

Long-Range Ordered Magnet of a Charge-Transfer  $\text{Ru}_2^{4+}/\text{TCNQ}$  Two-Dimensional Network CompoundHitoshi Miyasaka,<sup>\*,†,‡</sup> Toru Izawa,<sup>§</sup> Nao Takahashi,<sup>§</sup> Masahiro Yamashita,<sup>†,‡</sup> and Kim R. Dunbar<sup>||</sup>

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The design of magnetic/conducting materials based on  $d\pi$ – $p\pi$  electronic interactions through a metal–organic backbone is a long-standing theme in the field of molecule-based solid-state chemistry. One way to obtain such materials is to form charge-transfer complexes between metal donors and polycyano organic acceptors with the formation of coordination frameworks. In the case of a one-electron transfer, the 1:1 donor (D)/acceptor (A) alternating array will likely lead to a charge-polarized state with localized spins,<sup>1</sup> whereas a 2:1 stoichiometry with the units being essentially the same electronically, possibly creates a charge-delocalized state owing to a resonance of the type  $[\text{D}^+-\text{A}^-\text{D} \leftrightarrow \text{D}-\text{A}-\text{D} \leftrightarrow \text{D}-\text{A}^-\text{D}^+]$  in  $\text{D}_2\text{A}$  systems and vice versa in  $\text{A}_2\text{D}$  systems (vide infra). Such charge-transfer compounds have been prepared, most notably the pioneering materials,  $[\text{Cu}^{\text{II}}(\text{DCNQI})_2]$  (where DCNQI is *N,N'*-dicyanoquinonediimine)<sup>2</sup> and the systems based on  $[\text{Ru}^{\text{III}}-\text{Dicyd}-\text{Ru}^{\text{III}}]$  (where Dicyd<sup>2-</sup> is 1,4-dicyanamidobenzene dianion),<sup>3</sup> and the bridging ligand can be either reduced (electron-type;  $\text{D}_2\text{A}$  system) or oxidized (hole-type;  $\text{A}_2\text{D}$  system), respectively. Our strategy for preparing 2:1 assemblies involve the use of electron-rich paddle-wheel-type dimetal units and polycyano molecules (i.e.,  $\text{D}_2\text{A}$  system) which yield favorable charge-transfer materials with  $\text{M}-\text{L}$   $\pi$  back-bonding.<sup>4</sup> In this vein, we reported the first two-dimensional (2D) network compound composed of  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4]$  and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), which may be represented by the resonance scheme  $[\text{Ru}_2^{5+}-(\text{TCNQ}^{\cdot-})-\text{Ru}_2^{4+} \leftrightarrow \text{Ru}_2^{4+}-(\text{TCNQ})-\text{Ru}_2^{4+} \leftrightarrow \text{Ru}_2^{4+}-(\text{TCNQ}^{\cdot-})-\text{Ru}_2^{5+}]$ :  $[\{\text{Ru}_2(\text{O}_2\text{CCF}_3)_4\}_2\text{TCNQ}]\cdot 3(\text{toluene})$  (**1a**).<sup>4b</sup> The “partial” charge-transfer, however, leads to a lack of long-range 2D or 3D magnetic order and high conductivity mediated by transferred electrons. We reasoned that the oxidation potential of TCNQ was insufficient to allow for reduction of the  $[\text{Ru}_2(\text{O}_2\text{CCF}_3)_4]$  molecules, thus it becomes an important issue to fine-tune the redox chemistry of both types of units.

On the basis of the aforementioned hypothesis, we prepared a new charge-transfer 2D network compound,  $[\{\text{Ru}_2(\text{O}_2\text{CCF}_3)_4\}_2\text{TCNQF}_4]\cdot 3(p\text{-xylene})$  (**2**), where  $\text{TCNQF}_4$  is 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane, a much more powerful oxidant than TCNQ. The result is long-range magnetic ordering owing to the full electron-transfer from  $\text{Ru}_2$  units to  $\text{TCNQF}_4$  molecules.

