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# Long-Range Ordered Magnet of a Charge-Transfer $Ru_2^{4+}$/TCNQ Two-Dimensional Network Compound

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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,[1] 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 [$D^+$-$A^-$-D ↔ D-A-D ↔ D-$A^-$-$D^+$] in $D_2A$ systems and vice versa in $A_2D$ systems (vide infra). Such charge-transfer compounds have been prepared, most notably the pioneering materials, [$Cu^{II}$(DCNQI)$_2$] (where DCNQI is *N*,*N′*-dicyanoquinonediimine)[2] and the systems based on [$Ru^{III}$−Dicyd−$Ru^{III}$] (where Dicyd$^{2-}$ is 1,4-dicyanamidobenzene dianion),[3] and the bridging ligand can be either reduced (electron-type; $D_2A$ system) or oxidized (hole-type; $A_2D$ 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., $D_2A$ system) which yield favorable charge-transfer materials with M−L $\pi$ back-bonding.[4] In this vein, we reported the first two-dimensional (2D) network compound composed of [$Ru_2^{II,II}(O_2CCF_3)_4$] and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), which may be represented by the resonance scheme [$Ru_2^{5+}$-(TCNQ•$^-$)-$Ru_2^{4+}$ ↔ $Ru_2^{4+}$-(TCNQ)-$Ru_2^{4+}$ ↔ $Ru_2^{4+}$-(TCNQ•$^-$)-$Ru_2^{5+}$]: [{$Ru_2(O_2CCF_3)_4$}$_2$TCNQ]•3(toluene) (**1a**).[4b] 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 [$Ru_2(O_2CCF_3)_4$] 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, [{$Ru_2(O_2CCF_3)_4$}$_2$-TCNQF$_4$]•3(*p*-xylene) (**2**), where 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 $Ru_2$ units to TCNQF$_4$ molecules.

Compound **2** was synthesized under anaerobic conditions by a diffusion of a solution of [$Ru_2(O_2CCF_3)_4$] in *p*-xylene (top layer) and TCNQF$_4$ in $CH_2Cl_2$ (bottom layer) in a 2:1 molar ratio. The infrared spectrum of **2** reveals two $\nu$(C≡N) stretches at 2217 and 2179 cm$^{-1}$, which are shifted to lower energy than the stretches at 2227 cm$^{-1}$ ($b_{1u}\nu_{18}$) and 2214 cm$^{-1}$ ($b_{2u}\nu_{32}$) observed for neutral TCNQF$_4$.[5] Furthermore, two $\nu$(C═C) stretches of 1540 and 1492 cm$^{-1}$ are very similar to 1539 ($b_{2u}\nu_{33}$) and 1500 ($b_{1u}\nu_{19}$) cm$^{-1}$ of the TCNQF$_4^-$ radical anion (neutral TCNQF$_4$: 1602 and 1549 cm$^{-1}$, respectively). The shift to lower energies for **2** is in accord with increased $Ru_2$-TCNQF$_4$ $\pi$ back-bonding and with the reduction of 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 Ru−Ru bond and a $C_2$ axis and mirror plane that serve to quadrisect the TCNQF$_4$ moiety ($Z = 2$), leading to a single unique $Ru_2$ unit and one TCNQF$_4$ molecule per formula (ORTEP in Figure S1),[6] as was also observed for **1a**. All four cyano groups of TCNQF$_4$ coordinate to $Ru_2$ molecules with a distance of 2.260(6) Å for Ru(1)−N(1) and an angle of 171.9(5)° for Ru(1)−N(1)−C(5) to form a fishing-net-like 2D network (Figure 1). The interlayer distance is ca. 6.6 Å. The Ru−Ru bond distance is 2.3020(6) Å which is slightly longer than the corresponding distances in [$Ru_2^{II,II}(O_2CCF_3)_4(thf)_2$] (2.276(3) Å),[7] **1a** (2.2875(7) Å), and [{$Ru_2(O_2CCF_3)_4$}$_2$TCNQ]•3(*p*-xylene) (**1b**) (2.2915(3) Å) which was synthesized for the sake of comparison (Figure S1). The Ru−O$_{\mathrm{equatorial}}$ bond distance, which is strongly influenced by the oxidation state of the $Ru_2$ core, is in the middle range between those observed for [$Ru_2^{II,II}(O_2CCF_3)_4$-(thf)$_2$] (2.070(6)-2.076(6) Å)[7] and [$Ru_2^{II,III}(O_2CCF_3)_5$] (1.995(12)−2.032(12) Å),[8] clearly indicating a partially oxidized feature (i.e., formally, [$Ru_2$]$^{4.5+}$). It is noteworthy that the Ru−O$_{\mathrm{equatorial}}$ 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 [$Ru_2^{II,II}(O_2CCF_3)_4(thf)_2$] (i.e., likely assigned to [$Ru_2$]$^{4+}$).[7] The degree of charge transfer from [$Ru_2^{II,II}(O_2CCF_3)_4$] to TCNQF$_4$ was estimated from the Kistenmacher relationship, $\rho = A[c/(b + d)] + B$ with $A = -46.729$ and $B = 22.308$,[9] based on neutral TCNQF$_4$ ($\rho = 0$)[10] and (*n*-Bu$_4$N)[TCNQF$_4$] ($\rho = -1$)[11] (where $b$, $c$, and $d$ are 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 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 [$Ru_2^{II,II}(O_2CCF_3)_4$] units to one TCNQF$_4$ in **2** has occurred; that is, it is formally, [$Ru_2^{4.5+}$-(TCNQ•$^-$)-$Ru_2^{4.5+}$].

