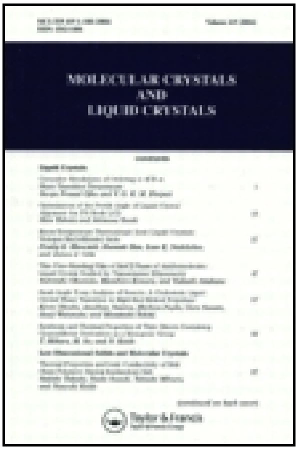

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Synthesis and Magnetic Property of Adducts of Ruthenium(II,III) Pivalate with 9,10-Anthraquinone

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Reaction of tetrakis(pivalato)diruthenium(II,III) cation dimer and 9,10-anthraquinone (aq) gave two kinds of adducts, $[\{Ru_2(piv)_4(H_2O)\}_2(aq)]\text{-}(BF_4)_2$ (**1**) (pivH = pivalic acid) and $[Ru_2(piv)_4(aq)]_n$ (**2**), depending on the condition. Very weak antiferromagnetic interaction was observed for **1**. The X-ray crystal structure of **2** shows an one-dimensional chain structure.

Keywords: ruthenium(II, III) pivalate; 9,10-anthraquinone; crystal structure; magnetic property

INTRODUCTION

There has been considerable interest in molecular magnetic materials[1]. One of the fascinating strategies toward the design of molecular magnetic materials is the use of metal carboxylates with a metal-metal bond as a building block. However, most of them were unsuccessful in producing one-dimensional ferro- or ferrimagnetic compounds based on the interaction between the paramagnetic metal carboxylates through the bridging ligands[2-8]. Electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (abbreviated as tcnq) and 9,10-

anthraquinone (abbreviated as aq) are quite interesting as bridging ligands for paramagnetic metal dimers. Recently, we succeeded in isolating an adduct of ruthenium(II,III) pivalate with tcnq[9], although the complex was found to be a tetranuclear species of "dimer-of-dimers". In this paper, we report synthesis and magnetic property of a diruthenium(II,III) complex with aq, $[\{Ru_2(piv)_4(H_2O)\}_2(aq)](BF_4)_2$ (**1**). The X-ray crystal structure of $[Ru_2(piv)_4(aq)]_n$ (**2**), which has been found out during the crystallization process, is also reported.

EXPERIMENTAL

Synthesis

The starting material $[Ru_2(piv)_4(H_2O)_2]BF_4$ was prepared by the method described elsewhere[6]. 9,10-Anthraquinone (aq) was recrystallized from ethanol before use. Benzene was dried over CaH_2 and distilled according to the standard method.

$[\{Ru_2(piv)_4(H_2O)\}_2(aq)](BF_4)_2$ (**1**).

A benzene solution (5 cm^3) of aq (10 mg) was added to a benzene solution (5 cm^3) of $[Ru_2(piv)_4]BF_4$ (30 mg) under argon. The solution was stirred overnight at room temperature. The solution gave green precipitate which was filtered off and washed with benzene and dried *in vacuo* : Yield, 21 mg (60%). Found: C, 39.71; H, 5.07%. Calcd for $C_{54}H_{84}B_2F_8O_{20}Ru_4$: C, 39.76; H, 5.19 %.

$[Ru_2(piv)_4(aq)]_n$ (**2**).

$[Ru_2(piv)_4]BF_4$ (30 mg) and aq (10 mg) was slowly diffused into 20 cm^3 of benzene by using an H-type tube at room temperature. After several days reddish-brown crystals of **2** were deposited.

Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanaco CHN corder MT-5. Infrared spectra were measured with a Jasco FT/ IR350 in the 4600—400 cm^{-1} region on a KBr disk. Diffused reflectance spectra were measured with a Shimadzu UV-3100 Spectrometer with ISR-3100, using barium sulfate ($BaSO_4$) as reference. Magnetic susceptibilities were measured over the 4—300 K temperature range by the Faraday method.