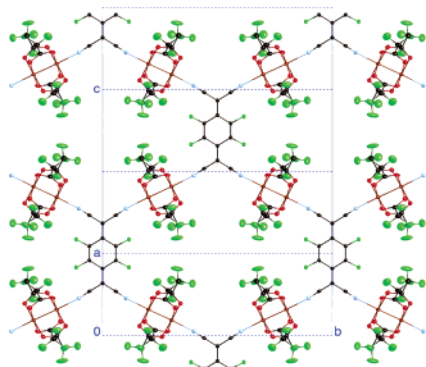
Compound **2** was synthesized under anaerobic conditions by a diffusion of a solution of  $[\text{Ru}_2(\text{O}_2\text{CCF}_3)_4]$  in *p*-xylene (top layer) and  $\text{TCNQF}_4$  in  $\text{CH}_2\text{Cl}_2$  (bottom layer) in a 2:1 molar ratio. The infrared spectrum of **2** reveals two  $\nu(\text{C}\equiv\text{N})$  stretches at 2217 and 2179  $\text{cm}^{-1}$ , which are shifted to lower energy than the stretches at

2227  $\text{cm}^{-1}$  ( $b_{1u}\nu_{18}$ ) and 2214  $\text{cm}^{-1}$  ( $b_{2u}\nu_{32}$ ) observed for neutral  $\text{TCNQF}_4$ .<sup>5</sup> Furthermore, two  $\nu(\text{C}=\text{C})$  stretches of 1540 and 1492  $\text{cm}^{-1}$  are very similar to 1539 ( $b_{2u}\nu_{33}$ ) and 1500 ( $b_{1u}\nu_{19}$ )  $\text{cm}^{-1}$  of the  $\text{TCNQF}_4^{\cdot-}$  radical anion (neutral  $\text{TCNQF}_4$ : 1602 and 1549  $\text{cm}^{-1}$ , respectively). The shift to lower energies for **2** is in accord with increased  $\text{Ru}_2$ – $\text{TCNQF}_4$   $\pi$  back-bonding and with the reduction of  $\text{TCNQF}_4$  moiety in **2**.

