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Magnetic/Conducting Bifunctionality due to π/σ-Conjugated Functional Moieties in a Stacked Ferrimagnetic Chain

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An alternating chain of a paddlewheel $[Ru_2^{II,III}(O_2CEt)_4]^+$ ($EtCO_2^-$ = propionate) complex and $[Pt(mnt)_2]^-$ (mnt^{2-} = maleonitriledithiolate) has a ferrimagnetic spin arrangement of $S = {}^3/_2$ and ${}^1/_2$ local spins, respectively, as well as three-dimensional antiferromagnetic ordering with a canting mode at 8.6 K. This chain is stacked at the $[Pt(mnt)_2]^-$ units to form a slipped column in the vertical direction against the chain, which acts as a pathway for electrical conduction.

Magnetic/conducting molecular materials, of which two properties are mutually coupled, are some of the most challenging targets in materials science. A few methodologies toward the rational design of such materials have been reported, in which the desired materials could be categorized as follows: (i) hybrid (layered); (ii) conjugated; (iii) coframework. Hybrid systems can be prepared by combining alternating functional layers in the same crystal.[1,2] Nevertheless, it is still not easy to control rationally the interplay between functional layers because of sufficient separation of these layers and weak through-space dipolar interactions. In the case of conjugated systems, Sugawara et al. have designed a spin-carrying donor molecule (called ESBN), which is a diselena analogue of benzotetrathiafulvalene with nitronyl nitroxide in a cross-conjugating manner, and have obtained its mixed-valence salt, $(ESBN)_2ClO_4$.[3] This is the first pure organic system that exhibits negative magnetoresistance. The use of coordination compounds to prepare conjugated or cross-conjugated systems using a moiety with a local d spin and an electron-transport module has been extensively studied,[4] but no remarkable system involving bi- or cofunctionality was reported. Drawing upon these results, a direct fabrication of magnetic/conducting coframeworks may be the best route. In order to design such a system, we have prepared charge-transfer metal−organic frameworks (MOFs) composed of carboxylate-bridged paddlewheel diruthenium(II,II) complexes and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) derivatives[5] and have obtained relatively high T_c magnets with semiconducting properties,[6] in which the two-dimensional MOF plays a role for both magnetic and conducting pathways.

Here a new conjugated system is reported. We synthesized a one-dimensional (1D) chain using $[Ru_2^{II,III}(O_2CEt)_4]^+$ (abbreviated as $[Ru_2^{II,III}]^+$; $EtCO_2^-$ = propionate) and $[Pt(mnt)_2]^-$ (mnt^{2-} = maleonitriledithiolate): $[\{Ru_2^{II,III}(O^2CEt)_4\}\{Pt(mnt)_2\}]$ (**1**). Both $[Ru_2^{II,III}]^+$ and $[Pt(mnt)_2]^-$ are paramagnetic with $S = {}^3/_2$ and ${}^1/_2$, respectively, which could allow adequate magnetic coupling along the 1D framework owing to a π-bonding overlap between a π^* orbital of $[Ru_2^{II,III}]^+$ and a singly occupied molecular orbital (SOMO) of $[Pt(mnt)_2]^-$ with π character. It is known that stacks of $[Pt(mnt)_2]^{\delta-}$ units with noninteger valence states are capable of acting as conducting pathways with σ-bonding bands of lowest unoccupied molecular orbitals.[7] Thus, the vertical direction of the magnetic framework of $[\{Ru_2\}\{Pt(mnt)_2\}]$ has the potential to be a conducting pathway with support of charge transfer between $[Ru_2^{II,III}]^+$ and $[Pt(mnt)_2]^-$ (Scheme 1), in which itinerant electrons would be associated with the spin ordering in the magnetic framework. The present compound **1** is a model for such materials, in which the magnetic/conducting bifunctionality due to π/σ-conjugated functional moieties in a stacked chain structure was observed.

