A Chain Complex of Ruthenium(II,III) Cation Dimer Linked by a Nitroxide Radical, $[Ru_2(O_2CCMe_3)_4(NITPh)]_n(BF_4)_n$ (NITPh=2-Phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide)

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A chain complex of ruthenium(II,III) cation dimer linked by the nitroxide radical, $[Ru_2(O_2CCMe_3)_4(NITPh)]_n(BF_4)_n$ (NITPh=2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide) has been prepared and characterized. The structure with the alternated alignment of S=3/2 (Ru(II,III) core) and S=1/2 (NITPh) has been confirmed by the X-ray crystal analysis. The magnetic moment decreases monotonously with decrease of temperature.

As shown for Krogmann's salt,[1] one-dimensional polymer complex with infinite metal-metal bond extended to a definite direction has unique physical (magnetic, electronic, optical) properties.[2] Recently, several efforts to mimic such properties by preparing compounds with metal-metal bonds linked by bridging ligands have been made.[3] We have much interest in applying the nitroxide radicals for linking the dimetal cores including direct metal-metal bond to produce the chain complexes.[4] To date, the chain compounds of rhodium carboxylates ($Rh_2(O_2CCR)_4$, R=CF_3) bridged by the nitroxide radicals have been reported.[5] The dimetal center is diamagnetic and propagate the antiferromagnetic interaction between the nitroxide radicals through the metal-metal bond. If the diamagnetic dimetal center is changed to the paramagnetic dimetal center such as Ru(II,II) carboxylate (S=1) or Ru(II,III) carboxylate cation (S=3/2), the magnetic properties of the chain complexes will be very interesting. We previously reported a nitroxide complexes of Ru(II,III) carboxylate cation, $[Ru_2(O_2CCMe_3)(tempo)_2][Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (tempo=2,2,6,6-tetramethyl-piperidine-1-oxyl) (**1**).[6] Here, a chain complex $[Ru_2(O_2CCMe_3)_4(NITPh)]_n(BF_4)_n$ (NITPh=2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide) (**2**) is presented. To our knowledge, this is the first example of the chain complex of paramagnetic dimetal center with the metal-metal bond linked by the nitroxide radical.

Complex **2** was obtained as follows. A benzene solution (5 ml) of NITPh (8.2 mg, 0.035 mmol) was added to a benzene