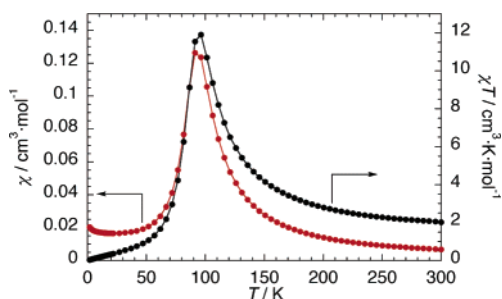
Compound **2** crystallizes in the monoclinic space group  $C2/m$  with an inversion center located at the midpoint of the  $\text{Ru}-\text{Ru}$  bond and a  $C_2$  axis and mirror plane that serve to quadrisect the  $\text{TCNQF}_4$  moiety ( $Z = 2$ ), leading to a single unique  $\text{Ru}_2$  unit and one  $\text{TCNQF}_4$  molecule per formula (ORTEP in Figure S1),<sup>6</sup> as was also observed for **1a**. All four cyano groups of  $\text{TCNQF}_4$  coordinate to  $\text{Ru}_2$  molecules with a distance of 2.260(6) Å for  $\text{Ru}(1)-\text{N}(1)$  and an angle of 171.9(5)° for  $\text{Ru}(1)-\text{N}(1)-\text{C}(5)$  to form a fishing-net-like 2D network (Figure 1). The interlayer distance is ca. 6.6 Å. The  $\text{Ru}-\text{Ru}$  bond distance is 2.3020(6) Å which is slightly longer than the corresponding distances in  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4(\text{thf})_2]$  (2.276(3) Å),<sup>7</sup> **1a** (2.2875(7) Å), and  $[\{\text{Ru}_2(\text{O}_2\text{CCF}_3)_4\}_2\text{TCNQ}]\cdot 3(p\text{-xylene})$  (**1b**) (2.2915(3) Å) which was synthesized for the sake of comparison (Figure S1). The  $\text{Ru}-\text{O}_{\text{equatorial}}$  bond distance, which is strongly influenced by the oxidation state of the  $\text{Ru}_2$  core, is in the middle range between those observed for  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4(\text{thf})_2]$  (2.070(6)–2.076(6) Å)<sup>7</sup> and  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_5]$  (1.995(12)–2.032(12) Å),<sup>8</sup> clearly indicating a partially oxidized feature (i.e., formally,  $[\text{Ru}_2]^{4.5+}$ ). It is noteworthy that the  $\text{Ru}-\text{O}_{\text{equatorial}}$  bond distances in **1a** (2.063(2)–2.072(2) Å) and **1b** (2.062(2)–2.078(2) Å) are very close to those of  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4(\text{thf})_2]$  (i.e., likely assigned to  $[\text{Ru}_2]^{4+}$ ).<sup>7</sup> The degree of charge transfer from  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4]$  to  $\text{TCNQF}_4$  was estimated from the Kistenmacher relationship,  $\rho = A[c/(b + d)] + B$  with  $A = -46.729$  and  $B = 22.308$ ,<sup>9</sup> based on neutral  $\text{TCNQF}_4$  ( $\rho = 0$ )<sup>10</sup> and  $(n\text{-Bu}_4\text{N})[\text{TCNQF}_4]$  ( $\rho = -1$ )<sup>11</sup> (where  $b$ ,  $c$ , and  $d$  are  $\text{TCNQF}_4$  bond distances defined in Table S1). The estimated  $\rho$  value is  $-1.05$  for **2**, while the value similarly estimated on the basis of neutral TCNQ and  $\text{RbTCNQ}$  for **1b** is  $-0.25$  ( $\rho = -0.5$  for **1a**). These IR data and the metrical parameters of the X-ray structure support that a one-electron charge transfer from two  $[\text{Ru}_2^{\text{II,III}}(\text{O}_2\text{CCF}_3)_4]$  units to one  $\text{TCNQF}_4$  in **2** has occurred; that is, it is formally,  $[\text{Ru}_2^{4.5+}-(\text{TCNQ}^{\cdot-})-\text{Ru}_2^{4.5+}]$ .

The magnetic properties of **2** were examined; Figure 2 depicts  $\chi$  and  $\chi T$  vs  $T$  plots. The  $\chi T$  value increases below 300 K (2.02  $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ ) to reach a maximum at 96 K (11.9  $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ ). Below the maximum temperature,  $\chi T$  decreases abruptly and then gradually to 0.037  $\text{cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$  at 1.8 K. The increase of  $\chi T$  at high temperatures is due to strong coupling between spins in a layer, mediated by the  $\text{TCNQF}_4^{\cdot-}$  radical. Notably  $\chi T$  for **1b** decreases continuously with decreasing temperature from 300 to 1.8 K, which is in accord with two isolated  $[\text{Ru}_2]^{4+}$  units with  $S = 1$  (Figure S2).

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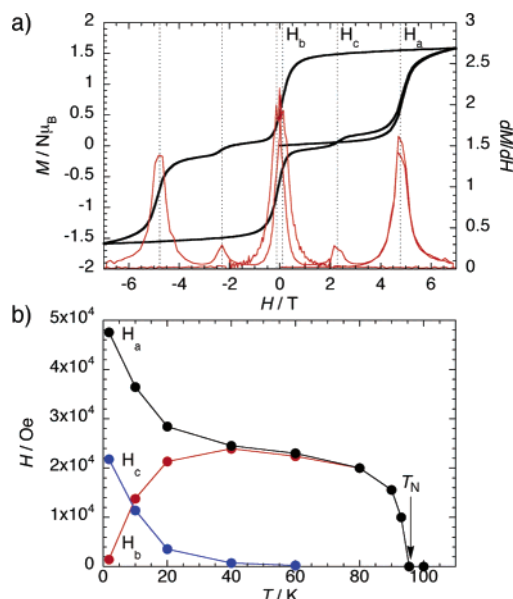


**Figure 1.** 2D network structure of **2** (black, C; red, O; blue, N; green, F; orange, Ru). The *p*-xylene molecules as crystallization solvents are omitted for clarity.



