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A ladder based on paddlewheel diruthenium(II, II) rails connected by TCNQ rungs: a polymorph of the hexagonal 2-D network phase†

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The slow diffusion reaction of \([\text{Ru}_2(\text{OCCF}_3)_6](\text{THF})_2]\) with TCNQ in \(\text{CH}_2\text{Cl}_2/4\)-chlorotoluene, respectively, leads to the formation of ladder chain composed of \([\text{Ru}_2]\) rails and TCNQ rungs in a 2:1 ratio.

Inorganic/organic hybrid molecule-based materials that exhibit dn/pt electronic delocalization are excellent prospects for the pursuit of solids that exhibit both conducting and magnetic properties. If one considers the field of candidates for exhibiting such behavior, it is clear that assemblies of metal ions or complexes with \(\pi\)-conjugated polycyano molecules such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), and \(N,N\)-dicyanoquinondimine (DCNQI) are particularly promising.† A leading example in the realm of conducting materials is the series of metallic materials of general formula \([\text{Cu}(\text{DCNQI})_n]\)\(^{−}\), which exhibit a three-dimensional structure consisting of mixed-valence tetrahedral \(\text{Cu}^{II}\) ions and partially reduced DCNQI. The high conductivity of this material is related to the columnar \(\pi\)-\(\pi\) stacking of DCNQI molecules and the 1:2 ratio of donor (Cu: D)/acceptor (DCNQI: A), combined with a charge-transfer resonance of the type \([A−D−A ↔ A−D+−A ↔ A−D−−A]\), plays a key role in the partial occupancy of the conducting band based on the DCNQI columns.

In contrast to the aforementioned possibility, the use of a \(D: A\) ratio of 2:1 with a single electron conjugation between the metal and the organocyanoide units is also an excellent strategy for obtaining delocalized metal–organic framework solids. In order to promote electronic resonance in such systems, the use of electron-rich metal–metal bonded complexes as a donor building block is an effective strategy. In this vein, we have capitalized on the use of paddlewheel diruthenium(II, II) complexes, \([\text{Ru}_{2}^{II,II}]\), which act as linear connecting units through the axial positions and undergo a reversible redox transformation from \([\text{Ru}_{2}^{II,II}]\) \(\leftrightarrow [\text{Ru}_{2}^{III,III}]\) without significant structural changes.† Most importantly, both \([\text{Ru}_{2}^{II,II}]\) and \([\text{Ru}_{2}^{III,III}]\) are paramagnetic with ground states of \(S = 1\) in the former case and \(S = 3/2\) or \(S = 1/2\) in compounds of the latter type. This approach has led to the synthesis of 2:1 assemblies, \([\text{Ru}_2(\text{OCCF}_3)_6]\)·TCNQ·3(solv) (solv = toluene; 1a, p-xylene; 1b)\(^{5,6}\) and \([\text{Ru}_2(\text{OCCF}_3)_6]\)·TCNQF\(_3\)·3(p-xylene) (TCNQF\(_4\) = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane; 2), which exhibit two-dimensional (2-D) hexagonal layered structures. While 1a and 1b do not undergo appreciable \([\text{Ru}_2]\)−TCNQ charge-transfer, compound 2 exhibits a significant degree of electron transfer and behaves as a metamagnet with \(T_N = 95\) K and a field-induced ferromagnet.\(^6\)

It has been a longstanding goal of our research in this area to isolate another type of 2:1 product with diruthenium units using the same combination of precursors. Specifically we are interested in “ladder-type chains”, which represent a polymorphic analogue of the 2D network previously noted for 1 and 2 (Scheme 1). In fact, previous studies in one of our laboratories revealed that a ladder-type motif crystallizes from the self-assembly reaction of \([\text{Mo}^{II}(\text{OCCF}_3)_6]\) with TCNQ, albeit with very weak axial interactions providing the basis for the extended structure.\(^7\) Given the proper choice of donor (D) and acceptor (A) building blocks, this type of 1-D compound can be exploited for the design of electron-delocalized conducting ladders\(^8\) or isolated magnetic ladders.\(^9,10\) In the vein of extending the known examples of such systems, herein we have prepared a new ladder compound, heretofore unknown for diruthenium chemistry, namely \([\text{Ru}_2(\text{OCCF}_3)_6]\)·TCNQ·4(4-chlorotoluene) (3), which, interestingly, is obtained from the same starting materials as the 2-D phase that we reported in earlier studies.\(^5,6\)

