Rational synthesis of a two-dimensional honeycomb structure based on a paramagnetic paddlewheel diruthenium complex†

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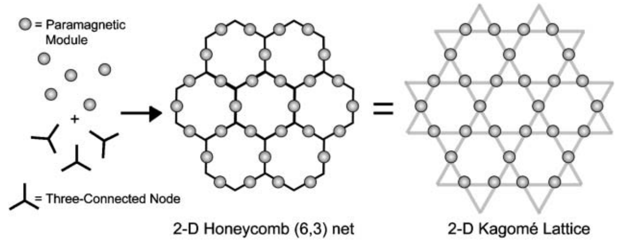
A novel 2-D coordination polymer with honeycomb (6,3) net topology is constructed from a paramagnetic paddlewheel diruthenium tetrabenzoate, $[\mathrm{Ru^{II}}_2(\mathrm{O_2CPh})_4]$, as a linear linker motif and triazine as a three-connected node; the $\mathrm{Ru^{II}}_2$ cores are positioned on nodes of a 2-D Kagomé lattice.

Considerable effort has been devoted to the design and synthesis of self-assembled coordination polymers with specific network topologies due to their potential applications as functional materials.[1] In particular, 2-D Kagomé or triangular lattices with the paramagnetic centers interacted antiferromagnetically with each other are of great interest because of spin-frustrated systems.[2] However, few examples of molecular Kagomé lattices have been reported to date[3] whereas inorganic solids such as iron sulfates are thoroughly investigated.[4] Therefore, we focused on the establishment of a rational synthetic method to arrange the paramagnetic centers on the appropriate positions in the coordination network. Our strategy is to construct a 2-D honeycomb (6,3) network with the paramagnetic centers located on the midpoint of the sides, which is interpreted as a magnetic 2-D Kagomé lattice (Scheme 1). Here, we report the synthesis and the magnetic study of a novel 2-D honeycomb (6,3) network, $[\{\mathrm{Ru^{II}}_2(\mathrm{O_2CPh})_4\}_3(\mathrm{trz})_2]_n$ (**1**) (trz = triazine), constructed from a paddlewheel diruthenium complex as a linear linker with a paramagnetic center and a triazine as a three-connected node.

The key feature of this successful synthesis is the simple but rational choice of assembling modules: triazine as a node and the paddlewheel diruthenium tetrabenzoate complex, $[\mathrm{Ru^{II}}_2(\mathrm{O_2CPh})_4]$, as a linker. Whereas triazine is the simplest candidate for the organic three-connected node, there are few examples[5] of infinite coordination polymers with triazine derivatives coordinating to three metal ions and there is no example of those coordinating to three paramagnetic centers because of their electron deficiency or low coordinating ability. Meanwhile, the neutral paddlewheel diruthenium complexes are intriguing molecular building blocks for supramolecular assemblies[6] not only due to their rigid motifs as the linear linker with a strong preference for axial coordination from N- or O-donating atoms but also their characteristic physical properties: the strong electron-donating ability and their spin states (S = 1) with two unpaired spins on the degenerated π^* orbitals,[7] which could show a significant interaction with a π-orbital of the aromatic molecules on the axial position. From these advantages of our strategy, the two-dimensional honeycomb network is constructed through a molecular self-assembled process.‡



Scheme 1 Synthetic strategy for a 2-D Kagomé lattice.

X-Ray crystal structure analysis§ revealed that **1** crystallized in a triclinic crystal system with an inversion center at the midpoint of the Ru–Ru bond. An asymmetric unit consists of one triazine molecule and three ruthenium moieties, therefore, each ruthenium atom possesses a distinct coordination environment. A view of the fundamental building unit of **1** is shown in Fig. 1. All three nitrogen atoms of triazine are coordinated to independent $\mathrm{Ru_2}$ molecules, the result of which is a plane and flawless hexagonal honeycomb network on the (2,2,2) plane (Fig. 2(a)). Within the layer, the ring diagonal distance is *ca.* 20 Å and each hexagonal cavity is filled with twelve phenyl groups of the $\mathrm{Ru_2}$ unit. The two-dimensional honeycomb layers are stacked in parallel in ABC

