7) The Ru(II,II) core has a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electron configuration (spin triplet ground state) and the magnetic moment (μ_{eff}) rapidly decreases with the decrease of temperature and approaches zero because of a large zero field splitting ($D=$ca. 300 cm^{-1}).2b,2c,7) However, the Ru(II,III) core has a $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ configuration (quartet ground state) with a relatively small D value (ca. 70 cm^{-1}), and shows an appreciable μ_{eff} value even at ca. 0 K.4b,5b) The difference may be important for the magnetic study of this type of nitroxide complex. Here, we present a nitroxide complex of Ru(II,III), $[Ru_2(O_2CCMe_3)_4(tempo)_2]$-$[Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (**3**). To our knowledge, this is the first example of a bis-tempo adduct complex having the mixed valent dimetal center.

Experimental

The starting material, $[Ru_2(O_2CCMe_3)_4]BF_4$, was prepared by a similar procedure to that described in the literature.3f)

Preparation of $[Ru_2(O_2CCMe_3)_4(tempo)_2]$ $[Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (3). A benzene solution of tempo (17 mg, 0.11 mmol) was added to a benzene solution of $[Ru_2(O_2CCMe_3)_4]BF_4$ (29 mg, 0.042 mmol) under

Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/Å^2$ [a)]	Atom	x	y	z	$B_{eq}/Å^2$ [a)]
Ru1	0.92061(3)	0.45633(2)	0.93970(3)	2.661(8)	C8	1.2716(7)	0.4498(6)	0.7686(8)	11.6(2)
Ru2	0.48299(3)	0.00584(3)	0.09317(3)	3.275(8)	C9	1.1654(8)	0.3136(6)	0.726(1)	21.0(3)
F1	0.3691(4)	0.0542(3)	0.5329(4)	10.2(1)	C10	1.085(1)	0.426(1)	0.6128(8)	26.9(7)
F2	0.2879(4)	0.0925(3)	0.3475(3)	11.0(1)	C11	0.2789(4)	−0.0016(3)	−0.1269(4)	3.6(1)
F3	0.1885(4)	0.0364(5)	0.4457(6)	15.0(2)	C12	0.1512(4)	−0.0047(3)	−0.2042(5)	4.2(1)
F4	0.2608(6)	0.1681(3)	0.5149(5)	17.5(2)	C13	0.0822(5)	−0.0183(5)	−0.1209(6)	6.4(2)
O1	0.8569(2)	0.5553(2)	0.8426(3)	3.22(7)	C14	0.1247(5)	−0.0763(5)	−0.3210(6)	6.7(2)
O2	0.9868(3)	0.3597(2)	1.0388(3)	3.39(7)	C15	0.1259(6)	0.0844(5)	−0.2470(7)	7.4(2)
O3	1.0003(3)	0.4131(2)	0.8124(3)	3.48(7)	C16	0.5240(4)	0.1720(3)	0.0363(4)	4.0(1)
O4	0.8438(2)	0.5020(2)	1.0676(3)	3.45(7)	C17	0.5541(5)	0.2706(4)	0.0665(5)	5.2(1)
O5	0.3134(3)	0.0063(2)	−0.0051(3)	3.87(8)	C18	0.5388(7)	0.3063(4)	−0.0538(7)	8.9(2)
O6	0.4974(3)	0.1388(2)	0.1180(3)	4.13(8)	C19	0.4896(7)	0.3207(5)	0.1421(7)	10.3(2)
O7	0.4681(3)	−0.1269(2)	0.0656(3)	4.00(8)	C20	0.6816(8)	0.2781(5)	0.149(1)	11.5(3)
O8	0.6527(3)	0.0058(2)	0.1889(3)	3.96(8)	C21	0.6365(4)	0.3718(3)	0.6291(5)	4.5(1)
O9	0.7818(3)	0.3589(2)	0.8266(3)	4.16(8)	C22	0.5361(5)	0.3120(4)	0.5314(6)	6.8(2)
O10	0.4593(3)	0.0107(3)	0.2829(3)	4.86(9)	C23	0.5688(7)	0.2252(4)	0.4767(6)	8.3(2)
N	0.7134(3)	0.3174(2)	0.7192(4)	3.57(9)	C24	0.6264(6)	0.1750(4)	0.5838(6)	6.7(2)
C1	0.9164(4)	0.6270(3)	0.8715(4)	3.1(1)	C25	0.7359(4)	0.2217(3)	0.6833(5)	4.4(1)
C2	0.8713(4)	0.7005(3)	0.7961(4)	3.6(1)	C26	0.7049(6)	0.4110(4)	0.5616(5)	6.2(2)
C3	0.7623(5)	0.6711(4)	0.6840(6)	6.2(2)	C27	0.5934(5)	0.4453(4)	0.7072(6)	6.1(2)
C4	0.8542(7)	0.7785(4)	0.8874(7)	8.6(2)	C28	0.7705(6)	0.1801(4)	0.8033(6)	6.3(2)
C5	0.9617(6)	0.7256(4)	0.7460(6)	7.6(2)	C29	0.8334(6)	0.2174(4)	0.6324(7)	7.4(2)
C6	1.1010(4)	0.4420(3)	0.8324(4)	3.4(1)	B	0.2779(6)	0.0905(5)	0.4636(6)	6.0(2)
C7	1.1567(5)	0.4075(4)	0.7356(5)	5.3(1)					

a) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

argon atmosphere. After stirring the solution overnight at room temperature, a precipitate was filtered, washed with benzene, and dried in vacuo. Yield: 33 mg (90% (based on $[Ru_2(O_2CCMe_3)_4]BF_4$)). Anal. Found: C, 40.22; H, 6.38; N, 1.64%. Calcd for $C_{58}H_{112}N_2B_2F_8O_{20}Ru_4$: C, 40.14; H, 6.51; N, 1.61%. The hydrate water may come from the solvent. In the preparation, the reaction using the hydrate precursor $[Ru_2(O_2CCMe_3)_4]BF_4{\cdot}2H_2O$ as the starting material also gave a compound having the same formula as **3**.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanako CHN CORDER MT-5. Magnetic susceptibilities were measured by the Faraday method over the 5—300 K temperature range. The apparatus was calibrated using $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$.[8] The susceptibilities were corrected for diamagnetism of the constituent atoms using Pascal's constants.[9] ESR was measured on a home-made K-band apparatus with a magnetic field modulation frequency of 100 kHz and an intensity of 0.5 gauss.

X-Ray Crystal Structure Analysis. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at 25±1 °C. The intensity data were collected by the ω–2θ scan technique and were corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $Ru_4F_8O_{20}N_2C_{58}B_2H_{112}$, F.W.=1735.42, triclinic, space group $P\bar{1}$, a=12.480(6), b=15.440(7), c=11.272(6) Å, α=100.37(3), β=110.40(2), γ=88.79(3)°, V=2000(2) Å^3, Z=1, D_m=1.45 (by floating in n-C_6H_{14}–CCl_4), D_c=1.44 g cm^{-3}, μ(Mo $K\alpha$)=8.03 cm^{-1}, crystal dimensions 0.33×0.43×0.11 mm^3. Of the 5551 reflections measured in the range $2.0\leq2\theta\leq46.0°$, 4174 with $I\geq3\sigma(I)$ were assumed as observed. The structure was solved by direct methods and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at their calculated positions and fixed at their positions. A weighting scheme $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$ was employed. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.029$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.031$.

All the calculations were carried out on a VAX station 4000(90A) with the MolEN program package.[10] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and thermal parameters of hydrogen atoms, and F_o-F_c tables have been deposited as Document No. 68027 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The reaction of the Ru(II, III) dimer and tempo in benzene gave the complex **3** with the formula of $[Ru_2(O_2CCMe_3)_4]^+$: tempo = 1 : 1 in spite of the use of excess tempo in the reaction. The reason is unclear at the present stage. Crystals of **3** suitable for single-crystal X-ray determination were grown from benzene. The X-ray analysis shows that the crystal consists of two kinds of Ru(II, III) cation units: $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$, and tetrafluoroborate an-