† Electronic supplementary information (ESI) available: ORTEP drawing and powder reflection spectrum of 3. CCDC reference number 688082. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808503j

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Compound 3 was synthesized as needle-shaped crystals by slow diffusion of a CH2Cl2 solution of [Ru2(O2CCF3)4(THF)2] (4 mM, bottom layer) into a 4-chlorotoluene solution of TCNQ (2 mM, top layer) in a narrow diameter glass tube (<8 mm). The use of glass tubes with wider diameters accelerates the diffusion rate of the reactant solutions and leads exclusively to the formation of the 2-D network phase ([Ru2(O2CCF3)4]2+:TCNQ):3(4-chlorotoluene) (1c), as the main product (the same is observed for 1a and 1b). It was further noted that diffusion of more dilute solutions has a greater tendency to produce 3 rather than 1c (crystals of 3 and 1c are distinguishable from their different crystal morphologies).

It is interesting to note that identical reactions with toluene and p-xylene in the solvent mixture instead of 4-chlorotoluene result only in the formation of crystals of 1a and 1b, respectively.

While the hexagonal 2-D net 1c crystallizes in the monoclinic space group C2/m with Z = 2 (Fig. S1†), compound 3 crystallizes in the triclinic space group P1̅1 with Z = 1 and one unique [Ru2] unit due to the presence of an inversion center located at the midpoint of the phenyl ring of TCNQ. A thermal ellipsoid plot of the asymmetric unit in 3 is depicted in Fig. 1 with selected bond distances and angles being listed in the figure caption. The TCNQ moiety in 3 acts as a µ-bridging group, as is the case of 1 and 2, but its bridging mode is repeated only along the b axis to form a ladder-type chain (Fig. 2a), in contrast to the structures of 1 and 2 which extend in two directions to form a 2-D hexagonal network. The Ru–Ru distance in 3 is 2.2930(3) Å, similar to that observed in [Ru2(O2CCF3)4(THF)2] (2.289 Å) (average is 2.289 Å). The obvious difference between these structures occurs in the axial angles Ru–N–C. In 1a–c with the 2-D network, the Ru–N–C angle is in the range 175.6–177.1°. In contrast, the corresponding Ru–N–C angle in 3 is much more acute as evidenced by the values Ru(1)–N(1)–C(9) = 149.7(2)° and Ru(2)≡N(2)–C(14) = 161.5(2)°, which are 15–30° less than those in 1a–c. The Ru–Ru–N bond angle is also considerably non-linear in 3 with Ru(2)–Ru(1)–N(1) = 173.38(6)° and Ru(1)–Ru(2)–N(2) = 174.75(7)°, whereas in 1a–c, it is 178.04–178.45°. The Ru–N distances in 3 are Ru(1)–N(1) = 2.290(2) Å and Ru(2)–N(2) = 2.254(2) Å, which are comparable to that in 1a (2.277(3) Å), 1b (2.281(2) Å) and 1c (2.279(3) Å) (symmetry operations # and ## are given in the caption of Fig. 1).

Fig. 2 depicts the side and the top views of the chain projected along the a and b axes, respectively. Each ladder is arranged in a parallel orientation along the b axis. The nearest [Ru2]···[Ru2] distance (defined as the distance between the midpoints of the Ru–Ru bonds) is 11.214 Å for the rail (leg) direction and 8.646 Å for the intra-ladder rung direction and 8.451 Å for inter-ladder. As can be seen in Fig. 2b, four interstitial 4-chlorotoluene solvent molecules are interleaved between the N≡C–C–≡C=N groups of TCNQ with distances between least-squares planes of 3.270 and 3.155 Å. It appears that the extra stabilization of these weak π–π interactions serves to stabilize the formation of ladders over the more conventional 2-D architecture. In contrast, 1c contains only three crystallization solvent molecules, only one of them is involved in a π–π stack (3.301 Å) with the phenyl ring of TCNQ.

