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Structural effects on magnetism of pyridyl nitroxide complexes of ruthenium(II, III) pivalate dimers*

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The 1:1 reactions in molar ratio of ruthenium(II, III) pivalate dimer and pyridyl nitronyl nitroxide gave chain complexes, $[Ru_2(O_2CCMe_3)_4(L)]_n(BF_4)_n$, L = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*–oxide and 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*-oxide. For the complex with the former radical, the chain structure made up by an alternated dimer-radical arrangement due to the axial co-ordination of pyridyl nitrogen and one of two nitroxide oxygens of the radical was confirmed by the X-ray diffraction method. Magnetic properties of the compounds were analyzed by considering magnetic interactions between Ru(II, III) dimer and radical through pyridyl and N–O groups, respectively.

Key words*: Ru(II, III) dimer; pyridyl niroxide radical; chain complexes*

1. Introduction

There has been much interest devoted to the metal complexes with nitroxide radicals because of their interesting magnetic properties based on the interaction between the paramagnetic metal centers and radicals [1–3]. We have been engaged in the magnetic study on ruthenium(II, III) pivalate dimers ($[Ru_2(O_2CCMe_3)_4]^+$) co-ordinated by the radicals; the Ru(II, III) dimeric cation has three unpaired electrons residing in its degenerated π^* and δ^* orbitals and has a large zero-field splitting ($D \sim 60$ cm^{-1}) [4, 5]. We have shown that the axial bond angle $\angle$Ru–O_{ax}–N (nitroxide) is the most important structural factor to affect their magnetic behaviours, the observed axial bond angles

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being in the range of 120–180° for the nitroxide Ru(II, III) complexes. The ferromagnetic interaction is operative between Ru(II, III) dimer and radical when the angle is decreased to be close to ∠Ru–O_{ax}–N = 120°. On the other hand, the antiferromagnetic interaction is operative when the angle ∠Ru–O_{ax}–N is close to 180° [6]. This result indicates that ferri- or ferromagnetic behaviour would be observed if the alternated chain structure of the Ru(II, III) dimer and the radical could be achieved in this combination [3]. However, the chain complex $[Ru_2(O_2CCMe_3)_4(nitph)]_n(BF_4)_n$ (**1**) (nitph = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*-oxide) revealed only a constant decrease of the magnetic moment until 3 K; neither ferri- nor ferromagnetic behaviour was observed. The temperature-dependent profile was concluded to be due to the fact that one of the two axial bond angles happened to be located at the angle giving no magnetic interaction through the axial bond [7, 8]. In spite of our efforts to obtain the alternated chain complex with various nitroxide radicals, the chain complex with niroxide oxygens at the both axial positions of Ru(II, III) dimers has not been obtained so far other than the complex **11**[6-10]. As an alternative way to produce such chain complexes, we selected the nitroxide radicals with a pyridyl group (2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*-oxide (*p*-nitpy) and 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*-oxide (*m*-nitpy)), which may take part in the axial co-ordination to the Ru(II, III) dimer together with the N–O group. Here, we report the Ru(II, III) chain complexes obtained by the use of the nitroxide radicals with the pyridyl group. A preliminary report has been published for a complex with *p*-nitpy [11].

2. Experimental

Preparation. The tetrafluoroborate salt $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ was prepared according to the method described in the literature [12]. The nitronyl nitroxide radicals *p*-nitpy and *m*-nitpy were obtained according to the method described in the elsewhere [13, 14].

