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Structure and Magnetic Property of Ru(II,III) Dimer Axially Coordinated by the Niroxide Radical and Water $[Ru_2(O_2CCMe_3)_4(nitph)(H_2O)]BF_4$, nitph = 2-Phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-*N*-oxide

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A ruthenium(II,III) pivalate dimer axially coordinated by a nitroxide radical and a water molecule, $[Ru_2(O_2CCMe_3)_4(nitph)(H_2O)]BF_4$ (nitph = 2-phenyl-4,4,5, 5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-*N*-oxide), has been prepared and characterized. The magnetic interaction between the Ru(II,III) core and the radical through the coordinated N–O group was estimated to be $J = -45$ cm^{-1}.

Nitroxide radicals have been producing fruitful magnetic results in combination with transition-metal complexes.[1] We have employed the ruthenium(II,III) pivalate cationic dimer ($[Ru_2(O_2CCMe_3)_4]^+$) as the metal complex for the combination, and engaged in the synthesis of nitroxide Ru(II,III) complexes with the expectation that three unpaired electrons within the Ru(II,III) core would interact with the radical to give rise to interesting magnetic properties.[2] The most important point of using the Ru(II,III) dimer is that the σ^* and π^* orbitals constructed by the direct Ru–Ru bond can give different magnetic pathways at the same time. Here, we report on an Ru(II,III) dimer with a nitroxide radical and a water molecule, $[Ru_2(O_2CCMe_3)_4(nitph)(H_2O)]BF_4$ (**1**), nitph = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-*N*-oxide. This complex presents an interesting example to purely estimate the Ru(II,III)-radical interaction based on the π^* orbitals because the effect of the radical-radical interaction through the Ru_2 core based on the σ^* orbital is excluded, the Ru(II,III) unit bearing only one nitroxide radical at one of the axial sites.

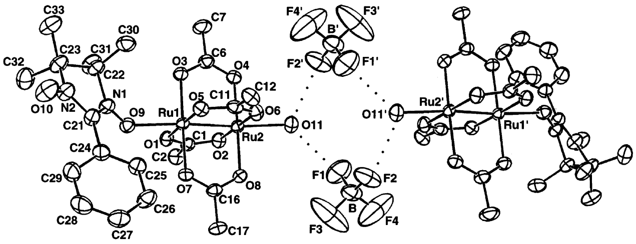

Fig. 1. View of structure of $[Ru_2(O_2CCMe_3)_4(nitph)(H_2O)]^+$ cation units in **1**·$2CH_2Cl_2$, which are connected with hydrogen bonds using BF_4^- ions. Primed and unprimed atoms are related by the inversion. Pivalate methyl groups and CH_2Cl_2 molecules are omitted for clarity.

The X-ray crystal structure of **1**·$2CH_2Cl_2$ is depicted in Fig. 1. The nitroxide radical nitph coordinates to the Ru(II,III) dimer at one of its two axial sites with an Ru1–O9 distance of 2.260(6) Å, which is comparable to one of those in the chain complex of nitph, $[Ru_2(O_2CCMe_3)_4(nitph)]_n(BF_4)_n \cdot n(C_6H_6)$ (**2**·$n(C_6H_6)$) (2.264(8) and 2.236(8) Å).[2c] The nitroxide oxygen, designated as O10, does not participate in coordination to the metal ion. The other axial site of the Ru(II,III) dimer is occupied by a water molecule, the Ru2–O11 distance being 2.281(6) Å. The Ru1–Ru2 (2.265(1) Å) and equatorial Ru–O_{eq} (2.013(5)–2.033(5) Å) bond lengths are characteristic of the Ru(II,III) cationic dimer.[3] The N–O bond lengths (1.298(8) (N1–O9) and 1.257(9) Å (N2–O10)) ensure that the axial nitph ligand exists as a genuine radical.[1a] The axial Ru1–O9–N1 (nitph) angle is 137.7(5)°, which is in the range of those for the nitroxide Ru(II,III) complexes we have reported (121.5(6)–151.5(3)°).[2] As shown in Fig. 1, two dimeric units, $[Ru_2(O_2CCMe_3)_4(nitph)(H_2O)]^+$, are crystallographically related to each other and connected to be a tetramer, described as $[\{(Ru_2(O_2CCMe_3)_4(nitph)(H_2O)\}_2(\mu\text{-}BF_4)_2]$, using hydrogen bonds of the coordinated water molecules and two tetrafluoroborate counter ions (2.71(1) (O11···F1 (BF_4^-)) and 2.74(1) Å (O11···F2′ (BF_4^-)).