To estimate the oxidation state of [Ru2] and TCNQ moieties in the material, one must evaluate the characteristic bond lengths. In

Fig. 1 ORTEP drawing of an asymmetric unit of 3 (50% probability ellipsoid; symmetry operations (*) −x + 1, −y + 1, −z; (**) −x + 1, −y + 2, −z; (***) −x + 1, −y, −z; (*) x, y + 1, z; (**) x, y − 1, z). Hydrogen atoms and 4-chlorotoluene molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) = 2.2930(3), Ru(1)–O(1) = 2.070(2), Ru(1)–O(3) = 2.075(2), Ru(1)–O(5) = 2.074(2), Ru(1)–O(7) = 2.063(2), Ru(1)–N(1) = 2.290(2), Ru(2)–O(2) = 2.079(2), Ru(2)–O(4) = 2.081(2), Ru(2)–O(6) = 2.063(2), Ru(2)–O(8) = 2.066(2), Ru(2)–N(2) = 2.254(2), Ru(2)–Ru(1)–N(1) = 173.38(6), Ru(1)–Ru(2)–N(2) = 174.75(7), Ru(1)–N(1)–C(9) = 149.7(2), Ru(2)≡N(2)–C(14) = 161.5(2).

Fig. 2 Packing views projected on the a axis (a) and the b axis (b). 4-Chlorotoluene molecules are described only in (b), and fluorine and hydrogen atoms are omitted for clarity.
that the TCNQ ligand, infrared data for in these compounds. respectively, indicating that the TCNQ moiety is close to neutral modes are observed at 2198 and 2140 cm\(^{-1}\) overlaps with the TCNQ at \(\sim\) roughly estimated as being 

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\text{Ru}_2^{14}(\text{O}_2\text{CFCF}_3)_2(\text{THF})_2] (2.073 \text{ Å})^{11} \text{ rather than that in the related } \text{Ru}_2^{11}(\text{O}_2\text{CFCF}_3)_2(\text{O}_2\text{CFCF}_3) (2.021 \text{ Å}).^{12} \text{ On this basis, the charge on the [Ru] moiety in 3 is assigned as 4+. Additional evidence for this conclusion can be derived from the C–C bond lengths of TCNQ which are excellent "reporters" of the oxidation state of TCNQ due to the fact that the ring character becomes more benzene-like (aromatic) than quinone-like with increasing charge.}^{13} \text{ The charge of TCNQ has been estimated by the Kistenmacher relationship } \rho = A(\sqrt{b + d}) + B,^{14} \text{ where } A = -41.667 \text{ and } B = 19.833 \text{ for TCNQ} \text{ by referring to neutral TCNQ (}\rho = 0\text{)}^{15} \text{ and RbTCNQ (}\rho = -1\text{)}^{16} \text{ with the definitions of bonds } b, d \text{ and } e \text{ being denoted in Fig. 1. The charge for the TCNQ bridges in 3 estimated from this method is } -0.19, \text{ whereas the values for 1a–c are } -0.42, -0.25, \text{ and } -0.21, \text{ respectively, indicating that the TCNQ moiety is close to neutral in these compounds.}