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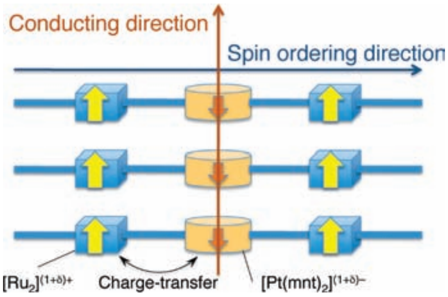
Scheme 1. Model of Conjugated 1D Chains in **1**



Compound **1** crystallized in the monoclinic space group $C2/c$ (see the Supporting Information). The formula unit is comprised of one [Ru_2] unit and one [$Pt(mnt)_2$] unit, which have an inversion center on the midpoint of the Ru−Ru bond and a C_2 axis through the platinum center ($Z = 4$). The [$Pt(mnt)_2$] unit coordinates to the [Ru_2] unit using two *trans*-positioned cyano groups of the mnt ligand, forming a 1D chain motif with a [−{Ru_2}−{$Pt(mnt)_2$}−] repeating unit (Figure 1a). The chain is almost linear with a Ru−N bond length of 2.260(7) Å and a Ru−N−C angle of 168.8(6)°. The [$Pt(mnt)_2$] unit, being nearly flat, is nearly in-plane with the equatorial blades (two of the four RCO_2^- ligands) of the paddlewheel [Ru_2] unit, giving rise to sufficient overlap between a frontier π^* orbital of [Ru_2], which has an unpaired spin, and the SOMO of [$Pt(mnt)_2$], which has π character, needed for magnetic exchange coupling (vide infra). The Ru−Ru distance is 2.2656(10) Å, and the Ru−O_{eq} (O_{eq} = carboxylate oxygen) bond distances are in the range of 2.01−2.03 Å, which are consistent with $[Ru_2^{II,III}]^+$, as reported in the literature (av. ⟨Ru−O_{eq}⟩ = 2.022 Å).[8] The Pt−S distances are in the range of 2.25−2.27 Å, indicating that the [$Pt(mnt)_2$] unit is an anion ([$Pt(mnt)_2$]$^-$). This assignment was supported by IR spectra, in which ν(C≡N) was observed as a sharp band at 2215 cm^{-1}.[7a]

The chains run along the (201) plane, where in-plane chains are parallel to each other (parallel to the (1−10) plane). On the other hand, as seen in Figure 1b, chains in the perpendicular direction stack, crossing each other at an angle of ca. 65° (parallel to the (110) plane). Because of this arrangement, the [$Pt(mnt)_2$] units, which are located at the crossover points between chains, form an interchain column with a slipped motif along the c axis with a plane-to-plane distance of 3.586 Å (Figure 1c). In this stacking mode, the Pt···Pt distance is 4.52(2) Å and the shortest S···S contact (S(1)···S(1)**) is 3.553(2) Å (symmetry operation **: x, $-y + 1$, $z - 0.5$). $CHCl_3$ and 1,1,2,2-tetrachloroethane, which are located in the void space of the pores along the c axis surrounded by chains, show positional disordering.

The temperature dependence of the direct-current (dc) magnetic susceptibility was measured on a polycrystalline sample of **1** by applying a field of 1 kOe, and a χT versus T plot is shown in Figure 2a. The Curie constant obtained from the data of χ^{-1} (300−50 K) is 2.34 $cm^3\cdot K\cdot mol^{-1}$, and the Weiss constant (θ) is −16.3 K. The χT value of 2.24 $cm^3\cdot K\cdot mol^{-1}$ at 300 K gradually decreases upon lowering of the temperature and reaches a minimum value of 1.53 $cm^3\cdot K\cdot mol^{-1}$ at 17.0 K. Then it suddenly increases to a maximum of 8.01 $cm^3\cdot K\cdot mol^{-1}$ at 5.4 K, followed by a decrease (3.85 $cm^3\cdot K\cdot mol^{-1}$ at 1.82 K). The χT versus T behavior with $\theta < 0$ clearly indicates that the dominant magnetic interaction, to which the intrachain exchange coupling between $[Ru_2^{II,III}]^+$ $S = {}^3/_2$ and $[Pt(mnt)_2]^-$ $S = {}^1/_2$ units contributes, is antiferromagnetic, thus affording a ferrimagnetic spin arrangement. The exchange coupling constant (J) was roughly estimated from a simulation of the χT data in the temperature range of 10−300 K using an alternating spin model with $S_{Ru_2} = S_i = {}^3/_2$ and $S_{Pt(mnt)_2} = S_{i+1} = {}^1/_2$ ($H = -2\sum_{i=1}^{N} \hat{S}_i\cdot\hat{S}_{i+1}$), reported by Drillon et al.,[9]