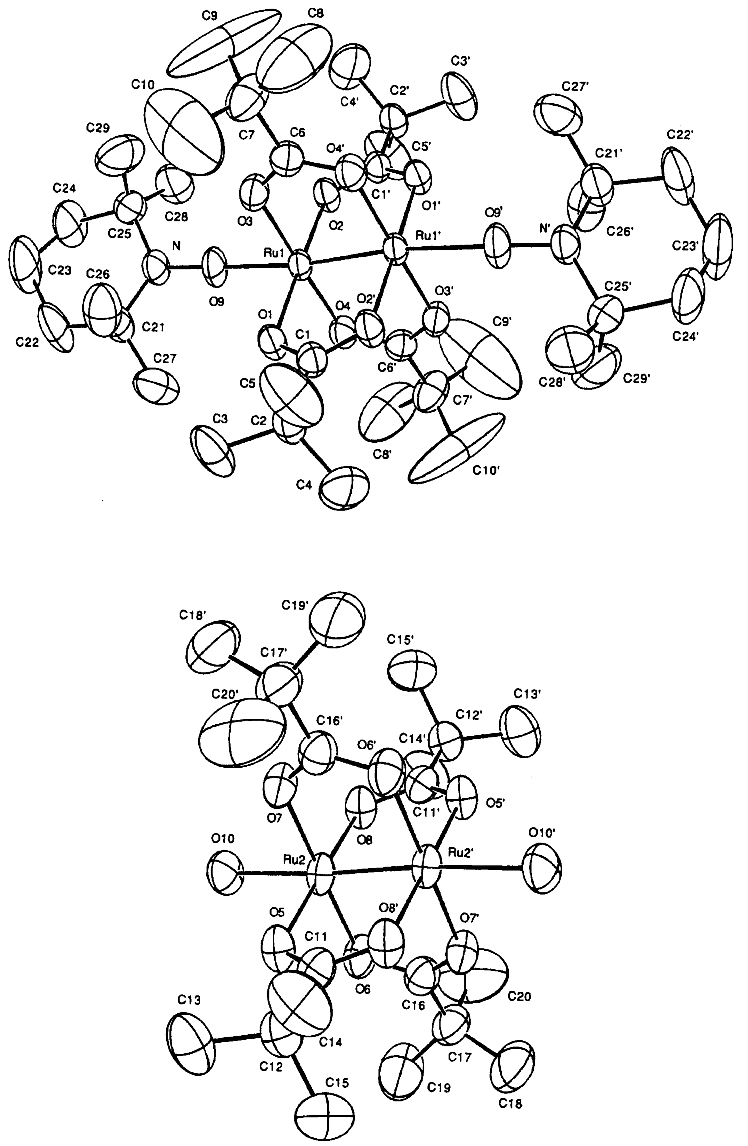

Fig. 1. Structures of Ru(II,III) cation units in **3**, $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ (upper side) and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$ (lower side).

ions. The structures of the two cation units are shown in Fig. 1. Selected bond distances and angles are given in Table 2. Crystallographic inversion centers are located at the midpoints of the Ru–Ru bonds of the Ru(II,III) cations. In $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$, the axial positions of the Ru(II,III) core are occupied by the oxygen atoms of tempo with a separation of 2.184(3) Å, relatively large compared with that of **1** (2.136(5) Å (201 K), 2.162(4) Å (293 K). In $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$, the axial positions are occupied by the oxygen atoms of water molecules with a separation of 2.247(4) Å. The Ru–Ru bond distances are 2.273(1) Å (for Rul–Rul′) and 2.260(1) Å (for Ru2–Ru2′), which are in the range of those reported for $[Ru_2(O_2CR)_4]^+$ compounds (2.24—2.30 Å).[1] The N–O bond length 1.275(4) Å (in tempo) comfirms that the axial ligand exists as a free radical.[6,7] The Ru–O–N angle is 151.5(3)°, comparable to that of **1** (158.2(3)° (201 K), 157.9(3)° (293 K)).