The variable temperature (VT) magnetic moment per the dimeric unit (2–300 K) for **1** is shown in Fig. 2. The steady decrease in the moment in accordance with decreasing temperature is explained based on the antiferromagnetic interaction between the Ru(II,III) core and the radical as well as the zero-field splitting.[2] The solid line in Fig. 2 is drawn with the pa-

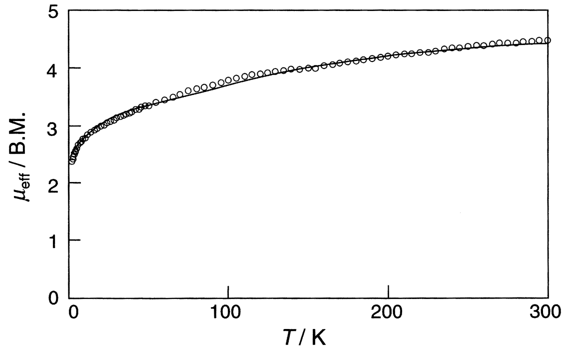

Fig. 2. Temperature dependence of magnetic moment per the dimeric unit for **1**. The solid line is drawn with the parameters noted in the text.

rameters $J = -45\ \mathrm{cm^{-1}}$, $g_{\mathrm{Ru}} = 2.34$, $g_{\mathrm{nit}} = 2.00$, $D = -30\ \mathrm{cm^{-1}}$,[4] where J is the spin-coupling constant for the interaction between the Ru(II,III) core and nitph, g_{Ru} and g_{nit} are the g factors of the Ru(II,III) core and the nitroxide ligand, respectively, and D is the zero-field splitting within the Ru(II,III) core. The observed VT behavior of the moment is well reproduced with these parameters. This result indicates that the hydrogen bonds connecting two Ru(II,III) dimer units do not mediate any important interaction, which makes the dimeric unit, $[\mathrm{Ru_2(O_2CCMe_3)_4(nitph)(H_2O)}]^+$, magnetically isolated. The distances, O10···O10″ = 3.43(1) and O10···N2″ = 3.47(1) Å, between the uncoordinated N–O groups of the neighboring tetramers $[\{\mathrm{(Ru_2(O_2CCMe_3)_4(nitph)(H_2O)}\}_2(\mu\text{-}\mathrm{BF_4})_2]$ are also considered to be long enough so as not to affect the magnetic behavior of **1**.[2f] We previously reported that the Ru(II,III)-radical interaction (J) is dependent on the axial Ru–$\mathrm{O_{ax}}$–N (nitroxide) angle; the larger the angle is, the more antiferomagnetic the interaction is[2c] (e.g., $J = -130\ \mathrm{cm^{-1}}$ when ∠Ru–$\mathrm{O_{ax}}$–N = 151.5(3)° ($[\mathrm{Ru_2(O_2CCMe_3)_4(tempo)_2}]^+$, tempo = 2,2,6,6-tetramethylpiperidine-1-oxyl),[2a] $J = -100\ \mathrm{cm^{-1}}$ when ∠Ru–$\mathrm{O_{ax}}$–N = 147.5(7)° (**2**)[2c], $J = 0\ \mathrm{cm^{-1}}$ when ∠Ru–$\mathrm{O_{ax}}$–N = 131.7(7)° (**2**),[2c] and $J = 20\ \mathrm{cm^{-1}}$ when ∠Ru–$\mathrm{O_{ax}}$–N = 121.5(6)° ($[\mathrm{Ru_2(O_2CCMe_3)_4(nitme)_2}]^+$, nitme = 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-*N*-oxide).[2e]
This is due to the fact that the Ru(II,III)-radical interaction operates using the π^* orbitals of the $\mathrm{Ru_2}$ core and the π^* orbital of the nitroxide radical; the larger Ru–$\mathrm{O_{ax}}$–N angle is favored for the antiferromagnetic interaction, which has been shown based on the overlap integral between the π^* orbitals of the $\mathrm{Ru_2}$ core and the radical.[2c] The estimated $J = -45\ \mathrm{cm^{-1}}$ value for **1** is almost that expected from the axial bond angle, Ru–$\mathrm{O_{ax}}$–N = 137.7(5)°. The radical-radical interaction through the $\mathrm{Ru_2}$ core is more antiferromagnetic when the Ru–$\mathrm{O_{ax}}$–N angle decreases because the overlap between the σ^* orbital of the $\mathrm{Ru_2}$ core and π^* orbital of the nitroxide radical becomes larger.[1a,2c] In the present case, the interaction can be neglected, since the radical does not exist at one axial site of the dimer. The minus D value ($-30\ \mathrm{cm^{-1}}$), which is in contrast to those for the previous nitroxide Ru(II,III) complexes, might be related to the fact that **1** has two different axial ligands, $\mathrm{H_2O}$ and nitph, within the same cation unit.