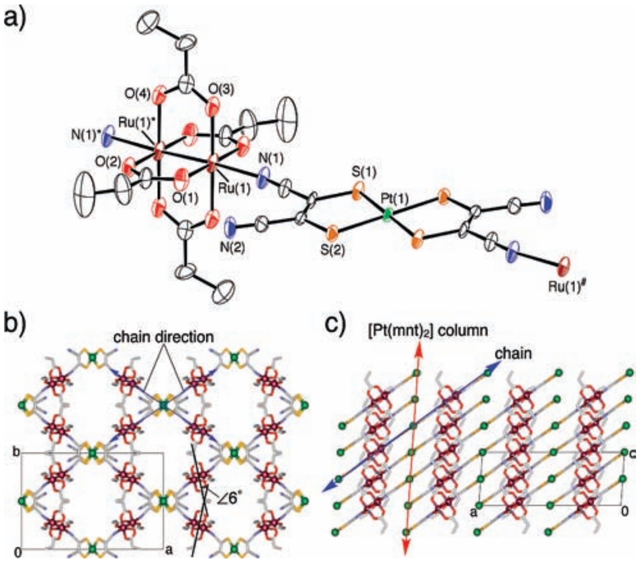


Figure 1. (a) Thermal ellipsoid drawing of **1** with 50% ellipsoid representations and packing arrangements of 1D chains projected along the (b) c and (c) b axes. Hydrogen atoms and solvent molecules are omitted for clarity. The blue and red arrows indicate the chain and stacking column directions, respectively.

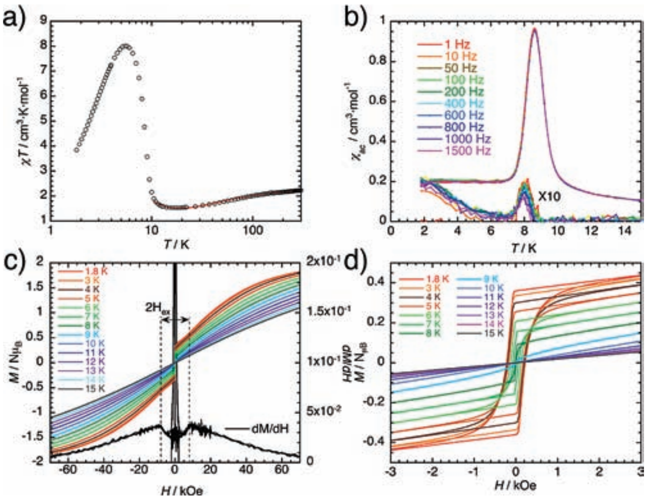


Figure 2. (a) χT vs T measured at 1 kOe, where the solid red line represents a simulation curve modeled for an alternating chain of $S = {}^3/_2$ and ${}^1/_2$ (see the text). (b) χ' and χ'' vs T measured at zero dc field and an oscillating field of 3 Oe. (c) M vs H measured at several temperatures from 1.8 to 15 K. The dM/dH curve is for the data at 1.8 K. (d) Close-up view of the low-field region of Figure 2c.

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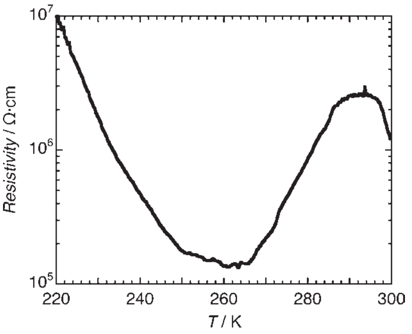

Figure 3. Temperature dependence of the resistivity (cooling process) of a single crystal of **1** (along the *c* axis) using a two-probe wiring method with platinum wires and carbon paste.

and an estimated value of J of −9.20(10) K with g_{Ru_2} = 2.025(1) and $g_{\mathrm{Pt(mnt)}_2}$ = 2.102(8) (solid red line in Figure 2a).