In order to gain more information on the oxidation state of the TCNQ ligand, infrared data for 3 were measured. It is known that the \(\delta(C–H)\) mode is quite sensitive to the redox state. The \(\delta(C–H)\) modes of TCNQ\(^{-}\) and TCNQ\(^{-}\) are observed to occur at \(\sim\) 860 cm\(^{-1}\) and between 820 and 825 cm\(^{-1}\), respectively.\(^{17} \text{ In 3, the corresponding bending mode was observed at 860 cm}^{-1}, \text{ indicating a neutral valence for TCNQ. Moreover, the } \nu(C=C) \text{ mode (}\nu_{as}\) of 3 at 1539 cm\(^{-1}\) (\(\omega_{as}\)), which is a good indicator to evaluate the degree of charge-transfer was compared to the corresponding frequency of neutral TCNQ (\(\omega = 1545 \text{ cm}^{-1}\)) and LiTCNQ (\(\omega = 1504 \text{ cm}^{-1}\)); using } \rho = -1/2(\omega_{as} - \omega_{p})/(\omega_{as} - \omega_{p}),^{18} \text{ the } \rho \text{ value of 3 was estimated to be } -0.146, \text{ consistent with the value from the X-ray structure. Finally, two } \nu(C=C) \text{ stretching modes are observed at 2198 and 2140 cm}^{-1}, \text{ which are shifted from the mode in free TCNQ (2222 cm}^{-1}\) but one must appreciate the fact that } \nu(C=C) \text{ modes are strongly affected by metal-binding as well as the oxidation state of TCNQ.}^{17} \text{ It is safe to say, however, that the shift to lower energies results from back-donation from the [Ru\(_{14}\)] unit, suggesting the occurrence of partial charge transfer, albeit a very small degree as } \rho = -0.15 \text{ to } -0.2. \text{ Indeed, the powder reflection spectra of 3 exhibit a strong, broad absorption indicative of a MLCT band in the range of 480–1400 nm (Fig. S2f), which overlaps with the TCNQ\(^{-}\) chromophore at 500–900 nm. These results are consistent with the conclusions of the structural analysis.}

\text{The charge distribution between the [Ru\(_2\)] and TCNQ parts is estimated by the Kistenmacher relationship } \rho = A(\sqrt{b + d}) + B,^{14} \text{ where } A = -41.667 \text{ and } B = 19.833 \text{ for TCNQ} \text{ by referring to neutral TCNQ (}\rho = 0\text{)}^{15} \text{ and RbTCNQ (}\rho = -1\text{)}^{16} \text{ with the definitions of bonds } b, d \text{ and } e \text{ being denoted in Fig. 1. The charge for the TCNQ bridges in 3 estimated from this method is } -0.19, \text{ whereas the values for 1a–c are } -0.42, -0.25, \text{ and } -0.21, \text{ respectively, indicating that the TCNQ moiety is close to neutral in these compounds.}

The temperature dependence of the dc susceptibility of 3 was measured in the temperature range of 1.8–300 K at 0.5 T. Fig. 3 displays the \(\chi\) and \(\chi' T\) vs \(T\) plots. The \(\chi' T\) value at 300 K is 2.5 cm\(^3\) K mol\(^{-1}\), which, upon cooling, decreases smoothly to 0.042 cm\(^3\) K mol\(^{-1}\) at 1.82 K. The qualitative features of the \(\chi' T\) vs \(T\) plot are similar to that observed for isolated [Ru\(_{14}\)] complexes with a triplet S = 1 ground state. In these compounds it is known that the decrease of \(\chi' T\) is due primarily to a strong orbital contribution, with a few examples being reported with zero-field splitting parameters (ZFS, \(D\)) as large as 300 cm\(^{-1}\).\(^{19} \text{ The increase of } \chi \text{ at low temperatures is ascribed to a paramagnetic impurity of a [Ru\(_{14}\)] species with } S = 3/2. \text{ The magnetic data were simulated by a Curie paramagnetic model with } S = 1 \text{ taking into account ZFS, temperature-independent paramagnetism (TIP), an impurity of } S = 3/2 (\(\rho\)), \text{ and inter-molecular interactions (}\(zJ\)) commonly used for magnetically-isolated or weakly-interacting [Ru\(_{14}\)] complexes.\(^{20}−22\) \text{ The inter-molecular interaction (}\(zJ\)) was introduced in the framework of the mean-field approximation. The best fit of parameters were with } g = 2.00 \text{ (fix), } D = 157.6 \text{ cm}^{-1}, \text{ } zJ = -32.7 \text{ cm}^{-1}, \text{ } TIP = 2.4 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}, \text{ and } \rho = 0.016. \text{ The } D \text{ value is somewhat small, but acceptable given the range of values reported for [Ru\(_{14}\)] complexes.\(^{22} \text{ Conversely, the observed TIP value is rather large compared to a TIP value of } \approx 10^{-5}−10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ for the } 1\text{A}_2 \text{ ground state of [Ru\(_{14}\)] complexes, but it is noted that the value is larger for magnetically interacting systems.}^{23} \text{ The } zJ \text{ value in 3, indeed, is fairly strong, indicating the presence of inter-[Ru\(_{14}\)] antiferromagnetic interactions, although the absolute value of the obtained } zJ \text{ is not very accurate because of the impossibility of separating the effect of this parameter from magnetooomisotropic effects in the simulation of the decreasing } \chi' T \text{ values. Considering the fact that very weak interactions were observed in 1b with a similar } \mu, \text{TCNQ bridge and a partially reduced form, the observed behavior could be due to through-space interactions as well as inter-chain interaction and/or intra-chain rung–rung directional interactions.}

