# A New "Dimer-of-Dimers" Complex Derived from Axial Coordination of 7,7,8,8-Tetracyanoquinodimethane to Ru(II,III) Cation Dimer

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(Received June 28, 1999; CL-990564)

The "dimer-of-dimers" complex of ruthenium(II,III) pivalate cation dimer [{$Ru_2(O_2CCMe_3)_4$}$_2$(μ-tcnq)($H_2O$)$_2$]($BF_4$)$_2$ (**1**) (tcnq=7,7,8,8-tetracyanoquinodimethane) has been prepared and characterized. The X-ray structure analysis of **1** showed that tcnq connects the Ru(II,III) dimers with an Ru-N distance of 2.323(7) Å. The Ru-Ru distance 2.263(1) Å is nearly the same as that of the parent cation dimer [$Ru_2(O_2CCMe_3)_4$]$^+$ (2.260(1) Å). The antiferromagnetic interaction between the Ru(II,III) cores through the tcnq molecule is fairly weak.

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Recently, much interest has been devoted to use of tetra-μ-carboxylatodimetal complexes with a metal-metal bond as building blocks for metal assembled complexes.[1] The complexes obtained in combination with the electron acceptors tetracyanoethylene (tcne), 7,7,8,8-tetracyanoquinodimethane (tcnq), and 2,5-dimethyl-*N,N'*-dicyanoquinone diimine (dmdcnqi) have been reported on the crystal structures for the Rh and Mo systems.[2] Although the study on the interaction between the dimer units through the bridging ligand has been considered important, they were all diamagnetic so that no investigation on the interaction between the dimer units in the solid state had been done based on the magnetic data. We have first succeeded in isolating the complex of the paramagnetic dimer having the metal-metal bond linked with tcnq using ruthenium(II,III) pivalate cation ([$Ru_2(O_2CCMe_3)_4$]$^+$) as crystals suitable for X-ray analysis. The complex was found out to have the "dimer-of-dimers" structure. The tetranuclear structure incorporating metal-metal bond units bridged by the electron acceptor is very rare because the complex [{$Re_2Cl_4$(dppm)$_2$}$_2$(μ-tcnq)] (dppm=bis(diphenylphosphino)methane), in which tcnq exists as an anion radical, has been only known until now.[3] Here we report the structure of the tetranuclear complex [{$Ru_2(O_2CCMe_3)_4$}$_2$(μ-tcnq)($H_2O$)$_2$]($BF_4$)$_2$ (**1**) and its magnetic properties.

The complex was prepared as follows. A solution of tcnq (8 mg, 0.039 mmol) in dichloromethane (10 cm$^3$) was added to a solution of [$Ru_2(O_2CCMe_3)_4$]$BF_4$[1c] (28 mg, 0.041 mmol) in dichloromethane (10 cm$^3$) under argon. After it was stirred overnight, addition of hexane (5 cm$^3$) to the solution gave brown microcrystals, which were collected by filtration, washed with hexane, and dried in *vacuo*. The yield was 10 mg (30% (based on [$Ru_2(O_2CCMe_3)_4$]$BF_4$)). Anal. Found: C, 37.21; H, 4.78; N, 3.36%. Calcd for $C_{52}H_{84}B_2F_8N_4O_{20}Ru_4$: C, 37.55; H, 5.09; N, 3.37%. Diffuse reflectance spectrum: $\lambda_{max}$/nm 410, 550sh, 900.

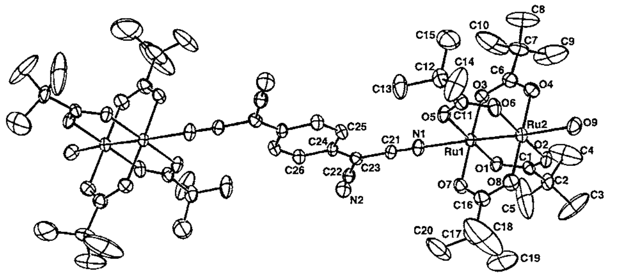

**Figure 1.** Perspective view of the teranuclear cation unit of **1**. Thermal ellipsoids are drawn to the 35 % probability level. Selected interatomic distances (*l*/Å) and angles (ϕ/°): Ru1-Ru2 2.263(1), Ru1-O1 2.022(5), Ru1-O3 2.017(5), Ru1-O5 2.023(6), Ru1-O7 2.016(5), Ru1-N1 2.323(7), Ru2-O2 2.008(6), Ru2-O4 2.002(5), Ru2-O6 2.015(6), Ru2-O8 2.009(6), Ru2-O9 2.273(6), Ru2-Ru1-N1 172.0(1), Ru1-Ru2-O9 175.8(2).

The tetranuclear structure of **1** is shown in Figure 1.[4] The Ru(II,III) dimers are bridged by tcnq with an Ru-N distance of 2.323(7) Å. The crystallographic inversion center is located at the center of the tcnq molecule. The bond length 1.38(1) Å of C23-C24 indicates that the tcnq molecule exists as a neutral one.[5,6] The other axial sides of the dimer units are coordinated by water molecules with an Ru-O distance of 2.273(6) Å. The Ru-Ru (2.263(1) Å) and equatorial Ru-$O_{eq}$ (2.002(5)—2.023(6) Å) bond lengths are nearly the same as those in [$Ru_2(O_2CCMe_3)_4(H_2O)_2$]$^+$ cation (Ru-Ru=2.260(1) Å and Ru-$O_{eq}$=2.014(3)—2.024(3) Å).[7] These results show that Ru dimer maintains the valence state (II,III) on the reaction with tcnq which are also kept neutral.

