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Molecule-based magnets with diruthenium building blocks in two and three dimensions

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Several molecule-based magnets can be constructed from diruthenium tetracarboxylate building blocks. We study two such materials with antiferromagnetic interactions between Cr(III) ions and diruthenium paddle-wheel complexes. While collinear magnetic ordering in the three-dimensional compound is frustrated by the easy-plane anisotropy on the diruthenium paddle wheel, the two-dimensional compound has a collinear ferrimagnetic ground state because of the dominant coupling between the Cr ions and the in-plane diruthenium species.

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Molecule-based magnets provide the unprecedented opportunity to design and construct multifunctional materials with a wide variety of physical behavior.[1,2] Due to their different topologies, molecule-based magnets constructed with the same molecular building block may exhibit quite different magnetic behavior. For example, the oxalate ion $C_2O_4^{2-}$ bridging transition-metal ions M(II) and M'(III) provides the building block for two- and three-dimensional (2D and 3D) M(II)M'(III) bimetallic oxalates with rather different properties.[3] Whereas the 3D Fe(II)Fe(III) bimetallic compounds may exhibit magnetic compensation due to the spin-orbit coupling on the Fe(II) sites, the 2D Fe(II)Fe(III) compounds show no signs of magnetic compensation despite the same crystal-field environment. The diruthenium paddle-wheel complex $Ru_2(O_2CX)_4$ (X=Me or tBu) bridging transition-metal ions M(III) (M=Co, Fe, or Cr) has also been used to synthesize both 2D[4] and 3D[5–8] materials. Compared to a 3D compound with H_{cr}=470 Oe and T_c=33 K, a 2D compound with M=Cr has a much larger coercive field H_{cr}=2 T and a significantly higher transition temperature T_c=39.5 K.[4]

The mixed-valent $Ru(II/III)_2$ complex has total spin S=3/2 with easy-plane anisotropy in the plane that bisects the two Ru ions. In earlier work,[9] we studied the metamagnetic transition in a 3D $Cr(Ru_2)_3$ compound with interpenetrating lattices. In this Rapid Communication, we compare the properties of 2D and 3D $Cr(Ru_2)_3$ compounds. Whereas collinear magnetic order in the 3D cubic compound was frustrated by the easy-plane anisotropy on the Ru_2 complexes, a collinear ferrimagnetic ground state is obtained for the 2D compound due to the dominance of the in-plane coupling.

An in-plane xy layer of the 2D structure is shown in Fig. 1(a). Compared to the 3D structure, the in-plane Ru_2 complexes are rotated by 30° about the z axis. Each Cr(III) ion with spin S=3/2 is also coupled to another Ru_2 complex alternatively in the $\pm z$ directions, as shown in Fig. 1(b). So if one Cr ion is coupled to a Ru_2 complex above the plane, then its four neighboring Cr ions are coupled to Ru_2 complexes below the plane. Because the protruding Ru_2 species are chemically capped by oxygen atoms, neighboring 2D layers are weakly magnetically coupled by dipolar interactions.

In a single lattice of the 3D compound, the Cr(III) ions lie at the corners of a cube and the Ru_2 easy plane is perpendicular to the axis joining the Ru_2 complex to the neighboring Cr(III) ions. Although the single-lattice 3D compound is amorphous,[4] a 3D compound with interpenetrating sublattices has been prepared. In this compound, a second identical lattice occupies the open space of the first lattice resulting in a body-centered cubic structure. The interpenetrating-lattice compound exhibits an unusual "wasp-waisted" hysteresis loop that is caused by the weak antiferromagnetic (AF) coupling between sublattices.