In summary, we report a ladder material which constitutes a second polymorph for the [Ru\(_{14}\)]/TCNQ system. Given the fact that a product with complete charge-transfer was realized by us in the case of the 2-D hexagonal [Ru\(_{14}\)]/TCNQF\(_4\) compound (2) by tuning the redox activity of the building blocks, this new phase represents a prototype for entry into a 1-D ladder with extensive d\(n\)/p\(n\) electron conjugation.

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Notes and references

\(^{†}\) Calcd (found) for 3: C\(_{66}\)H\(_{42}\)Cl\(_6\)F\(_{12}\)N\(_6\)O\(_{15}\)Ru\(_4\); C, 33.31 (33.48); H, 1.60 (1.75); N, 2.78 (2.85%).

\(^{‡}\) X-Ray structure determination: A single crystal (0.2 \times 0.05 \times 0.05 mm) of 3 was mounted in a loop. Data were collected on a Rigaku CCD diffractometer (Saturn70) with graphite-monochromated Mo-K\(_\alpha\)
radiation. The structures were solved by and expanded using Fourier techniques (DIRDIF99). The non-hydrogen atoms were refined anisotropically, except for some disordered fluorine atoms of CF₃CO₂. Full-matrix least-squares refinements on \( F^2 \) converged with unweighted and weighted agreement factors of \( R_1 = \sum|F_o| - |F_c|/\sum|F_o| \) (I > 2.00o(I) and all data), and \( wR^2 = \sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^{0.5} \) (all data). A Sheldrick weighting scheme was used. All calculations were performed using the CrystalStructure crystallographic software package. Crystal data for 3: \( \text{CaH}_{12}\text{Cl}_{3}\text{Ni}_{2}\text{O}_{17} \cdot \text{Ru} \), \( M = 2018.94 \), triclinic \( P1 \) (no. 2), \( T = 93 \pm 1 \text{K}, \alpha(\text{Mo-K}α) = 0.71075\text{Å}, a = 10.0147(4)\text{Å}, b = 11.2143(4)\text{Å}, c = 16.1954(7)\text{Å}, \alpha = 75.1093(9)^{\circ}, \beta = 81.2134(10)^{\circ}, \gamma = 86.8650(10)^{\circ}, V = 1736.94(12)\text{Å}^3, Z = 1, D_{calc} = 1.930 \text{g cm}^{-3}, F_{200} = 984.00, 2\theta_{\text{max}} = 55^{\circ}. \) Final \( R_1 = 0.0410 \) (I > 2.00o(I)), \( R = 0.0526 \) (all data), \( wR^2 = 0.1228 \) (all data), GOF = 1.011 for 515 parameters and a total of 14149 reflections, 7621 unique (\( R_{int} = 0.029 \)).