**Figure 2.** Temperature dependence of  $\chi$  and  $\chi T$  measured at 1 T of **2**. The solid line is only a guide for the eyes.

A fitting led to the parameters,  $g = 2.0$  (fixed),  $D = 271 \text{ cm}^{-1}$ ,  $\text{TIP} = 44 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $\rho = 0.0079$ ). It should be noted that the peak in  $\chi T$  for **2** does not imply any long-range ferromagnetic ordering given the absence of an  $ac \chi''$  signal down to 1.8 K at zero dc field, but rather an antiferromagnetic ordering with  $T_N = 95 \text{ K}$  as shown in  $\chi$  versus  $T$  ( $\chi'$  shows a peak only at this temperature. Figure S3). To probe the detail of magnetic properties, the field dependence of the magnetization was measured at several temperatures below 100 K (Figures 3 and S4). At 1.82 K, the initial sweep from 0 to 7 T shows a sigmoidal increase of the magnetization with a critical field of 4.74 T, indicating a spin flip from an antiferromagnetic phase (AF) to a paramagnetic phase (P), that is, metamagnetic nature. Moreover, during the forward and reverse sweeps between 7 T and  $-7 \text{ T}$ , three kinds of steps at  $\pm 0.20$  ( $H_b$ ),  $\pm 2.38$  ( $H_c$ ), and  $\pm 4.74$  ( $H_a$ ) T are observed with a large butterfly-type hysteresis. The presence of three steps indicates the existence of a canted spin phase (CS):  $\text{P} \rightarrow \text{CS}$ ,  $\text{CS}(+) \rightarrow (\text{AF}) \rightarrow \text{CS}(-)$ , and  $\text{CS} \rightarrow \text{P}$ , respectively. Upon increasing the temperature, the hysteresis and spin flip at  $H_c$  disappear relative to one another at ca. 60 K, and the metamagnetic spin flip ( $\text{AF} \rightarrow \text{P}$  or  $\text{CS} \rightarrow \text{P}$  at  $H_a$ ) disappears at ca. 95 K (Figure 3b), consistent with the peak temperature in  $\chi T$  (Figure 2). Thus, the metamagnetic-like nature with a large hysteresis in **2** likely originates from interlayer antiferromagnetic interactions coupled with a strong anisotropy arising from the  $[\text{Ru}_2]^{n+}$  units; each layer allows for a long-range ferromagnetic order. Such a high-temperature long-range ordering is possible in cases involving double-exchange interaction, and the resonance scheme of charge transfer (probably, due to electron-hopping transfer), which possibly occurs with a charge delocalization spreading over a layer, is expected to play a critical role in **2**. As a preliminary experiment, the conductivity of pellets of **1b** and **2** was measured at room temperature, and a value 100 times larger was observed for **2** ( $4.6 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ ) than was observed for **1b**.



**Figure 3.** Field dependence of  $M$  and  $dM/dH$  at 1.82 K of **2** (a) and temperature dependence of critical fields,  $H_a$ ,  $H_b$ , and  $H_c$  (b), where the value of  $(H_a - H_b)$  is a field-hysteresis of paramagnetic phase and the value of  $H_c$  is approximately corresponding to a coercive field.

Inspired by the concept of the resonance scheme in charge-transfer  $\text{D}_2\text{A}$  network systems, the first successful example of a magnet for  $\text{Ru}_2\text{-TCNQ}$  type systems was rationally designed by tuning the redox between  $[\text{Ru}_2]^{4+}$  and the TCNQ molecule by changing from TCNQ to  $\text{TCNQF}_4$ .

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**Supporting Information Available:** X-ray crystallographic data of **1b** and **2** in CIF format and additional supporting data (Table S1, Figures S1–S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The crystal structures of **1a**, **1b**, and **2** are basically isostructural with very similar cell dimensions on the same space group. The crystallographic details are described in cif files, which were deposited in CCDC (615251 for **1b** and 615250 for **2**).
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