Table 2. Selected Bond Distances (Å) and Angles (°) of **3**

Rul–Rul′	2.273(1)	Ru2–Ru2′	2.260(1)
Rul–O1	2.026(3)	Ru2–O5	2.018(3)
Rul–O2	2.015(3)	Ru2–O6	2.024(3)
Rul–O3	2.028(3)	Ru2–O7	2.019(3)
Rul–O4	2.016(3)	Ru2–O8	2.014(3)
Rul–O9	2.184(3)	Ru2–O10	2.247(4)
O9–N	1.275(4)	Rul′–Rul–O9	173.01(9)
Rul–O9–N	151.5(3)	Ru2′–Ru2–O10	175.85(9)

In Fig. 2, the variation of effective magnetic moments per Ru(II,III) dimer with temperature (5—300 K) for **3**[11] and $[Ru_2(O_2CCMe_3)_4]BF_4\cdot2H_2O$ are shown. The magnetic moments for **3** are considerably lower than those for $[Ru_2(O_2CCMe_3)_4]BF_4\cdot2H_2O$ in the whole temperature range, which shows the existence of an antiferromagnetic interaction between the dimetal cen-

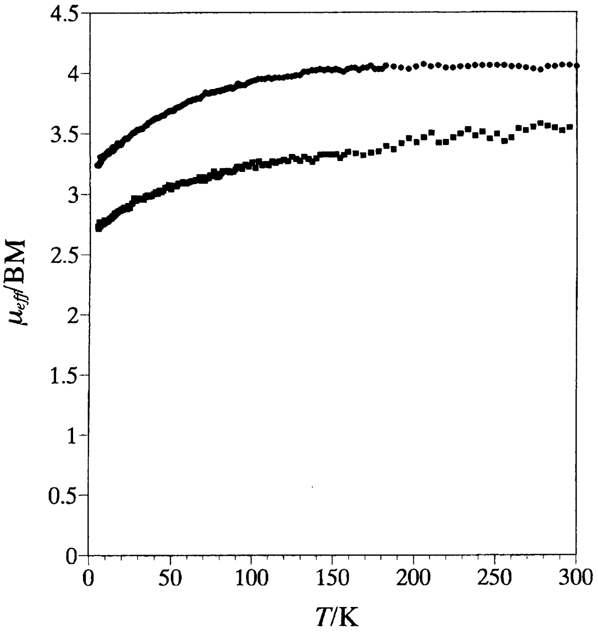

Fig. 2. Temperature dependence of magnetic moments per Ru(II,III) unit for **3** (■) and $Ru_2(O_2CCMe_3)_4BF_4 \cdot 2H_2O$ (●).

ter and the radical. In order to estimate the value of the exchange integral *J*, the magnetic susceptibility of $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ (χ(Ru-tem)) was calculated by subtracting the measured susceptibility value of $[Ru_2(O_2CCMe_3)_4]BF_4 \cdot 2H_2O$ (χ(Ru-H$_2$O)) from that of **3** (χ(**3**))[12] at each temperature point, considering the molar fraction of $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ (p) and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$ (q) ($p+q=2$) in the sample.[13] The equation is

$$\chi(\text{Ru-tem}) = (1/p)[\chi(\mathbf{3}) - q\chi(\text{Ru-H}_2\text{O})]. \quad (1)$$