Due to the paddle-wheel molecular environment, each

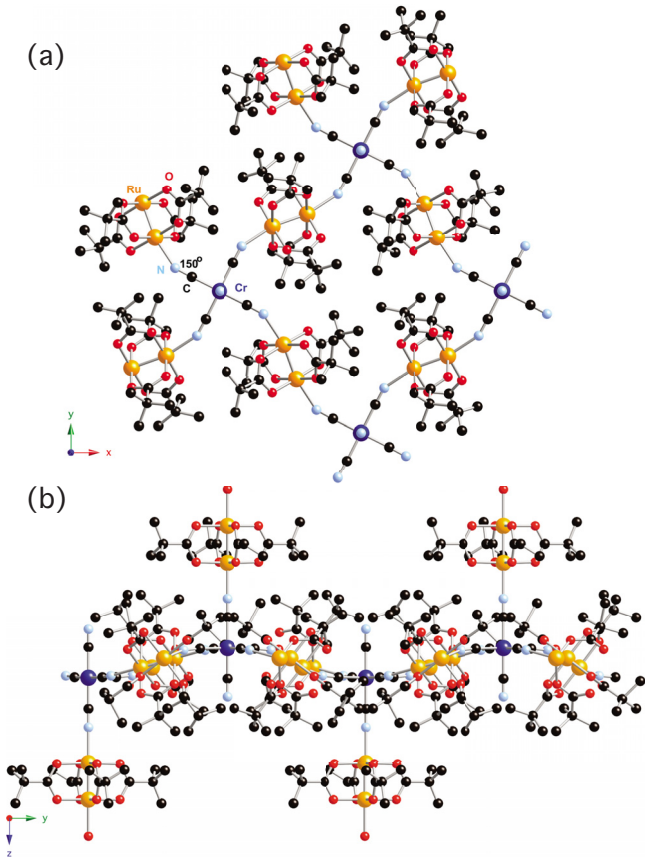

FIG. 1. (Color online) (a) The 2D layer structure with in-plane diruthenium complexes rotated by 30° in the xy plane and (b) a sideview of a single layer of the 2D structure. Hydrogen atoms are not shown for clarity.

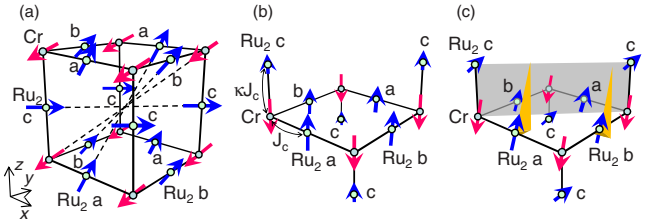

FIG. 2. (Color online) The magnetic ground states of (a) the 3D compound with net moment in the [111] direction [for classical spins with infinite anisotropy (Ref. 9)], (b) the collinear FEM ground state of the 2D compound showing the z exchange parameter κ, and (c) the noncollinear CAF ground state of the 2D compound.

Ru_2 moment experiences a strong easy-plane anisotropy with $D \approx 8.6$ meV.[10,11] Most properties of the 3D interpenetrating-lattice compound can be explained by a simple model[9] with strong easy-plane anisotropy D on the Ru_2 sites, AF intrasublattice exchange $J_c \approx 1.7$ meV between neighboring Cr and Ru_2 sites on each sublattice, and a weak AF intersublattice exchange $K_c \approx 2.8 \times 10^{-3}$ meV between moments on the two sublattices.

For classical spins with infinite anisotropy, the Ru_2 spins are confined to the easy planes and the predicted magnetic ground state of a single lattice of the 3D compound is shown in Fig. 2(a).[9] Collinear AF order is frustrated by the easy-plane anisotropy on each Ru_2 complex. Instead, the magnetic ground state is noncollinear, with the Cr spin pointing along one of the four diagonals of the cube and the sum of the Ru_2 a, b, and c spins (along the x, y, and z axes, respectively) pointing opposite. Accounting for the two orientations of the moment along each diagonal, there are eight domains in zero field.

To evaluate the ground state of the 2D compound, we allow the coupling κJ_c along the z direction between Cr and the protruding c Ru_2 complexes to be different than the coupling J_c within the xy plane between Cr and the a or b Ru_2 complexes. As discussed further below, the parameter κ can possibly be controlled by strain or pressure. Although the absence of a metamagnetic transition in the 2D compounds implies that the layers are ferromagnetically coupled below T_c, we neglect that weak dipolar coupling in the following discussion. The rotation of the a and b Ru_2 easy planes around the z axis can be trivially removed by working in a spin reference frame that is similarly rotated by 30°. The magnetic unit cell contains four spins: the a, b, and c Ru_2 spins and a Cr spin.