$[Ru_2(O_2CCMe_3)_4(p\text{-nitpy})]_n(BF_4)_n$ (2). 20 mg (0.027 mmol) of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ was put into a Schlenk tube and heated at 80 °C under vacuum (0.005 mm Hg) for 30 min in order to remove the axial water molecules. During the treatment the tetrafluoroborate salt turned yellowish brown from orange. The CH_2Cl_2 solution (3 cm^3) of *p*-nitpy (6.4 mg (0.027 mmol)) was subsequently added into the tube and stirred with the water-removed tetrafluoroborate salt under argon. Hexane (14 cm^3) was slowly added into the reacted solution; the resulting solution was allowed to stand for several days at room temperature to deposit dark-green crystals, which were collected by filtration and washed with hexane. The yield was 18 mg (72%). Anal. found C, 41.50; H, 5.64; N, 4.56. Calcd. for $C_{32}H_{52}BF_4N_3O_{10}Ru_2$: C, 41.43; H, 5.65; N, 4.53. IR (in KBr) ν(NO) 1361, ν(COO) 1484, 1452, 1418, ν(BF_4^-) 1057 cm^{-1}. Diffuse reflectance spectrum: λ_{max} 290 (sh), 380, 607, 1027 (br) nm.

$[Ru_2(O_2CCMe_3)_4(m\text{-nitpy})]_n(BF_4)_n \cdot nH_2O$ (3). This compound was obtained as dark-green crystals by the reaction of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ (20 mg, 0.027 mmol) with *m*-nitpy (6.7 mg, 0.029 mmol) in CH_2Cl_2/hexane using the same method as that of **2**. The yield was 20 mg (78% based on $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$). Anal. found C, 40.79; H, 5.49; N, 4.37. Calcd. for $C_{32}H_{54}BF_4N_3O_{11}Ru_2$: C, 40.64; H, 5.76; N, 4.44. IR (in KBr) ν(NO) 1363, ν(COO) 1483, 1452, 1418, ν(BF_4^-) 1056 cm^{-1}. Diffuse reflectance spectrum: λ_{max} 266, 367, 577, 621, 673, 1016 (br) nm.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using Perkin-Elmer Series II, CHN/O Analyzer. Infrared spectra (KBr pellets) and electronic spectra were measured with JASCO IR-700 and Shimadzu UV-3100 spectrometers, respectively. Temperature dependences of the magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T between 2 and 300 K. The susceptibilities were corrected for diamagnetism of constituent atoms using Pascal′s constant [3]. The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$, where χ is the magnetic susceptibility per Ru(II, III)-radical unit. The X-Ray Diffraction data for $\mathbf{2}\cdot 1.5n CH_2Cl_2$ were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K_α radiation at (25±1) °C. The crystal structure was solved by direct methods and refined by full-matrix least-squares. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed there. The calculations were carried out on a VAX station 4000 90A computer using a MolEN program package [15]. Crystallographic data for $\mathbf{2}\cdot 1.5n CH_2Cl_2$: $C_{33.5}H_{55}Cl_3BF_4N_3O_{10}Ru_2$, F.W. = 1055.32, monoclinic, space group $P2_1/c$, a = 11.421(3), b = 17.424(3), c = 26.358(8) Å, β = 98.75(1)°, V = 5184(2) $Å^3$, Z = 4, D_m =1.40, D_c = 1.35 g cm^{-3}, μ(Mo K_α) = 7.85 cm^{-1}, $F(000)$ = 2148, crystal dimensions 0.40×0.39×0.32 mm, 8932 reflections collected ($2\theta_{max}$ = 49°), 4973 independent reflections, R [$I \geq 3\sigma(I)$] = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.061, R_w [$I \geq 3\sigma(I)$] = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$ = 0.079 ($w = 1/[\sigma^2(|F_o|)+(0.02|F_o|)^2 + 1.0]$).

3. Results and discussion

The crystal structure of $\mathbf{2}\cdot 1.5n CH_2Cl_2$ is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The zigzag chain with alternated arrangement of the Ru(II, III) dimer and the radical is extended along the *b* axis. The Ru1–Ru2 bond distance is 2.272(1) Å, which is in the range of those of the other $[Ru_2(O_2CR)_4]^+$ compounds (2.24–2.30 Å) [4, 5]. One of the axial sites of the Ru(II, III) dimer is occupied by the pyridyl nitrogen of *p*-nitpy with a separation of Ru2–N3" = 2.260(9) Å, which is comparable to those of bis-adduct Ru(II, III) dimers with *m*- and *p*-nitpy (2.269(3) Å for $[Ru_2(O_2CCMe_3)_4(m\text{-nitpy})_2]BF_4$ and 2.282(6) Å for $[Ru_2(O_2CCMe_3)_4(p\text{-nitpy})_2]BPh_4$) [16]. One of the two N–O groups is co-ordinated with a distance of