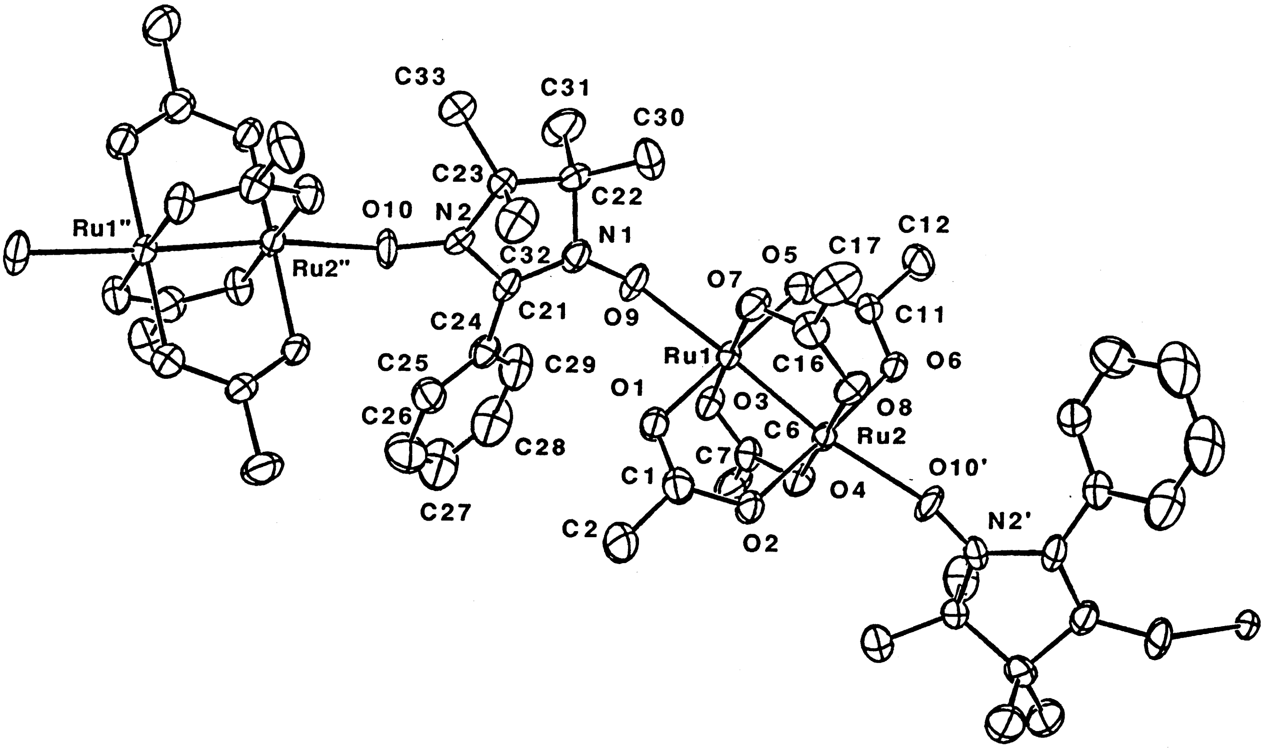

Figure 1. ORTEP view of a chain structure of $[Ru_2(O_2CCMe_3)_4(NITPh)]_n{}^{n+}$. CH_3 groups of the pivalate ions, $BF_4{}^-$ ions, and solvent benzene molecules are omitted for clarity. Selected interatomic distances (l/Å) and angles (ϕ/°): Ru1-Ru2 2.266(1), Ru1-O1 2.017(8), Ru1-O3 2.011(8), Ru1-O5 2.009(8), Ru1-O7 2.020(8), Ru1-O9 2.264(8), Ru2-O2 2.012(8), Ru2-O4 2.015(8), Ru2-O6 2.018(7), Ru2-O8 2.010(8), Ru2-O10' 2.236(8), O9-N1 1.30(1), O10-N2 1.28(1), Ru2-Ru1-O9 172.9(2), Ru1-O9-N1 131.7(7), Ru1-Ru2-O10' 170.9(2), Ru2-O10'-N2' 147.5(8).

solution (5 ml) of $Ru_2(O_2CCMe_3)_4BF_4$ (19.0 mg, 0.027 mmol) under argon atmosphere. After stirring the solution overnight at room temperature, a precipitate was filtered, washed with benzene, and dried in vacuo. Anal. $Ru_2(O_2CCMe_3)_4(NITPh)$-BF_4; Found: C, 42.58; H, 5.44; N, 3.00%. Calcd for $C_{33}H_{53}BF_4N_2O_{10}Ru_2$: C, 42.77; H, 5.76; N, 3.02%.

In Figure 1, the crystal structure of **2**•2*n*(benzene) is shown.[7] The $Ru_2(O_2CCMe_3)_4$ unit is axially coordinated by NITPh to form a chain structure. The axial positions of the Ru(II,III) core are occupied by the oxygen atoms of NITPh with a separation of 2.264(8) and 2.236(8) Å, respectively, relatively large compared with those of **1** (2.184(3) Å). The Ru-Ru bond distance is 2.266(1) Å, which is in the range of those reported for $[Ru_2(O_2CR)_4]^+$ compounds (2.24—2.30 Å).[8] The N-O bond lengths 1.30(1) and 1.28(1) Å shows that the NITPh exists as a free radical.[9] The Ru-O-N angles are 131.7(7) and 147.5(8)°, smaller than those of **1** (151.5(3)°).

The magnetic moment for **2** (per Ru(II,III)-NITPh unit) is 3.28 BM at 295 K.[10] This value is indicative of existence of an antiferromagnetic interaction between the Ru(II,III) core and the nitroxide radical because the spin only value is 4.24 BM for the two local spins, S=3/2 (Ru(II,III) core) and S=1/2 (NITPh). In Figure 2, the variation of the effective magnetic moments with temperature (5—300 K) is shown. It seems strange that the magnetic moment is monotonously decreased with lowering of temperature, because the alternative alignment of S=3/2 and S=1/2 should give a ferrimagnetic behavior (which shows the increase of μ_{eff} after reaching the minimum of μ_{eff} as temperature is lowered (c.f., ref. 4)). The crystal structure shows the existence of two kinds of bond parameters for linking the two Ru(II,III) cores by the nitroxide radical (e. g., the Ru-O distances and the Ru-O-N angles). Thus we have introduced an alternative chain model including two kinds of interactions between the Ru(II,III) core and the nitroxide radical (J and J') to interpretate the magnetic data. The best fit with J=-100 cm^{-1}, J'=0 cm^{-1}, D=65 cm^{-1}, g=2.00, g'=2.00, and p=0.045[11] is shown as the solid line in Figure 2. This result shows that the inequality in the two interactions between the Ru(II,III) core and the nitroxide radical may be the cause of such a strange behavior.

