Ferromagnetic Chain Complex of Ruthenium(II,III) Pivalate with Pyridyl Nitronyl Nitroxide

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A chain complex of ruthenium(II,III) dimer with pyridyl nitronyl nitroxide, $[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n$ (*p*-pynit = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) has been prepared and charactarized by the X-ray crystal structure analysis. The magnetic susceptibility data show that a ferromagnetic interaction is operative between the ruthenium(II,III) dimers and pyridyl nitronyl nitroxides.

Metal carboxylates with metal-metal bonding have been proved to be a good building-block for constructing one-dimensional chain compounds.[1] Recently some efforts to produce magnetic chain compounds have been done by using nitroxide radicals and metal carboxylates.[2-5] Such compounds may provide a new aspect of one-dimensional magnetic materials because of the presence of the metal-metal bonding. However, none of them are successful in producing ferromagnetic nor ferrimagnetic interaction between the nitroxide radicals and paramagnetic metal carboxylates, although a few radicals form a chain compounds with metal carboxylates.[4,5] In this study, we have introduced pyridyl group into nitroxide radicals in order to attempt to make new magnetic materials. Here we report a chain complex, $[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n$ (**1**) (*p*-pynit = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide), which is the first example of ferromagnetic chain compounds made up of nitronyl nitroxides and paramagnetic metal carboxylates.

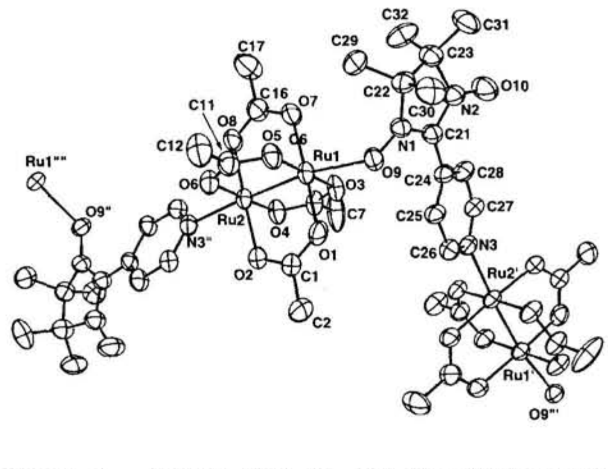

Figure 1. ORTEP view of $[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n\cdot1.5nCH_2Cl_2$ ($\mathbf{1}\cdot1.5nCH_2Cl_2$). Methyl groups of pivalic acid moieties, BF_4^- ions, and CH_2Cl_2 molecules are omitted. Selected bond distances (l/Å) and angles (ϕ/°): Ru1-Ru2 2.272(1), Ru1-O1 2.005(7), Ru1-O3 2.006(7), Ru1-O5 2.007(7), Ru1-O7 2.015(7), Ru2-O2 2.014(7), Ru2-O4 2.021(7), Ru2-O6 2.008(7), Ru2-O8 2.020(7), Ru1-O9 2.286(7), Ru2-N3" 2.248(9), O9-N1 1.30(1), O10-N2 1.27(1); Ru2-Ru1-O9 169.5(2), Ru1-Ru2-N3" 176.2(2), Ru1-O9-N1 125.3(6).

Complex **1** was prepared by a reaction of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$[6] and *p*-pynit[7] in a ratio of 1:1 in dichloromethane—hexane under Ar.[8]

The X-ray crystal structure of **1** shows that the complex is an extended zig-zag chain of alternating diruthenium carboxylate cation and nitroxide, elongated along the *b* axis (Figure 1).[9] The Ru1-Ru2 bond distance is 2.272(1)Å, which is in the range of those of other $[Ru_2(O_2CR)_4]^+$ compounds (2.24–2.30 Å).[10] The axial positions are occupied by pyridyl group and one of the two N-O groups of *p*-pynit with the Ru2-N3" and Ru1-O9 distances of 2.248(9) and 2.286(7) Å, respectively. The Ru1-Ru2-N3" and Ru2-Ru1-O9 angles are 176.2(2) and 169.5(2)°, respectively. The bonding parameters of *p*-pynit moiety show that the nitronyl nitroxide is in a free radical form, although the N-O bond coordinated to the Ru atom (N1-O9 1.30(1) Å) is a little longer than that of the non-coordinated N-O group (N2-O10 1.27(1) Å).[11]