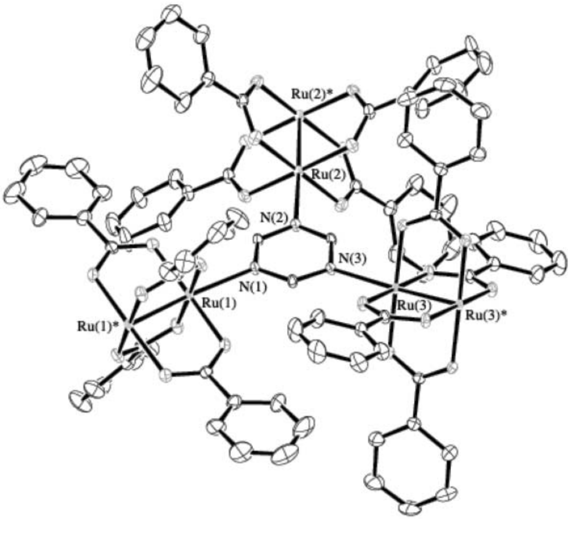


Fig. 1 Structure of one triazine molecule coordinated to three independent $[\mathrm{Ru^{II}}_2(\mathrm{O_2CPh})_4]$ units in **1** (ORTEP representation). Selected bond distances (Å) and angles (°): Ru(1)–Ru(1)* 2.2661(6), Ru(2)–Ru(2)* 2.2649(6), Ru(3)–Ru(3)* 2.2654(7), Ru(1)–N(1) 2.329(3), Ru(2)–N(2) 2.324(3), Ru(3)–N(3) 2.333(3), Ru(1)*–Ru(1)–N(1) 177.14(9), Ru(2)*–Ru(2)–N(2) 176.52(10), Ru(3)*–Ru(3)–N(3) 175.73(9).

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b415843a/
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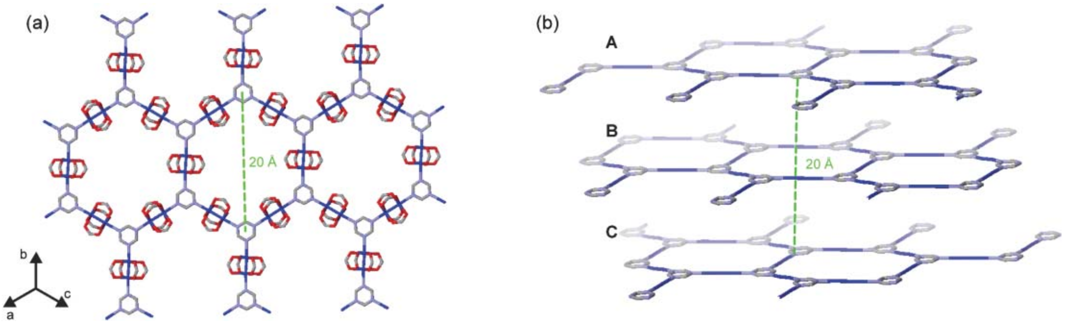

Fig. 2 (a) A view from above the honeycomb 2-D (6,3) net structure of **1**. The ring diagonals are *ca.* 20 Å. The phenyl groups of the Ru_2 cores are omitted for the sake of clarity. (b) The plane 2-D layer architectures of **1** are stacked in parallel in ABC alternations. The distance between each layer is *ca.* 10 Å. The benzoates of the Ru_2 cores are omitted for the sake of clarity. The ruthenium, oxygen, carbon and nitrogen atoms are denoted by blue, red, gray and sky blue, respectively.

alternations as shown in the rhombohedral graphite sheets arrangement (Fig. 2(b)).

The Ru–Ru distances of 2.2649(6)–2.2661(6) Å correspond to those of typical paddlewheel diruthenium complexes.[8] The Ru–N distances of 2.324(3)–2.333(3) Å are significantly shorter than that of $[\{Ru^{II}_2(O_2CCF_3)_4\}(\text{phenazine})]_n$ (2.425(2) Å),[6b] though the trifluoroacetate derivatives usually provide the shorter distances between the dimetal core and the axial ligand due to the strong electron-withdrawing properties of trifluoroacetate.[9] These obviously shorter Ru–N distances indicate that the π-back donation from the dπ* orbital to the pπ* orbital should stabilize the coordination of Ru–N. In order to avoid the steric hindrance among the phenyl groups located on the hexagonal cavities, each Ru_2 molecule turns with rotational angles between the carboxylate plane and the triazine plane of 24.0, 20.1, and 36.2° for Ru(1), Ru(2), and Ru(3) units, respectively. In spite of their rotational angles, dπ*–pπ* orbitals are fully overlapped because of the degenerated π* orbitals of the Ru^{II}_2 core.

The temperature dependence of the magnetic susceptibility of **1** measured between 1.8 K and 300 K is shown in Fig. 3. The overall magnetic behavior is very similar to that of the parent $[Ru^{II}_2(O_2CR)_4]$ compounds.[10] Although the nature of the ground state of such compounds has been a matter of debate over the years, it is reasonable to state that the Ru^{II}_2 complexes are doubly bonded species with the π* and δ* HOMO orbitals being nearly degenerate. The ground state electronic configuration is $(\pi^*)^2(\delta^*)^2$ which is an $S = 1$state with an appreciable zero-field splitting (ZFS). Compound **1** exhibits a continuous decrease of χT at lower temperatures from 1.365 $cm^3\ K mol^{-1}$ at 300 K to 0.015 $cm^3\ K mol^{-1}$ at 1.8 K, which is primarily due to the ZFS arising from the $^3A_{2g}$ ground state.