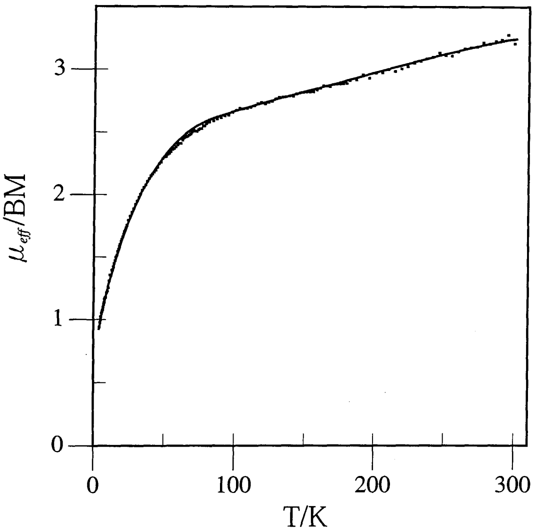

Figure 2. Temperature dependence of magnetic moments for **2**.

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References and Notes

1 K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969)

2 "Extended Linear Chain Compounds," ed by J. S. Miller, Plenum, New York (1982), Vol. 1.

3 M. Handa. M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 2567 (1995) and references therein.

4 A. Caneschi, D. Gatteschi, and P. Rey, *Prog. Inorg. Chem.*, **39**, 331 (1991).

5 A. Cogne, A. Grand, P. Rey, and R. Subra, *J. Am. Chem. Soc.*, **109**, 7927 (1987); A. Cogne, A. Grand, P. Rey, and R. Subra, *J. Am. Chem. Soc.*, **111**, 3230 (1989).

6 M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **68**, 1647 (1995).

7 Crystal data for **2**•2*n*(benzene): $C_{45}H_{65}BF_4N_2O_{10}Ru_2$, *F.W.*=1082.96, monoclinic, space group $P2_1/n$, a=23.582(8), b=20.528(3), c=11.087(4) Å, β=93.33(2)°, V=5358(3) Å^3, Z=4, D_m=1.35, D_c=1.34 gcm^{-3}, μ(Mo-Kα)=6.14 cm^{-1}, crystal dimensions 0.42x0.25x0.17 mm^3. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using a graphite-monochromated Mo-Kα radiation. A total of 8676 reflections were collected, of which 4106 reflections with $I \geq 3\sigma(I)$ were considered as observed. The structure was solved by the direct method and refined by the full-matrix least-square method. There are disorders at two carbon atoms on *t*-butyl group of pivalate and hence they are divided into two positions with same weights, respectively. The refinement converged at R=0.061 and R_w=0.069. All the calculations were performed on a VAX station 4000(90A) with the MolEN program package.

8 F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms," 2nd ed, Oxford Univ. Press, New York (1993).

9 W. Wong and S. F. Watkins, *J. Chem. Soc., Chem. Commun.*, **1973**, 888; A. Zheludev, V. Barone, M. Bonnet, B. Delley, A. Grand, E. Ressouche, P. Rey, R. Subra, and J. Schweuzer, *J. Am. Chem. Soc.*, **116**, 2019 (1994).

10 The magnetic moment for $Ru_2(O_2CCMe_3)_4BF_4$•$2H_2O$ is 4.06 BM at 295 K.

11 The parameters, J, J', D, g, g', and p are exchange integrals for the interactions between the Ru(II,III) core and the nitroxide radical, zero-field splitting parameter, g factors for the Ru(II,III) core and the nitroxide radical, and the fraction of the dinuclear Ru(II,III) impurity, respectively. The details for the procedure will be described elsewhere.