Ru1–O9 = 2.286(7) Å. The nitroxide oxygen O10 stays free from any co-ordination. The N–O bond distances 1.30(1) (for N1–O9) and 1.27(1) Å (for N2–O10) imply that the *p*-nitpy ligand exists as a genuine radical [1]. The axial bond angle Ru1–O9–N1 = 125.3(6)° is in the range for giving ferromagnetic interaction between the Ru(II, III) dimer core and the radical (*vide infra*).

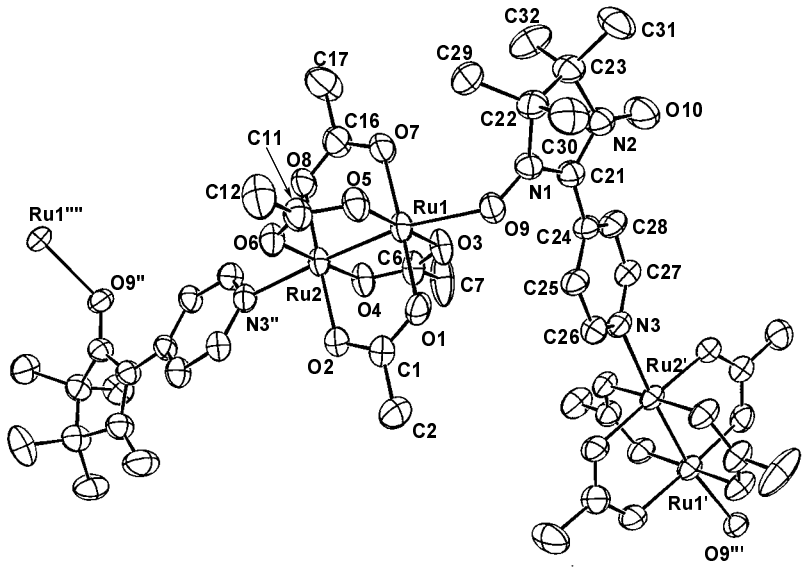


Fig. 1. View of the structure of $[Ru_2(O_2CCMe_3)_4(p\text{-nitpy})]_n(BF_4)_n \cdot 1.5nCH_2Cl_2$ (**2**·$1.5nCH_2Cl_2$), showing the atom-labelling scheme. Thermal ellipsoids are at the 35% probability level. Methyl groups of pivalic acid moieties, BF_4 ions, and CH_2Cl_2 molecules are omitted for clarity. Primes and double primes refer to the equivalent positions (x, ½ – y, ½ + z) and (x, ½ – y, –1/2+z), respectively

Table 1. Selected bond distances (Å) and angles (°) of **2**·$1.5nCH_2Cl_2$ with their estimated standard deviations (in parentheses)

Bond	Value	Bond	Value
Ru1–Ru2	2.272(1)	Ru2–O6	2.008(7)
Ru1–O1	2.004(7)	Ru2–O8	2.020(7)
Ru1–O3	2.005(7)	Ru2–N3''[1]	2.260(9)
Ru1–O5	2.006(7)	N1–O9	1.30(1)
Ru1–O7	2.015(7)	N2–O10	1.27(1)
Ru1–O9	2.286(7)	Ru2–Ru1–O9	169.5(2)
Ru2–O2	2.015(7)	Ru1–Ru2–N3''[1]	175.7(2)
Ru2–O4	2.020(7)	Ru1–O9–N1	125.3(6)

[1]Double prime refers to the equivalent position (x, ½ – y, –1/2 + z).

Temperature dependences of magnetic moments for **2** and **3** are displayed in Figs. 2 and 3, respectively. Although the magnetic moments at a room temperature (300 K) are similar (4.89μ_B for **2** and 4.75μ_B for **3**), their temperature-dependent profiles are quite different. The moment of **2** increases upon lowering the temperature down to 8 K and then rapidly decreases from the maximum value of 5.70μ_B (at 8 K) to reach the value of 3.89μ_B (at 2 K). On the other hand, the moment of **3** is nearly constant down to 100 K, and then falls to the value of 2.83μ_B (at 2 K).