The theoretical magnetic susceptibility for this system is numerically calculated based on the Heisenberg model by the use of Van Vleck's formula (see Appendix 1). For the bis-tempo adduct unit, two different exchange integrals should be taken into consideration (Fig. 3); that is, the exchange integrals *J* for the nitroxide-metal interaction and *J*′ for the through-bond interaction between two tempo ligands. During fitting, the values of Lande g factors for Ru(II,III) core (g_{Ru}) and tempo (g_{tem}) were fixed at 2.117, and 2.0, respectively. The g_{Ru} value was evaluated by fitting the experimental data of $[Ru_2(O_2CCMe_3)_4]BF_4 \cdot 2H_2O$ to the equation taken from Ref. 14. The validity of these values is supported by the fact that the average of g_{Ru} and g_{tem}, 2.059 is almost equal to the average g value ($=(2.33+2\times1.92)/3=2.057$) obtained from an ESR spectrum of **3** (vide infra). The fitting showed that the quality of the fit was independent of the J' value as long as $J'>0$ and that the D value was at least less than half of the J value where the quality of the fit was also nearly independent of the D value. Hence, the J' and D values were set to zero. The result is shown in Fig. 4. The fitting parameters are summarized in Table 3. Although the J value (-130 cm^{-1}) is smaller than that for **1** (-263 cm^{-1}) and **2** (-234 cm^{-1}), a fairly large antiferromagnetic interaction has been also achieved in the combination of the Ru(II,III) carboxylate cation dimer $[Ru_2(O_2CR)_4]^+$ and the nitroxide radical. In the cases of **1** and **2**, the large interaction was interpreted with the mechanism of the pathway based on the π^* orbitals of the N–O group of the nitroxide and the diruthenium core, judging from the Ru–O–N bond angle of **1** (158.2(3)° (201 K) and 157.9(3)° (293 K))[7] which are significantly different from the values (ca. 120°) reported for the O-bonded nitroxide complexes of tetra-μ-carboxylato-dirhodium(II) with the σ-pathway mechanism.[6b] The close similarity of the Ru–O–N bond angle value of **3** (151.5(3)°) to that of **1** shows that the magnetic coupling observed for **3** also results from the same mechanism as for **1** and **2**, because both the Ru(II,II) and the Ru(II,III) cores have unpaired electrons in the π^* orbitals. The larger Ru–O (tempo) bond length of **3** compared with that of **1** may result in the smaller *J* value compared with those of **1** and **2**. In fact, the discontinuous drop in magnetic susceptibility with decrease of the temperature observed

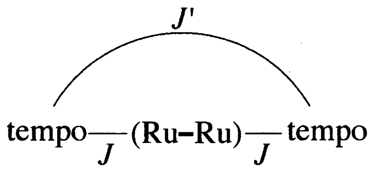

Fig. 3. Exchange integrals for the bis-tempo adduct system. *J* and *J*′ are for the nitroxide–metal interaction and the through-bond interaction between two tempo ligands, respectively.

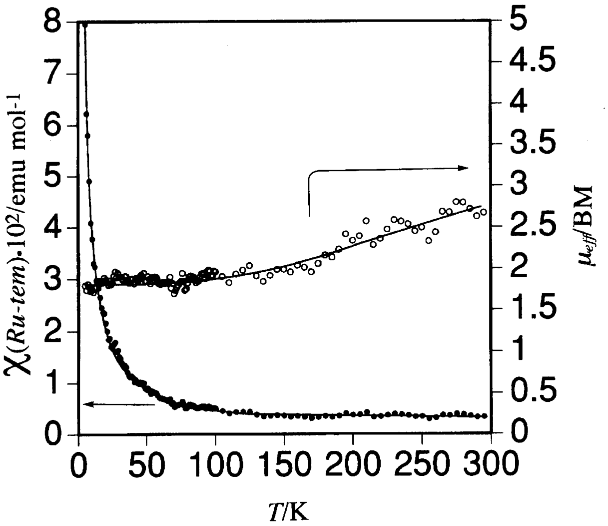

Fig. 4. Temperature dependence of the magnetic susceptibility (●) and effective magnetic moment (○) for $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$, which were obtained based on Eq. 1 (see text). The solid lines were calculated with the parameters listed in Table 3.

Table 3. Fitting Parameters for the Magnetic Data

	$Ru_2(O_2CCMe_3)_4BF_4 \cdot 2H_2O$	$Ru_2(O_2CCMe_3)_4$ $(tempo)_2^+$ [a]
g_{Ru}	2.117	2.117
g_{TEM}		2.0
D/cm^{-1}	61	0
p, q[b]		0.86, 1.14
J/cm^{-1}		−130
J'/cm^{-1}		0
$R/10^5$ [c]	2.54	129

a) The magnetic susceptibility (χ(Ru-tem)) was calculated by Eq. 1 (see text). b) Parameters for the molar fraction of $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$ in the measured sample of **3** (see text). c) $R=\Sigma(\chi_{exp}-\chi_{theo})^2/\Sigma\chi_{exp}^2$; χ_{exp} is χ(Ru-H$_2$O) or χ(Ru-tem) and χ_{theo} the theoretical magnetic susceptibility for $Ru_2(O_2CCMe_3)_4BF_4 \cdot 2H_2O$ or $Ru_2(O_2CCMe_3)_4(tempo)_2^+$ (see text and Appendix 1).