X-Ray Crystal Structure Analysis.

A crystal of **2** was sealed in a glass capillary together with mother liquor and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 < 2\theta < 30°$. Crystallographic data for **2**; $C_{34}H_{44}O_{10}Ru_2$, *F.W.* = 814.9, triclinic, space group $P\bar{1}$, $a = 9.450(4)$, $b = 9.634(5)$, $c = 10.646(7)$ Å, $\alpha = 81.61(4)$, $\beta = 70.78(4)$, $\gamma = 72.41(4)°$, $V = 871.2(9)$ Å^3, $Z = 1$, $D_m = 1.55$, $D_c = 1.55$ gcm^{-3}, μ(Mo $K\alpha$) = 9.02 cm^{-1}, crystal dimensions 0.29 × 0.17 × 0.15 mm, 3058 reflections measured ($2\theta_{max} = 50°$), 1819 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.060$, $R_w = 0.075$. The structure was solved by the direct method and refined by the full-matrix least-squares method using MolEN program package[10].

RESULTS AND DISCUSSION

In this study, we obtained complex **1** as green powder by stirring benzene solution of $[Ru_2(piv)_4]BF_4$ and aq. The analytical and infrared spectral data suggest that this complex has a composition of $[\{Ru_2(piv)_4(H_2O)\}_2(aq)](BF_4)_2$. The structure of **1** can be considered that both of the two oxygen atoms of aq are coordinated to one of the axial sites of the Ru_2 units and the other axial sites are occupied by water molecules, like the "dimer-of-dimers" complex $[\{Ru_2(piv)_4(H_2O)\}_2(tcnq)](BF_4)_2$[9]. The water molecules might come from the solvent or starting materials. Complex **1** was also obtained when excess amount of aq was added to a benzene solution of $[Ru_2(piv)_4]BF_4$.

In the infrared spectra of **1**, ν(COO) peaks are found at 1482, 1453, and 1416 cm^{-1}, which are almost in the same region as that of $[Ru_2(piv)_4(H_2O)_2]BF_4$. This suggests that Ru_2 core in **1** maintains the dimer structure. ν(C=O) peaks of aq, found at 1672, 1634, and 1569 cm^{-1}, are not appreciably shifted compared with those of free aq.

The reflectance spectra of **1** and $[Ru_2(piv)_4(H_2O)_2]BF_4$ are shown in FIGURE 1. Absorption band around 1000 nm may be attributed to the $\delta - \delta^*$ transition of the Ru_2 core, as in the case of $[Ru_2(piv)_4(H_2O)_2]BF_4$. The new bands at 607 and around 348 nm may be attributed to $n - \pi^*$ and $\pi - \pi^*$ transitions, respectively. The bands at 430 and 224 nm in $[Ru_2(piv)_4(H_2O)_2]BF_4$ are hidden by the broad band around 348 nm.

The temperature dependence of effective magnetic moments (μ_{eff}) for **1** is shown in FIGURE 2. The μ_{eff} value at 300K is 4.1 B.M., which is larger than that derived from spin-only equation, 3.87 B.M. When temperature is lowered, μ_{eff} is gradually decreased to 3.1 B.M. at

4K. This behavior can be attributed to the zero-field splitting rather than an antiferromagnetic interaction between the Ru_2 spins through the bridging ligand. The solid line is drawn with the parameters g (g factor for the Ru_2 core) = 2.1 and D (zero-field splitting parameter) = 70 cm^{-1}. The good fitting shows that antiferromagnetic interaction of **1** between the two Ru_2 cores through the bridging aq must be very weak. The weak antiferromagnetism has been also observed in $[\{Ru_2(piv)_4(H_2O)\}_2(tcnq)](BF_4)_2$[9].