Experimental

Synthesis of 1. A 20 mg (0.027 mmol) portion of water-coordinated parent complex $[\mathrm{Ru_2(O_2CCMe_3)_4(H_2O)_2}]\mathrm{BF_4}$ was used for the reaction. The axial water molecules were removed by heating under a vacuum and stirred with the radical nitph (15 mg, 0.064 mmol) in $\mathrm{CH_2Cl_2}$ (4 $\mathrm{cm^3}$) under argon. Onto the reacted solution was slowly added hexane (15 $\mathrm{cm^3}$); the resulting solution was kept quiet at −1 °C in a refrigerator for several days. Formed blackish-blue crystals were filtered off, washed with hexane, and dried under a vacuum. The yield was 17 mg (67% based on $[\mathrm{Ru_2(O_2CCMe_3)_4(H_2O)_2}]\mathrm{BF_4}$).[5] Anal. Found: C, 41.80; H, 5.93; N, 2.97%. Calcd for $[\mathrm{Ru_2(O_2CCMe_3)_4(nitph)(H_2O)}]\mathrm{BF_4}$ (**1**): C, 41.95; H, 5.87; N, 2.96%.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Perkin-Elmer Series II, CHN/O Analyzer. The magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer. The effective magnetic moments were calculated from the equation $\mu_{\mathrm{eff}} = 2.828\sqrt{\chi T}$, where χ is the magnetic susceptibility per $[\mathrm{Ru_2(O_2CCMe_3)_4(nitph)(H_2O)}]^+$.

X-ray Crystal Structure Analysis. The procedure of the X-ray analysis has been described previously.[2]

Crystallographic data: for $\mathbf{1}\cdot2\mathrm{CH_2Cl_2}$; $\mathrm{C_{35}H_{59}BCl_4F_4N_2O_{11}Ru_2}$, FW = 1114.82, triclinic, space group $P\bar{1}$, $a = 14.190(7)$, $b = 14.515(10)$, $c = 12.735(9)$ Å, $\alpha = 102.34(4)$, $\beta = 91.12(4)$, $\gamma = 85.01(4)$°, $V = 2553(3)$ Å^3, $Z = 2$, $D_{\mathrm{m}} = 1.45$, $D_{\mathrm{c}} = 1.45\ \mathrm{g\ cm^{-3}}$, $\mu(\mathrm{Mo}\ K\alpha) = 8.53\ \mathrm{cm^{-1}}$, $F(000) = 1136$, crystal dimensions 0.70 × 0.55 × 0.48 mm, 10014 reflections measured ($2\theta_{\max} = 52$°), 7537 [$I \geq 3\sigma(I)$] used in the refinement, $R = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}| = 0.071$, $R_{\mathrm{w}} = [\Sigma w(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2/\Sigma|F_{\mathrm{o}}|^2]^{1/2} = 0.086$. The X-ray analysis data have been deposited as Document No. 74050 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition number CCDC 167970.

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4 $R = \Sigma(\chi_{\mathrm{obsd}} - \chi_{\mathrm{calcd}})^2/\Sigma(\chi_{\mathrm{obsd}})^2 = 9.46 \times 10^{-3}$, where χ is the magnetic susceptibility.

5 The complex **1** could be also obtained when the reaction was performed with a mole ratio of $[\mathrm{Ru_2(O_2CCMe_3)_4}]\mathrm{BF_4}$: nitph = 1 : 1. However, the yield was low (43%).