for **1** qualitatively agreed with the decrease of the Ru–O bond length at low temperature.[7]

The ESR spectrum (powder at 5 K) of **3** is shown in Fig. 5. The signal at $g_\perp^e=4.40$, where g^e means the effective g value defined in Appendix 2, is assumed to arise from $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$ because $[Ru_2Cl(O_2C\text{-}n\text{-}Bu)_4]$[4b] and also $[Ru_2(O_2CCMe_3)_4]BF_4 \cdot 2H_2O$ show the identical $g_\perp^e$ value of 4.40. The signals at $g_\perp^e=2.33$ and $g_{/\!/}^e=1.92$ are attributed to $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$. The latter signal at $g=1.92$ does not originate from the $g_{/\!/}^e$ component of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$, because the $g_{/\!/}^e$ signal of $[Ru_2(O_2CCMe_3)_4]BF_4 \cdot 2H_2O$ is hardly discernible around there in the solid state. The observed $g_\perp^e$ and $g_{/\!/}^e$ values indicate that the present bis-tempo adduct is in $S=1/2$ ground state (see Appendix 2) in agreement with the susceptibility study.

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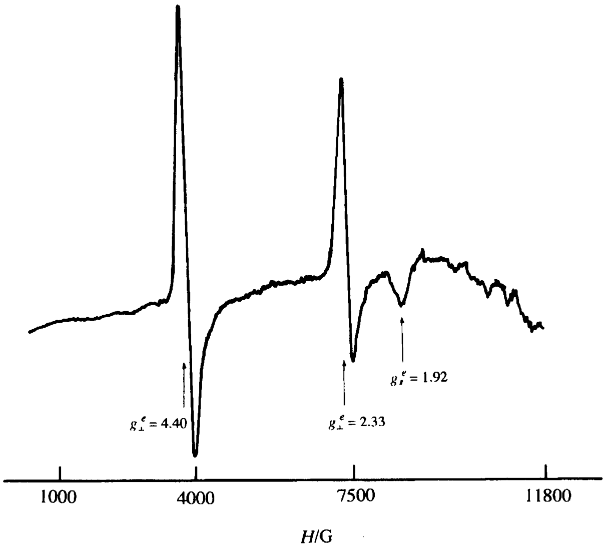

Fig. 5. K-band ESR spectrum of **3**, powder at 5 K. 1 G=1×10^{-4} T.

Appendix

Appendix 1. Susceptibility of $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$. The theoretical magnetic susceptibility of the present bis-tempo adduct is calculated in a procedure similar to that of Cogne et al.[7] using the Van Vleck formula. The Hamiltonian is

$$H = H_0 + \mu_B[g_M\vec{S} + g(\vec{S}_1+\vec{S}_2)]\vec{H}, \tag{A1}$$

with

$$H_0 = -2J\vec{S}(\vec{S}_1+\vec{S}_2) - 2J'\vec{S}_1\vec{S}_2 + D[S_z^2 - \frac{1}{8}\vec{S}^2], \tag{A2}$$

where $S_1=S_2=1/2$ are the nitroxide spins and $S=3/2$ is the spin of the diruthenium core. The difference from the case of Cogne et al. is that the present diruthenium core has the spin 3/2 instead of spin 1, which makes it impossible to obtain the analytic formula for the susceptibility, so that the calculation must be done numerically.

In order to use the Van Vleck's formula, the eigenvalues and the eigenstates of unperturbed Hamiltonian $\mathscr{H}_0$ must be obtained. Using a representation $|SS_{12}S_tM_t\rangle$, where

$$\vec{S}_{12} = \vec{S}_1 + \vec{S}_2, \tag{A3}$$

$$\vec{S}_t = \vec{S}_{12} + \vec{S}, \tag{A4}$$

and M_t is the eigenvalue of $(S_t)_z$, the energy levels become as follows.