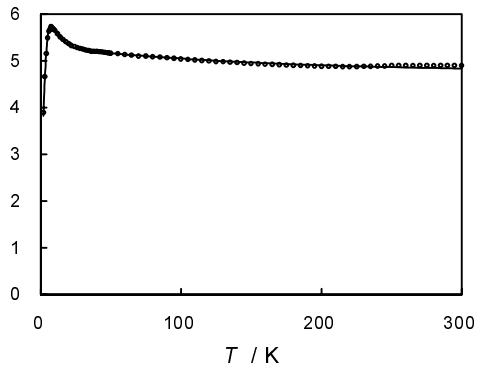


Fig. 2. Temperature dependence of effective magnetic moment (μ_{eff}/μ_B) of **2**. The solid line was calculated with the parameters listed in Table 2

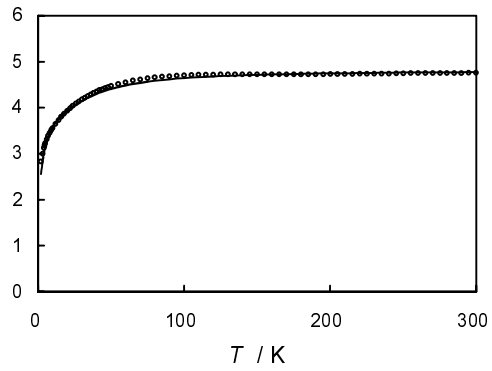
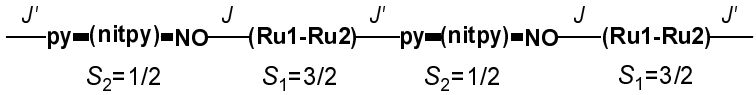


Fig. 3. Temperature dependence of effective magnetic moment (μ_{eff}/μ_B) of **3**. The solid line was calculated with the parameters listed in Table 2

Their magnetic behaviours were analyzed by taking two magnetic interactions between the Ru(II, III) dimer and the radical (Scheme 1) into account; one is through the axial N–O group and the other through the pyridyl group. The magnetic simulations of the behaviours were made using the parameters J and J' (in Scheme 1) together with the parameters g_M (g factor for Ru(II, III) dimer), g_R (g factor for radical), and D (zero-field splitting for Ru(II, III) dimer), where J' was considered to be substantially smaller in its absolute value than J and was evaluated based on the molecular–field approximation [3].



Scheme 1

The results are summarized in Table 2. The ferromagnetic interaction through the co-ordinated N–O group (J = 20 cm^{-1}) in **2** is reasonably explained by considering the axial bond angle (∠Ru1–O9–N1 = 125.3(6)°), which is located at the smaller end for those of the nitroxide Ru(II, III) complexes prepared by our research groups [6–11, 16, 17]; the interaction is ferromagnetic when the axial bond angle is decreased to be

close to 120°, though the interaction is antiferromagnetic when the angle is increased to be close to 180°. The complex **3** might have a larger axial bond angle compared with that of **2** because its ferromagnetic interaction (J = 0.3 cm^{-1}) is much weaker than that for **2**. The interactions through the pyridyl group are weak for both the present complexes like the cases of bis-addcut complexes $[Ru_2(O_2CCMe_3)_4(m\text{-nitpy})_2]X$ and $[Ru_2(O_2CCMe_3)_4(p\text{-nitpy})_2]X$ (X = BF_4 and BPh_4) [16], in which the interactions of Ru(II, III) dimer with *p*-nitpy are weakly ferromagnetic (J' = 0.8 and 1.4 cm^{-1}) and those with *m*-nitpy are weakly antiferromagnetic (J' = –1.0 cm^{-1}). The complex **2** has a ferromagnetic interaction through the pyridyl group of *p*-nitpy (J' = 0.45 cm^{-1}) as well as that through the N–O group (J = 20 cm^{-1}), which may be related to the relatively steep increase in the moment when the temperature goes down near its maximum temperature (8 K) (Fig. 2).