In an external field $\mathbf{H}=H\mathbf{m}$, the mean-field (MF) energy at each Ru_2 $k=a$, b, or c site is

$$\epsilon_k = -\mathbf{h}_k \cdot \mathbf{S}_k + D(\mathbf{S}_k \cdot \mathbf{n})^2 \tag{1}$$

($\mathbf{n}=\mathbf{x}$, $\mathbf{y}$, or $\mathbf{z}$ for $k=a$, b, or c) and the MF energy at each Cr site is $\epsilon_{\mathrm{Cr}}=-\mathbf{h}_{\mathrm{Cr}}\cdot\mathbf{S}_{\mathrm{Cr}}$. The effective fields $\mathbf{h}_k$ and $\mathbf{h}_{\mathrm{Cr}}$ are given by

$$\mathbf{h}_a = \mathbf{h}_b = -2J_c\mathbf{M}_{\mathrm{Cr}} + 2\mu_B\mathbf{H}, \tag{2}$$

$$\mathbf{h}_c = -\kappa J_c\mathbf{M}_{\mathrm{Cr}} + 2\mu_B\mathbf{H}, \tag{3}$$

$$\mathbf{h}_{\mathrm{Cr}} = -J_c(2\mathbf{M}_a + 2\mathbf{M}_b + \kappa\mathbf{M}_c) + 2\mu_B\mathbf{H}, \tag{4}$$

where $\mathbf{M}_k$ are the average Ru_2 spins and $\mathbf{M}_{\mathrm{Cr}}$ is the average Cr spin. Since each Ru_2 complex has spin 3/2, the eigenvalues of ϵ_k are obtained by diagonalizing a 4×4 matrix in spin space.[11] The robust anisotropy of the 2D $Cr(Ru_2)_3$ compound, demonstrated below, justifies the application of MF theory for a 2D system.

Within MF theory, the effective fields for a single lattice of the 3D compound are recovered by taking $\kappa=2$ so that there are effectively *two* Ru_2 c complexes for each Cr ion and *two* Cr ions for each Ru_2 c complex. Therefore, our MF treatment includes the 3D compound as a special case. For $\kappa=1$, the out-of-plane coupling in the 2D compound is the same as the in-plane coupling. For $\kappa<1$, the protruding Ru_2 complexes are more weakly coupled to the Cr ions than the Ru_2 complexes within the 2D layer.

The set of self-consistent equations for the order parameters $\mathbf{M}_k(T)$ and $\mathbf{M}_{\mathrm{Cr}}(T)$ are easily solved numerically. Since the $T=0$ Cr spin $M_{\mathrm{Cr}}(0)$ is always fully saturated at 3/2, there are 9 self-consistent relations with 9 unknown parameters in the presence of a magnetic field at $T=0$. In zero field, the collinear ferrimagnetic (FEM) and noncollinear canted AF (CAF) ground states of the 2D compound are sketched in Figs. 2(b) and 2(c). In the CAF state, the Cr spin bends away from the $-z$ direction along the diagonal in the xy plane. The Cr spin $\mathbf{M}_{\mathrm{Cr}}$ points opposite $\mathbf{M}_a+\mathbf{M}_b+(\kappa/2)\mathbf{M}_c$. As $\kappa\rightarrow2$, this state evolves into the ground state of the 3D compound in Fig. 2(a), where the Cr spin points opposite the total of the a, b, and c Ru_2 spins $\mathbf{M}_a+\mathbf{M}_b+\mathbf{M}_c$. In the FEM state, the Cr spin points down and the Ru_2 spins point up (or visa versa). Because of the easy-plane anisotropy, the c Ru_2 spin has an amplitude close to 0.5 whereas the amplitudes of the a and b Ru_2 spins are about twice as large, but still smaller than the fully saturated Cr spin.

After evaluating the temperature-dependent order parameters, we obtain the phase diagram in Fig. 3, where D/J_c is the relative strength of the anisotropy. When $\kappa=2$, the CAF phase is stable below T_c for all D/J_c. For $\kappa>1.1$, the CAF phase is stable for all D/J_c at $T=0$. As κ decreases below 1.1, the CAF phase rapidly shrinks to a region around the origin. For a fixed $\kappa<2$ and sufficiently small D/J_c, a CAF to FEM phase transition occurs at the transition temperature $\tilde{T}_c<T_c$. Since the FEM phase is absent when $\kappa=2$, $\tilde{T}_c=T_c$ in that case. The transition temperatures T_c from a FEM ($\kappa<2$) or CAF ($\kappa=2$) to a paramagnet (dashed curves) are relatively insensitive to κ.