In the alternating-current (ac) susceptibility data measured at zero dc field in a 3 Oe oscillating field in the temperature range of 1.8−15 K (Figure 2b), a distinct frequency-independent peak at 8.6 K is observed for in-phase (χ') susceptibilities involving the onset of out-of-phase (χ'') susceptibilities (but relatively weak), indicating long-range spin ordering. Moreover, in the field dependence of the magnetization measured at several temperatures (Figure 2c), the magnetization abruptly increased at low fields and shows hysteresis at temperatures below 8 K (Figures 2d and S1 in the Supporting Information). In the M/H curves, the magnetization only reaches a value of ca. 0.4 μ_{B} (1.8 K) for a saturation value (M_{s}) at low fields, followed by a sigmoidal curve with an inflection at around 0.8 T (H_{ex} from a dM/dH plot, Figure 2c; the phase diagram, Figure S2 in the Supporting Information), becoming M_{s} = 1.82 μ_{B} at 7 T. This M/H feature indicates that the interchain interaction is antiferromagnetic and that the spontaneous magnetization is due to a canting mode of antiferromagnetically ordered spins. The interchain interactions (zJ', where z is the numbers of neighbors) having an effective spin (S_{eff}) of 1 were estimated from H_{ex} to be −0.54 K (g = 2.0).[10] From a structural point of view, the stacking of the $[\mathrm{Pt(mnt)_2}]^-$ moieties is important for interchain interactions. The canting angle estimated using M_{s} was ~6°, which corresponds to a tilt angle of the $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ units (see Figure 1b), reflecting the effect of in-plane anisotropy of this unit. The M_{s} value at 7 T is smaller than the expected value of M_{s} (=gS_{eff}, where g = 2.0) of 2 due to a contribution of the strong anisotropy of $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ ($D \approx 60$ cm^{-1} with $S = {}^3/_2$).[8,11]

The temperature dependence of the electronic resistivity of a single crystal of **1** was measured using a two-probe method (Figure 3). Even at 300 K, the resistivity along the c axis was much higher (>10^6 Ω·cm) than that generally observed for $[\mathrm{Pt(mnt)_2}]^{\delta-}$ with noninteger valence states, conjuring up the image of general semiconductors.[7a] Interestingly, the resistivity decreases in the high-temperature region of 265−290 K (this behavior was confirmed on five crystals taken from different batches). This unusual electron transport property is distinctly anisotropic with $\rho > 10^7$ Ω·cm in the ab plane. The c axis direction corresponds to the stacking direction of the $[\mathrm{Pt(mnt)_2}]^-$ moieties; thus, the 1D column is a pathway for electron transport. If there is complete charge separation between the $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ and $[\mathrm{Pt(mnt)_2}]^-$ units even in the high-temperature region, a simple insulator or semiconductor with an invariant wide energy gap between valence and conducting bands is expected. Although the resistivity decreased, as if it was metallic, this compound should be a semiconductor over the entire temperature range measured, and we believe that the decrease in the resistivity is due to a continuous decrease in the band gap. Thus, we propose the following: A small amount of charge fluctuates between $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ and $[\mathrm{Pt(mnt)_2}]^-$ units to form a charge balance of $[-\{\mathrm{Ru_2}\}^{(1+\delta)+}-\{\mathrm{Pt(mnt)_2}\}^{(1+\delta)-}-]$ because the $[\mathrm{Pt(mnt)_2}]^{(1+\delta)-}$ columns form 1D conduction bands with an energy gap from the valence band (Scheme 1). Indeed, a strong charge-transfer band attributed to $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+ \rightarrow [\mathrm{Pt(mnt)_2}]^-$ newly appeared at ca. 0.9 eV in **1** (Figure S3 in the Supporting Information). Then, not only the degree of the charge separation (δ) but also the delocalization of the charge through the $[\mathrm{Pt(mnt)_2}]^{(1+\delta)-}$ column becomes thermally activated. However, they concomitantly compete with structural fluctuations at high temperatures particularly when electrons hop through the column. Thermally activated fluctuations were confirmed via IR spectra for a single crystal, as shown in Figures S4 and S5 in the Supporting Information. Hence, the decrease in the resistivity is closely associated with suppression of structural fluctuations when the temperature is decreased. In addition, δ should be thermally sensitive, and thus, upon cooling, the charge between $[\mathrm{Ru_2}]^{(1+\delta)+}$ and $[\mathrm{Pt(mnt)_2}]^{(1+\delta)-}$ should recouple to afford an electron-filled band with a wide gap. It acts as a semiconductor below 265 K. Note that this behavior is akin to what is observed in a three-dimensional $[\mathrm{Ru_2}]_2\mathrm{TCNQ}$ system.[12]

Even though two properties (spin order and meaningful electron transport) function separately in **1**, the conjugation via the interchain stacking played a crucial role in bringing about the two functions. Designing this type of structure is a good way to achieve multiple functionalities, especially of magnetic/conducting properties in materials.

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Supporting Information Available: Details of experiments, characterization, X-ray crystallographic data of **1** in CIF format, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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