Table 2. Fitting parameters for the magnetic data

Parameter	Compound	
	2	**3**
g_M	2.23	2.32
g_R	2.00	2.00
D/cm^{-1}	50	40
J/cm^{-1}	20	0.3
J'^{*}/cm^{-1}	0.45	–0.4
$R/10^{-3}$**	0.66	10.8

*Estimated by molecular field approximation.

**$R = \Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma(\chi_{obsd})^2$, where χ is the magnetic susceptibility per Ru(II, III)-radical unit.

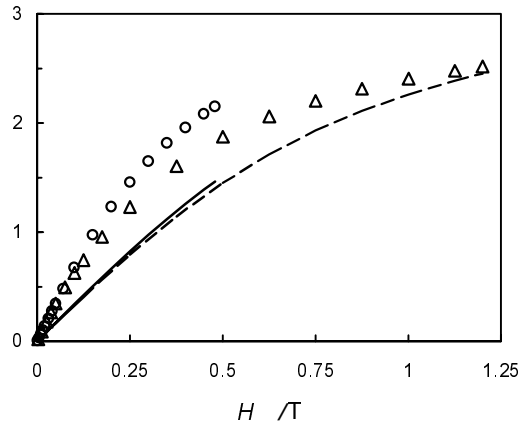


Fig. 4. Field (H/T) dependence of the magnetization ($M/N\mu_B$) for $[Ru_2(O_2CCMe_3)_4(p\text{-nitpy})]_n(BF_4)_n$ (**2**) at 4.0 K (Δ) and 10 K(O). Theoretical curves at 4.0 K (----) and 10 K (–) (g_M = 2.23, g_R = 2.00, and D = 50 cm^{-1})

The ferromagnetic behaviour of **2** was confirmed by measuring the magnetization of **2** versus the applied field (Fig. 4). The magnetization curve of **2** lies above the curve of the Brillouin function for the system of $S_1 = 3/2$ (for Ru(II, III) dimer) and $S_2 = 1/2$ (for *p*-nitpy) under the consideration of zero-field splitting. The rapid decrease in the moment below 8 K is considered to come from the zero-field splitting ($D = 40$ cm^{-1}) within the Ru(II, III) dimer (Fig. 2). The complex **3** has an antiferromagnetic interaction through the pyridyl group of *m*-nitpy ($J' = -0.4$ cm^{-1}). Both the interactions estimated with $J = 0.3$ cm^{-1} and $J' = -0.4$ cm^{-1} are weak, hence it may not be appropriate to estimate the J' value using the molecular-field approximation. However, it is certain that **3** has the ferro- and antiferromagnetic interactions although the antiferromagnetic interaction is slightly predominant because **3** does not show any ferrimagnetic behaviour, which should occur if both the interactions are antiferromagnetic in a similar magnitude [3]. The assignment of the antiferromagnetic interaction $J' = -0.4$ cm^{-1} is in accordance with the previous results for $[Ru_2(O_2CCMe_3)_4(m\text{-nitpy})_2]X$ (X = BF_4 and BPh_4), which have a weak magnetic interaction through the pyridyl group ($J' = -1.0$ cm^{-1}) [16].

4. Conclusions

The magnetic investigation on chain complexes with an alternated arrangement of ruthenium(II, III) pivalate dimers and pyridyl nitroxide radicals, 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*–oxide (*p*-nitpy) and 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-*N*-oxide (*m*-nitpy), was performed. It was found that the pyridyl group on the radical weakly mediates a ferro- or antiferromagnetic interaction with Ru(II, III) dimer depending on the employed radicals; *p*-nitpy gives the ferromagnetic interaction, but *m*-nitpy gives the antiferomagnetic interaction. The observed ferromagnetic interaction through the axially co-ordinated N–O group for the chain complex with *p*-nitpy (complex **2**) is concluded to be associated with the fact that the axial bond angle is located at ca. 120°.

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