The magnetic moment M_{av} in Fig. 4 is obtained by averaging $\mathbf{M}_{tot}=\mathbf{M}_a+\mathbf{M}_b+\mathbf{M}_c+\mathbf{M}_{\mathrm{Cr}}$ over all orientations $\mathbf{m}$ of a polycrystalline sample in a vanishingly small field. Hence,

$$M_{av} = \frac{1}{2}\{|M_{tot}^x| + |M_{tot}^y| + |M_{tot}^z|\}. \tag{5}$$

For the FEM ground state in Fig. 2(b), $M_{av}=M_{tot}/2$; for the 3D ground state in Fig. 2(a), $M_{av}=\sqrt{3}M_{tot}/2$. The transition between CAF and FEM states is clearly seen in Fig. 4 as a kink in the average moment for $D/J_c=4$ and $2>\kappa>1.02$. The absence of such a kink in the measured magnetization implies that the 2D compound remains in a FEM state, at

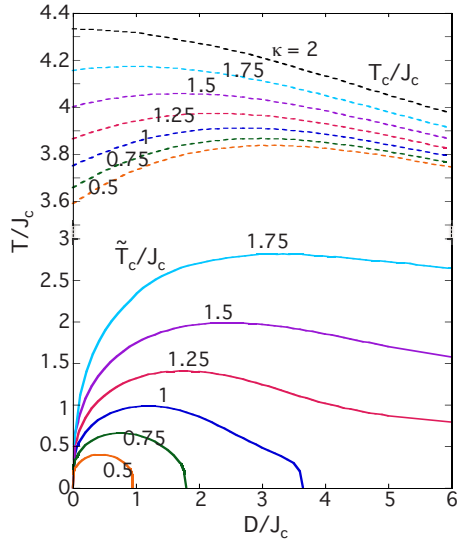

FIG. 3. (Color online) The transition temperatures T_c (dashed) and $\tilde{T}_c$ (solid) versus D/J_c for several values of κ. The CAF phase is stable for $T<\tilde{T}_c$ and the FEM phase is stable for $\tilde{T}_c<T<T_c$. For a 3D compound with $\kappa=2$, $\tilde{T}_c=T_c$ so only a dashed curve appears.

least down to 2 K. This places severe constraints on the anisotropy D and z exchange parameter κ.

To estimate the exchange J_c in the xy plane, notice that the transition temperature $T_c \approx 39.5$ K of the 2D compound is about 25% higher than the transition temperature $T_c \approx 33$ K of the 3D compound.[4] Based on Fig. 3, this suggests that J_c in the 2D compound is at least 25% higher than in the 3D compound. So we estimate that $J_c \approx 2.1$ meV. The larger coupling in the 2D compound is produced by the *t*Bu group, which has electron density closer to the Ru ions than does the Me group. Compared to Me in the 3D compound, *t*Bu raises the levels of the $4d$ electrons in the Ru_2 core, thereby enhancing the superexchange interaction with the neighboring Cr ions. With this enhanced value of J_c, we estimate that $D/J_c \approx 4$.

Because of the broken tetragonal crystal-field symmetry

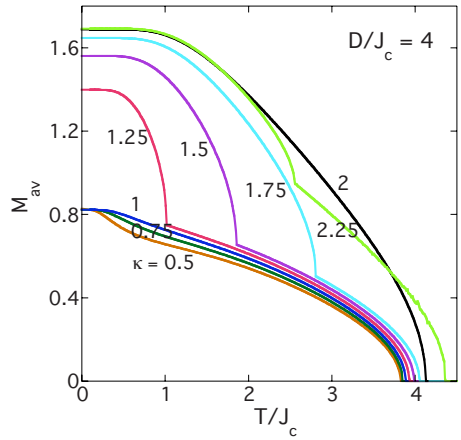

FIG. 4. (Color online) The temperature dependence of the zero-field average moment M_{av} for $D/J_c=4$ and several values of κ. The absence of a kink in the observed 2D magnetization due to the CAF-FEM transition suggests that $\kappa<1$.

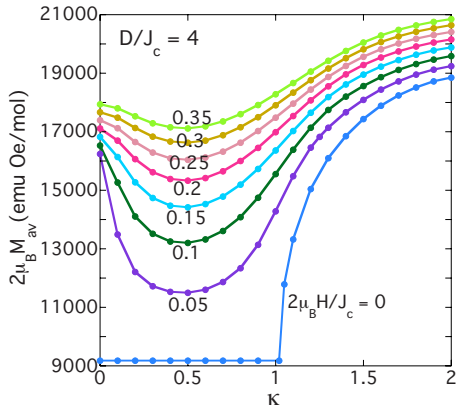

FIG. 5. (Color online) The $T=0$ average magnetization $2\mu_B M_{av}$ versus κ for $D/J_c=4$ and several values of the field $2\mu_B H/J_c$.