The room temperature magnetic moment is 4.88 BM, considerably higher than the value (4.24 BM) expected for non-interacting spins $S = 3/2$ ($Ru_2^{II,III}$ core) and $S = 1/2$ (*p*-pynit). In Figure 2, the variation of the effective magnetic moment with temperature (2–300 K) is shown. The effective magmetic moment of **1** increases with lowering of temperature, reaches a maximum at 8 K, and then decreases sharply down to 2 K. The magnetic data were analyzed by a $[-(S = 1/2)-J-(S = 3/2)-J'-]_n$ chain model, where J is the spin coupling constant through the N-O group of *p*-pynit and J' is the spin coupling constant through the pyridyl group of the nitronyl nitroxide, respectively. The

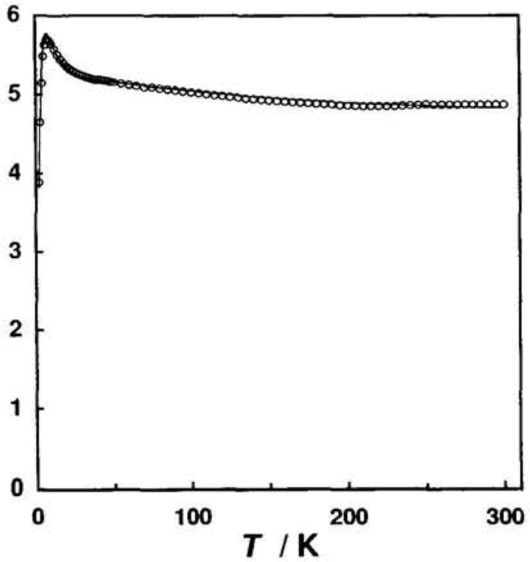

Figure 2. Temperature dependence of effective magnetic moment of **1**.

best fit with $J = 20$ cm^{-1}, $J' = 0.45$ cm^{-1}, $D = 50$ cm^{-1}, $g_{Ru} = 2.23$, and $g_{p\text{-}pynit} = 2.00$ for **1** was obtained as the solid line in Figure 2.[12] This result shows that **1** is a ferromagnetic chain compound and the ferromagnetic behavior comes mainly from the spin interaction through the N-O group of *p*-pynit. In this regard, it is noteworthy that the Ru1-O9-N1 angle is only 125.3(6)°. This angle is considerably smaller than those observed for the antiferromagnetic $Ru_2^{II,III}$ nitroxide complexes, where the Ru-O-N angles are 147.5(7) and 151.5(3)°, resulting in a substantial overlap between the π^* orbital of the Ru_2 core and the π^* orbital of the nitroxide radical.[3,5] It is very likely that the small Ru1-O9-N1 angle brings about the orthogonality of the Ru-Ru π^* and nitroxide π^* orbitals, leading to the ferromagnetic behavior of the present complex. Further studies are now under way.

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8 Satisfactory microanalytical data (C, H, N) were obtained. Anal. $[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n$ (**1**); Found: C, 41.50; H, 5.64; N, 4.56%. Calcd for $C_{32}H_{52}BF_4N_3O_{10}Ru_2$:C, 41.42; H, 5.65; N, 4.53%.

9 Crystallographic data for **1**•1.5nCH$_2$Cl$_2$; $C_{33.5}H_{55}BCl_3F_4N_3O_{10}Ru_2$, *F.W.* = 1049.3, 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 gcm^{-3}, μ(Mo Kα) = 7.85 cm^{-1}, 8932 reflections measured ($2\theta_{max} = 49°$), 4973 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.061, R_w = 0.079. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.

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12 The parameters, D, g_{Ru}, and $g_{p\text{-}pynit}$ are zero-field splitting parameter and g factors for the $Ru_2^{II,III}$ core and the nitroxide radical, respectively.