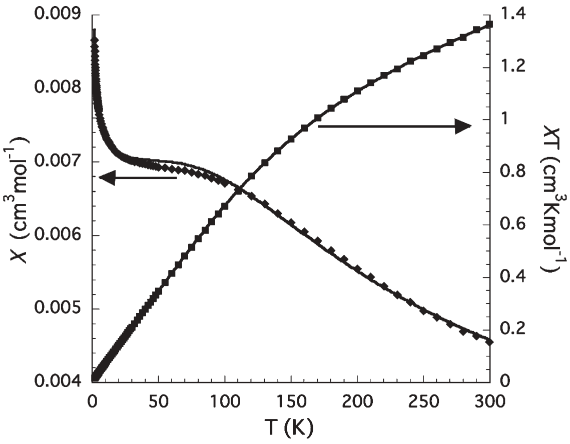

Fig. 3 Temperature dependence of χ and χT of **1** per Ru_2 unit. The solid line represents the theoretical fit.

The theoretical fitting is performed with a previously reported equation[6b] (see also the ESI†) which contains the following valuable parameters: g value,[11] the magnitude of ZFS (D), a temperature independent paramagnetic contribution (TIP), superexchange interaction in the layer considered by the molecular field approximation (zJ) and an extrinsic paramagnetic impurity (ρ) of a ubiquitous $Ru_2^{II,III}$ species ($S = 3/2$).[12] The theoretical fitting led to $g = 2.0$, $D = 254\ cm^{-1}$, $zJ = -2.2\ cm^{-1}$, TIP $= 1.6 \times 10^{-3}\ cm^3\ mol^{-1}$, and $\rho = 0.24\%$. The negative zJ value means that the antiferromagnetic interaction based on the spin delocalization mechanism between the dπ*–dπ* orbitals of the Ru_2 cores through the pπ* orbital is dominant rather than the spin polarization mechanism giving the ferromagnetic interaction between them. Such spin structure can give spin-frustration in the 2-D network, however, it has not been clearly observed because of the large ZFS contributions of the Ru^{II}_2 cores.

In conclusion, we have presented the rational design and synthesis of a novel honeycomb (6,3) network containing antiferromagnetically interacted paramagnetic centers arranged on a Kagomé lattice. The syntheses of the analogous structure of $Ru_2^{II,III}$ having smaller ZFS and its mixed-valence analogue with Ru^{II}_2 and $Ru_2^{II,III}$ are now in progress.

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Notes and references

‡ All syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. $[Ru_2(O_2CPh)_4(THF)_2]$ was prepared according to the literature procedure.[13] *Synthesis for* **1**: a CH_2Cl_2 solution of $[Ru_2(O_2CPh)_4(THF)_2]$ (29.8 mg, 0.036 mmol) was placed in a Schlenk tube,

and layered with a toluene solution that contained an excess of triazine (25.0 mg, 0.308 mmol), which gave red hexagonal plate crystals. Elemental analysis calcd for $C_{90}H_{66}N_6O_{24}Ru_6$: C 48.65, H 2.99, N 3.78, found: C 49.48, H 3.23, N 3.78.

§ *Crystal data for* **1**·$2CH_2Cl_2$: $C_{92}H_{66}Cl_4N_6O_{24}Ru_6$, $M = 1193.90$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.993(4)$, $b = 14.312(5)$, $c = 14.497(3)$ Å, $\alpha = 69.87(5)$, $\beta = 71.17(4)$, $\gamma = 73.15(5)^\circ$, $V = 2527.4(1)$ Å^3, $Z = 1$, $D_c = 1.569$ g cm^{-3}, $\mu = 1.051$ mm^{-1}. Data collection ($6.0 < 2\theta < 55^\circ$) was performed at 243 K on a Rigaku CCD diffractometer (Mo-Kα = 0.7107 Å). The structure was refined on F^2 and converged for 9810 unique reflections with $I > 2\sigma(I)$ and 580 parameters to give $R1 = 0.0607$ and $wR2 = 0.2160$. Large residual electron density peaks (*ca.* 4 e$^-$ Å^{-3}) were located near Ru(1), Ru(2), and Ru(3) atoms in the unit cell. CCDC 254230. See http://www.rsc.org/suppdata/cc/b4/b415843a/ for crystallographic data in .cif or other electronic format.

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11 In order to minimize the usual problem of refining many parameters (g, D, zJ, TIP, ρ), the g value is fixed as $g = 2.0$.

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