about the protruding Ru_2 complexes and the 30° rotation of the in-plane Ru_2 complexes, the z coupling κJ_c is not the same as the xy coupling J_c. The z exchange parameter κ can be estimated by comparing the predicted and observed average magnetizations in a field of 5 T. Using $D/J_c=4$, we plot the average magnetization $2\mu_B M_{av}$ versus κ for several fields $2\mu_B H/J_c$ in Fig. 5. Note that M_{av} always has a minimum at $\kappa=0.5$ for any nonzero field. For $H=0$, the flat region with $\kappa<1.02$ corresponds to the FEM phase. The predicted zero-field magnetization of $2\mu_B M_{av} \approx 9200$ emu Oe/mol in the FEM phase is higher than the observed remanent magnetization of 7500 emu Oe/mol[4] at 2 K. This difference is probably caused by the polycrystalline nature of the sample.[12]

With $J_c=2.1$ meV, a field of 5 T corresponds to $2\mu_B H/J_c=0.27$. So the observed average magnetization of 16 200 emu Oe/mol (Ref. 4) at 5 T requires $\kappa \approx 0.5$. While a larger coupling constant J_c for the 2D compound would allow a somewhat higher value of κ, Fig. 3 indicates that $\kappa=1$ produces a CAF ground state for $D/J_c<3.65$. Since the 2D compound shows no signature of the CAF-FEM transition with increasing temperature, it seems likely that $\kappa<1$ or that the z coupling is smaller than the in-plane coupling. We expect that future *ab initio* calculations will be able to confirm this prediction.

It may be possible to control the frustration induced by the z coupling by applying pressure to 2D compounds or strain to 3D compounds. When $\kappa>2$, the anisotropy in the protruding Ru_2 complexes will dominate the physical behavior just below T_c and create a coplanar CAF phase with moments confined to the xy plane. With increasing temperature, the transition from the CAF phase with components in all three directions to the coplanar CAF phase will appear as a kink in the average magnetization, seen in Fig. 4 for $\kappa=2.25$. So uniaxial compression applied to a 3D compound will induce either a FEM phase ($\kappa<2$) or a coplanar CAF phase ($\kappa>2$) close to T_c. By forcing the layers closer together, pressure applied to a 2D compound will raise κ, increasing both the transition temperature and the average magnetization at a fixed temperature and field. With sufficient pressure to raise κ above 1.02, the 2D CAF phase will be stabilized at low temperatures.

In order to qualitatively explain the difference in coercive fields for the 2D and 3D compounds, we evaluated the en-

ergy barrier between preferred orientations of the total magnetic moment. With the Cr moment forced away from its equilibrium position, the Ru_2 spins are then required to minimize the energy. In the 3D compound with $D/J_c=5$, the energy barrier for rotating the moment from the $[111]$ to the $[11\bar{1}]$ directions is $0.16J_c$ per Cr atom in one sublattice. For the 2D compound, the energy barrier for rotating the moment from the $[001]$ to the $[00\bar{1}]$ directions is $1.21J_c$ per Cr atom. So accounting for the 25% enhancement of J_c in the 2D compound, the 2D energy barrier is roughly 10 times higher than the 3D energy barrier. Since the coercive field H_{cr} of the 2D compound is about 40 times higher than that of the 3D compound, this explanation may not be complete.

To conclude, we have examined how the dimensionality affects the properties of molecule-based magnets built with diruthenium paddle-wheel complexes coupling hexacyanometallates. The estimated parameters for the 2D and 3D compounds are summarized in the Table I. While the frustration produced by the easy-plane anisotropy stabilizes a noncollinear ground state with net moment along a cubic diagonal in the 3D compound, the presence of only one protruding Ru_2 complex per Cr ion in the 2D compound stabilizes a collinear ferrimagnetic ground state. Pressure and strain may be able to control the magnetic frustration created by the z coupling and modify the properties of these compounds. We hope that this Rapid Communication can provide a roadmap for future experimental studies of the 2D and 3D $Cr(Ru_2)_3$ compounds.

TABLE I. Observed and estimated parameters for 2D and 3D $Cr(Ru_2)_3$ compounds. D and J_c in meV.

	$T_c(K)$	$H_{cr}(T)$	D	J_c	κ
2D	39.5	2	8.6	2.1	<1
3D	33	0.05	8.6	1.7	2

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