eigenvalues of $\mathscr{H}_0-C$	energy	eigenstates
E_1, E_2, E_3	Numerically calculated	$\left\{ s\lvert\frac{3}{2}1\frac{5}{2}\frac{1}{2}\rangle + t\lvert\frac{3}{2}1\frac{3}{2}\frac{1}{2}\rangle + u\lvert\frac{3}{2}1\frac{1}{2}\frac{1}{2}\rangle \right.$ $\left. s'\lvert\frac{3}{2}1\frac{5}{2}-\frac{1}{2}\rangle + t'\lvert\frac{3}{2}1\frac{3}{2}-\frac{1}{2}\rangle + u'\lvert\frac{3}{2}1\frac{1}{2}-\frac{1}{2}\rangle \right.$
E_4	$-3J-2J'+\frac{9}{4}D$	$\lvert\frac{3}{2}1\frac{5}{2}\frac{5}{2}\rangle$ $\lvert\frac{3}{2}1\frac{5}{2}-\frac{5}{2}\rangle$
E_5	$-\frac{1}{2}J-2J'+\frac{5}{4}D+\delta$	$\cos\theta\lvert\frac{3}{2}1\frac{5}{2}\frac{3}{2}\rangle + \sin\theta\lvert\frac{3}{2}1\frac{3}{2}\frac{3}{2}\rangle$ $\cos\theta\lvert\frac{3}{2}1\frac{5}{2}-\frac{3}{2}\rangle - \sin\theta\lvert\frac{3}{2}1\frac{3}{2}-\frac{3}{2}\rangle$
E_6	$-\frac{1}{2}J-2J'+\frac{5}{4}D-\delta$	$\cos\theta'\lvert\frac{3}{2}1\frac{5}{2}\frac{3}{2}\rangle + \sin\theta'\lvert\frac{3}{2}1\frac{3}{2}\frac{3}{2}\rangle$ $\cos\theta'\lvert\frac{3}{2}1\frac{5}{2}-\frac{3}{2}\rangle - \sin\theta'\lvert\frac{3}{2}1\frac{3}{2}-\frac{3}{2}\rangle$
E_7	$\frac{9}{4}D$	$\lvert\frac{3}{2}0\frac{3}{2}\frac{3}{2}\rangle$ $\lvert\frac{3}{2}0\frac{3}{2}-\frac{3}{2}\rangle$
E_8	$\frac{1}{4}D$	$\lvert\frac{3}{2}0\frac{3}{2}\frac{1}{2}\rangle$ $\lvert\frac{3}{2}0\frac{3}{2}-\frac{1}{2}\rangle$

(A5)

where

$$\delta=\sqrt{\frac{25}{4}J^2+JD+D^2},$$

$$\tan\theta=\frac{\frac{25}{2}J+D+5\delta}{2\sqrt{6}D},$$

$$\tan\theta'=\frac{\frac{25}{2}J+D-5\delta}{2\sqrt{6}D},$$

and C is a constant included in $\mathscr{H}_0$ defined by

$$C=J'(\vec{S}_1^2+\vec{S}_2^2)-\frac{1}{3}D\vec{S}^2.$$

The eigenvalues E_1, E_2, and E_3 and the eigenstates in the form of $s\lvert\frac{3}{2}1\frac{5}{2}\frac{1}{2}\rangle+t\lvert\frac{3}{2}1\frac{3}{2}\frac{1}{2}\rangle+u\lvert\frac{3}{2}1\frac{1}{2}\frac{1}{2}\rangle$ are obtained by numerically solving the eigenvalue problem of the matrix

$$\begin{bmatrix} -3J-2J'+\frac{9}{20}D & \frac{2}{5}D & \frac{\sqrt{5}}{5}D \\ \frac{2}{5}D & 2J-2J'+\frac{21}{20}D & \frac{2\sqrt{5}}{5}D \\ \frac{\sqrt{5}}{5}D & \frac{2\sqrt{5}}{5}D & 5J-2J'+\frac{5}{4}D \end{bmatrix}. \tag{A6}$$

Similarly, the eigenstates in the form of $s'\lvert\frac{3}{2}1\frac{5}{2}-\frac{1}{2}\rangle+t'\lvert\frac{3}{2}1\frac{3}{2}-\frac{1}{2}\rangle+u'\lvert\frac{3}{2}1\frac{1}{2}-\frac{1}{2}\rangle$ are obtained from the matrix

$$\begin{bmatrix} -3J-2J'+\frac{9}{20}D & -\frac{2}{5}D & \frac{\sqrt{5}}{5}D \\ -\frac{2}{5}D & 2J-2J'+\frac{21}{20}D & -\frac{2\sqrt{5}}{5}D \\ \frac{\sqrt{5}}{5}D & -\frac{2\sqrt{5}}{5}D & 5J-2J'+\frac{5}{4}D \end{bmatrix}, \tag{A7}$$

which has the same eigenvalues as the matrix (A6).