In Figure 2, the variation of the effective magnetic moment per Ru(II,III) core for **1** with temperature (5—300 K) is shown. The decrease of the moment with lowering of temperature mostly comes from the zero-field splitting within the dimer core. At the temperature close to 5 K, the extra decrease which cannot be explained only with zero-field splitting was considered to be due

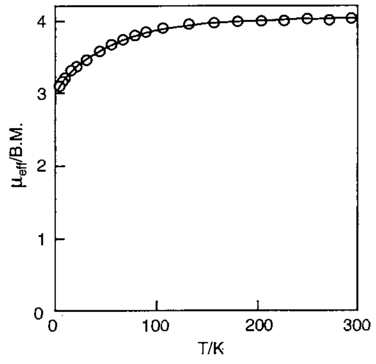

**Figure 2.** Temperature dependence of magnetic moments for **1**.

to the antiferromagnetic interaction through the tcnq bridging. The solid line is drawn with the parameters g=2.10 (g factor for $Ru_2$ core), D=65 $cm^{-1}$ (zero-field splitting parameter), and $J$=-0.15 $cm^{-1}$ (the parameter for the magnetic interaction, which was estimated based on the molecular field approximation). This result means that the interaction through the tcnq molecule is fairly weak. The weakness of the interaction was confirmed by the ESR spectrum (powder at 5 K) (Figure 3). The spectral feature is quite similar to that for $[Ru_2(O_2CPr^n)_4]Cl$.[8,9] The signal position at g=4.38 is very close to those for $[Ru_2(O_2CPr^n)_4]Cl$ (g=4.40) and $[Ru_2(O_2CCMe_3)_4]^+$ cation (g=4.40).[7,8]

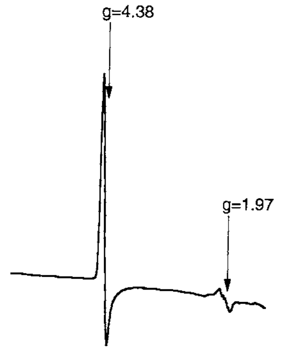

**Figure 3**. K-band ESR spectrum of **1**, powder at 5K. 1 G=$1\times10^{-4}$ T.

The pyrazine bridged chain complex $[Ru_2(O_2CMe_3)_4(pyrazine)]_n(BPh_4)_n$ has also shown a weak interaction ($J$=-2.3 $cm^{-1}$) through the bridging.[10] On the other hand, the considerably strong magnetic couplings have been achieved through the linkage ligands in the dinuclear ruthenium(III) complexes $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})](ClO_4)_4$ (**2**) (dicyd=1,4-dicyanamidobenzene dianion[11]) and its derivatives (-$J$ ranges from 61.9 to ≥400 $cm^{-1}$).[12] It is considered that, in **1** and $[Ru_2(O_2CMe_3)_4(pyrazine)]_n(BPh_4)_n$, the $\pi^*$ and $\delta^*$ orbitals of the unpaired electrons within the Ru(II,III) core do not match the $\pi^*$ orbital of tcnq or pyrazine in the orbital energies and/or symmetries to result in the weak interaction between the dimer cores. When taking into consideration that **1** and **2** have the same axial coordination atom (N) and number (10) of atoms intervening between the ruthenium ions through the each linkage ligand, the anionic and electron-rich ligand like dicyd could be favorable for the stronger interaction between the Ru(II,III) dimers. Further study is in progress in our laboratory to give rise to the one-dimensional antiferromagetism by use of electrons in the metal-metal bonds.

The present work was partially supported by a Grant-in Aid for Scientific Research (No. 10640547) and Grant-in Aid for Scientific Research on Priority Areas (Nos. 10157472 and 11136235 "Metal-assembled Complexes") from the Ministry of Education, Science and Culture.

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4 Crystal Data for **1**: $C_{52}H_{80}B_2F_8N_4O_{18}Ru_4$ F.W.=1627.51, monoclinic, space group $P2_1/c$, $a$=17.731(5), $b$=12.010(2), $c$=18.549(5) Å, $\beta$=112.98(1)°, $V$=3636(2) $Å^3$, $Z$=2, $D_m$=1.49, $D_c$=1.49 g $cm^{-3}$, $\mu$(Mo-$K\alpha$)=8.78 $cm^{-1}$, crystal dimensions 0.45×0.28×0.23 mm, $F$(000)=1644, $T$=298 K, $R$=0.045, $R_w$=0.051. A total of 7492 reflections were measured in the range $1\leq2\theta\leq52°$; 3695 with $I\geq3\sigma(I)$ were assumed observed. For the determination of structure, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation. The intensity data were corrected for Lorentz-polarization effects. The structure was solved by the direct method and refined by the full-matrix least-squares method using MolEN program package.

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6 The observation of ν(C≡N) band at 2230 $cm^{-1}$ for **1** in the IR spectrum (Nujol mull) (for neutral tcnq, ν(C≡N) 2230 $cm^{-1}$) confirms that the tcnq molecule exists as the neutral one in **1**.

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