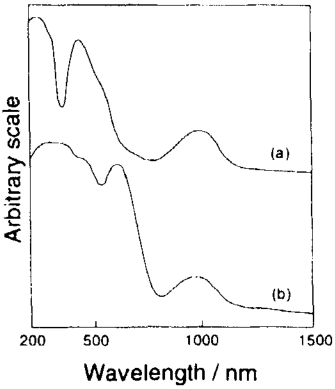

FIGURE 1 Diffused reflectance spectra of $[Ru_2(piv)_4(H_2O)_2]BF_4$ (a) and **1** (b)

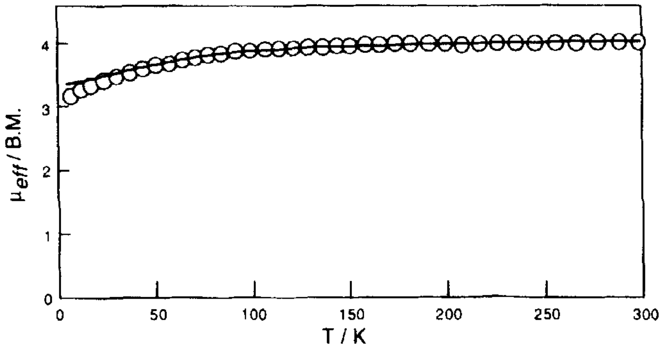

FIGURE 2 Temperature dependence of the effective magnetic moment of **1**.

On the other hand, complex **2** was obtained as reddish-brown crystals, when the reaction of $[Ru_2(piv)_4]BF_4$ and aq was performed by the diffusion method in benzene.

The crystal structure of **2** is shown in FIGURE 3. Because there are no BF_4^- anions in the crystal, it is suggested that aq molecule becomes anion radical. The zig-zag chain structure is made up by the alternating arrangement of $[Ru_2(piv)_4]^+$ and aq^-. The Ru—Ru bond length is 2.248(2) Å, which is in the range of those reported for $[Ru_2(O_2CR)_4]^+$ complexes (2.24—2.30 Å)[11]. The Ru—O5—C11 angle is 123.4(7) °. At present, it is not clear why the chain complex formed during the crystallization process. Further studies are in progress in our laboratories.

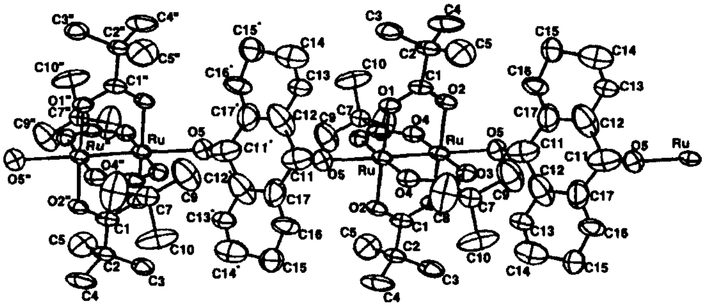

FIGURE 3 Molecular structure of **2**. Selected bond lengths (Å) and angles(°) are as follows: Ru–Ru 2.248(2), Ru–O1 2.008(6), Ru–O2 2.013(6), Ru–O3 2.017(7), Ru–O4 2.010(7), Ru–O5 2.28(1); Ru–Ru–O1 89.4(3), Ru–Ru–O2 89.5(3), Ru–Ru–O3 89.0(3), Ru–Ru–O4 91.1(3), Ru–Ru–O5 175.4(2), O1–Ru–O2 178.4(3), O1–Ru–O3 91.8(3), O1–Ru–O4 88.8(3), O1–Ru–O5 91.2(3), O2–Ru–O3 89.3(3), O2–Ru–O4 90.1(3), O2–Ru–O5 89.9(3), O3–Ru–O4 179.4(2), O3–Ru–O5 86.4(3), O4–Ru–O5 93.5(3), Ru–O1–C1 120.0(8), Ru–O2–C1 120.0(7), Ru–O3–C6 118.6(8), Ru–O4–C6 117.6(8), Ru–O5–C11 123.4(7).

Acknowledgments
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