Then, the susceptibility is calculated by using the Van Vleck formula which treats the term $\mu_B[g_M\vec{S}+g(\vec{S}_1+\vec{S}_2)]\vec{H}$ in (A1) as a perturbation. The effect of g-anisotropy has been neglected in the present calculation.

Appendix 2. Magnetic Resonance Conditions. (I) $[\mathbf{Ru_2(O_2CCMe_3)_4(H_2O)_2}]^+$ (S=3/2). Using the spin Hamiltonian,

$$\mathscr{H}=D[S_z^2-\frac{1}{3}\vec{S}^2]+\mu_B[g_{M\perp}(S_xH_{0x}+S_yH_{0y})+g_{M/\!/}SzH_{0z}], \tag{A8}$$

and considering the Zeeman term in (A8) as a perturbation, the resonance condition for the $S_z=\pm\frac{1}{2}$ ground state is easily obtained as follows.

$$h\nu=g_{M/\!/}\mu_BH_0 \quad \text{for } H_0/\!/\text{z}$$
$$h\nu=2g_{M\perp}\mu_BH_0 \quad \text{for } H_0/\!/\text{x,y}, \tag{A9}$$

where h is the Planck constant, ν the microwave frequency and μ_B the Bohr magneton. (A9) indicates that the effective g value, $g^e=h\nu/(\mu_BH_0)$, becomes $g_{M/\!/}$ for $H_0/\!/$z and $2g_{M\perp}$ for $H_0/\!/$x,y.

(II) $[\mathbf{Ru_2(O_2CCMe_3)_4(tempo)_2}]^+$. In the present bis-tempo adduct, the total spin S_t is a good quantum number, and the ground state is the doubly degenerate $S_t=1/2$ state, i.e., the $\lvert\frac{3}{2}1\frac{1}{2}\pm\frac{1}{2}\rangle$ state. Then, with the perturbation,

$$\mathscr{H}=\mu_B[g_{M\perp}(S_xH_{0x}+S_yH_{0y})+g_{M/\!/}S_zH_{0z} +g_\perp\{(S_{12})_xH_{0x}+(S_{12})_yH_{0y}\}+g_{/\!/}(S_{12})_zH_{0z}], \tag{A10}$$

the resonance condition is calculated to be

$$h\nu=2\mu_BH_0(\frac{5}{6}g_{M/\!/}-\frac{1}{3}g_{/\!/}) \quad \text{for } H_0/\!/\text{z}$$
$$h\nu=2\mu_BH_0(\frac{5}{6}g_{M\perp}-\frac{1}{3}g_\perp) \quad \text{for } H_0/\!/\text{x,y}. \tag{A11}$$

Now, using the values of $g_{M\perp}=2.20$, $g_{M/\!/}=1.95$ and $g_\perp=g_{/\!/}=2.00$ obtained from the ESR spectra of $[\mathrm{Ru_2Cl(O_2C{-}\mathit{n}{-}Bu)_4}]^{4b)}$ and tempo, we calculate the effective g values of bis-tempo adduct to be $g^e_{/\!/}=1.92$ and $g^e_\perp=2.33$, which are exactly the same as those observed in the present study.

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11) The magnetic moments of **3** were calculated as Ru(II, III) dimer unit in order to compare the values with those of $[Ru_2(O_2CCMe_3)_4]BF_4 \cdot 2H_2O$.

12) χ(**3**) is the magnetic susceptibility per $[Ru_2(O_2CCMe_3)_4(tempo)_2][Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$.

13) The introduction of parameters, p and q, improved the fitting of the data to the theoretical susceptibilities for $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$. The ratio of $[Ru_2(O_2CCMe_3)_4(tempo)_2]^+$ and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$ seems to be not exactly 1 : 1 in a powder sample used for the measurement.

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