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 cm$^3$•K•mol$^{-1}$) to reach a maximum at 96 K (11.9 cm$^3$•K•mol$^{-1}$). Below the maximum temperature, $\chi T$ decreases abruptly and then gradually to 0.037 cm$^3$•K•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 TCNQF$_4^-$ radical. Notably $\chi T$ for **1b** decreases continuously with decreasing temperature from 300 to 1.8 K, which is in accord with two isolated [$Ru_2$]$^{4+}$ units with $S = 1$ (Figure S2.

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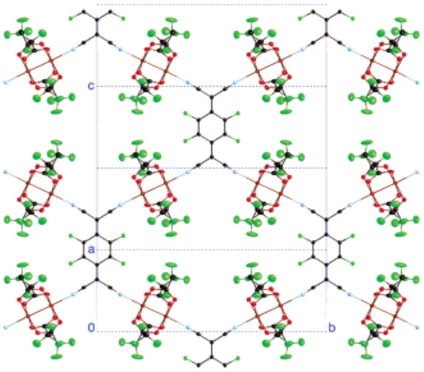

***Figure 1.*** 2D network structure of **2** (black, C; red, O; blue, N; green, F; orange, Ru). The *p*-xylene molecules as crystallization solvents are omitted for clarity.

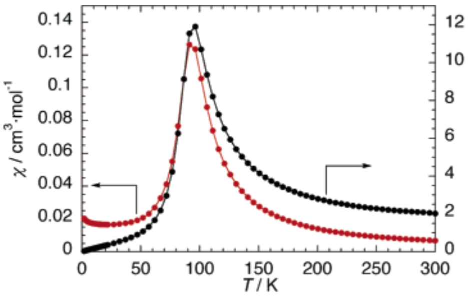

***Figure 2.*** Temperature dependence of $\chi$ and $\chi T$ measured at 1 T of **2**. The solid line is only a guide for the eyes.

A fitting led to the parameters, $g = 2.0$ (fixed), $D = 271$ cm$^{-1}$, TIP $= 44 \times 10^{-6}$ cm$^3$•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 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 T, three kinds of steps at ±0.20 ($H_b$), ±2.38 ($H_c$), and ±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): P→CS, CS(+)→(AF)→CS(−), and CS→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 (AF→P or CS→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 $[Ru_2]^{n+}$ 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** ($4.6 \times 10^{-4}$ S•cm$^{-1}$) than was observed for **1b**.

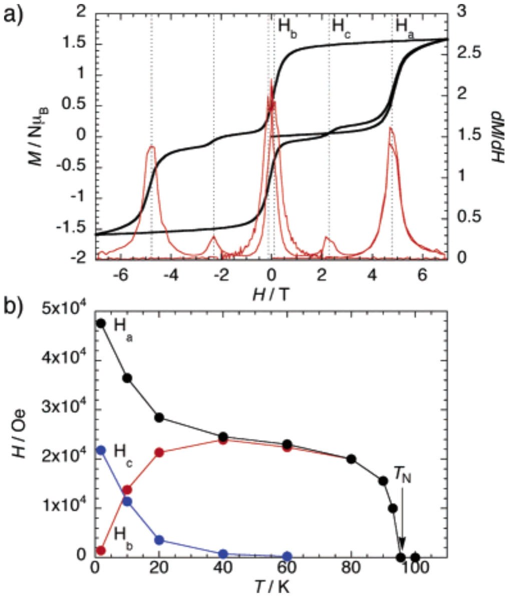

***Figure 3.*** Field dependence of $M$ and d$M$/d$H$ at 1.82 K of **2** (a) and temperature dependence of critical fields, $H_a$, $H_b$, and $H_c$ (b), where the value of ($H_a - H_b$) is a field-hysteresis of paramagnetic phase and the value of $H_c$ is approximately corresponding to a coercive field.

Inspired by the concept of the resonance scheme in charge-transfer $D_2A$ network systems, the first successful example of a magnet for $Ru_2$-TCNQ type systems was rationally designed by tuning the redox between $[Ru_2]^{4+}$ and the TCNQ molecule by changing from TCNQ to 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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