Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rational Synthesis of Two-Dimensional Honeycomb Structure Based on Paramagnetic Paddlewheel Diruthenium Complex

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Experimental Section

Chemicals and reagents

The chemicals used were of reagent quality. Reactions were carried out under a dry dinitrogen atmosphere. Dichloromethane and toluene were distilled under N_2 before use by the conventional method. $[Ru_2(O_2CPh)_4(THF)_2]$ was synthesized by the our previously reported method (ref 13).

The preparation of $[\{Ru_2(O_2CPh)_4\}_3(trz)_2]$ is described in the main text.

Physical measurements

The magnetic susceptibility measurements were carried out with the use of a Quantum Design SQUID magnetometer MPMS. Polycrytalline sample (26.055 mg) was used in the range 1.8–300K at 500 G. The data were corrected for the sample holder from experimental data and for the diamagnetic contribution of the sample using Pascal's constants.

X-ray crystallographic analysis

Measurements were conducted on Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The data were collected up to 55º. The structures were solved by Patterson methods (DIRDIF92/PATTY) and expanded using Fourier techniques. Non-hydrogen atoms except solvents were refined anisotropically, whereas solvent molecules were refined isotropically. Hydrogen atoms were introduced as fixed contributors. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

Theoretical fitting of the temperature dependence of the magnetic susceptibility

The magnetic susceptibility for $S = 1$ centers with ZFS and a temperature independent paramagnetic (TIP) contribution can be expressed as in eqn. (1)

$$\chi = \frac{2Ng^2\beta^2}{3k_BT}\frac{e^{-x}+\frac{2}{x}(1-e^{-x})}{1+2e^{-x}} + \text{TIP} \qquad (1)$$

where $x = D/k_BT$ and D is the magnitude of ZFS. Superexchange in these layers can be considered by the molecular field approximation (2) where z is the number of neighbors

$$\chi' = \frac{\chi}{1-(\frac{2zJ}{Ng^2\beta^2})\chi} \qquad (2)$$

and J the magnitude of the intermolecular interaction, which is assumed to be interaction magnetic interactions of the $S = 1$ centers. The abrupt increase of χ at low temperature that can be observed in Fig. 3 is attributed to an extrinsic paramagnetic impurity (ρ) of a ubiquitous $Ru_2^{II,III}$ species ($S = 3/2$). This is taken into account by eqn. (3). The value of g_{imp} is assumed to be 2.0 by convention. In order to minimize the usual problems of refining many parameters (g, D, zJ, TIP, ρ), the least–squares calculation was performed in a parameter range of $g = 2.0$ based on previously reported magnetic data. The best fitting parameters for the magnetic behavior of **1** were determined from eqn. (3). The best χT fitting was described in the main text.

$$\chi'' = (1-p)\chi' + p(\frac{5Ng_{imp}{}^2\beta^2}{4k_BT}) \qquad (3)$$