Inorganic Chemistry
Communication
pubs.acs.org/IC

Peculiar Field-Dependent Magnetic Behavior of Cyano-Bridged Coordination Polymer $Er(H_2O)_4[W(CN)_8]$

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S *Supporting Information*

ABSTRACT: The two-dimensional cyano-bridged coordination polymer $Er(H_2O)_4[W(CN)_8]$ exhibits a magnetic transition at 12 K and an unusual field-dependent transition from short-range to ferromagnetic ordering.

The design and study of two- and three-dimensional molecule-based magnets exhibiting long-range magnetic ordering have attracted a great deal of attention, and numerous ferro- or ferrimagnets with various critical temperatures have been reported in the last 40 years.[1] Comparatively, a much reduced amount of molecular systems exhibits magnetic-field-induced transitions in which one magnetic behavior may be switched to another by applying a critical field and thus can be controlled by external stimuli. Such behavior usually occurs in two-dimensional systems, presenting ferromagnetic interactions between the spin carriers and an antiferromagnetic or canted spin orientation between the planes,[2] or, more rarely, in three-dimensional compounds with spin noncolinearity. Most previously investigated compounds exhibit a crossover from antiferro- or ferrimagnetic ordering to a ferromagnetic state[3] (i.e., metamagnet), and only a handful of cases show more complex behavior with a field-induced transition from a paramagnetic state or weak ferromagnetic ordering to a superparamagnetic regime[4] or from spin-glass to paramagnetic behavior.[5]

One of the promising systems in the field of molecular magnetism are cyano-bridged networks, in which several examples of field-induced behavior in two- or three-dimensional systems based on hexa-,[2,6] hepta-,[7] or tetracyanometallates[2c] associated with bivalent transition-metal ions or lanthanides have been reported. To the best of our knowledge, a field-induced behavior in the octacyanometallate systems has never been observed despite the high structural diversity of the obtained networks.[8] Recently, we explored the potential of the association of the octacyanometallate building blocks with lanthanides and investigated a new family of two-dimensional coordination polymers $Ln(H_2O)_5[M(CN)_8]$ (Ln = Tb, Sm, Gd; M = Mo, W).[9] In most cases, these compounds present a long-range ferro- or ferrimagnetic ordering at low temperature (below 3 K). In the present Communication, we report a new cyano-bridged coordination polymer of this family $Er(H_2O)_4[W(CN)_8]$ obtained by the combination of the octacyanotungstate building block with a Er^{3+} ion, which has a doubly degenerate and high-magnitude ground state ($J = {}^{15}/_2$). The resulting coordination network presents a two-dimensional crystal structure different from those previously reported by Kepert et al.[11] This compound exhibits a magnetic transition at 12 K and an unprecedented field-induced magnetic behavior.

The crystals of $Er(H_2O)_4[W(CN)_8]$ were obtained by the slow diffusion of diethyl ether into an acetonitrile solution of the precursors $[(N(C_4H_9)_4]_3[W(CN)_8]\cdot 2H_2O$[10] and $[Er(H_2O)_5](NO_3)_3$ (see the Supporting Information, SI). Single-crystal X-ray diffraction studies unequivocally show that this compound crystallizes in the tetragonal space group $P4/nmm$ with $a = b = 10.45950(10)$ Å and $c = 7.77690(10)$ Å. The structure may be viewed as an assembly of two-dimensional cyano-bridged undulated layers placed in the *ab* plane of the unit cell and formed by the alternation of two crystallographically independent coordination polyhedra, slightly distorted $\{ErN_4O_4\}$ square antiprisms, and $\{WC_8\}$ dodecahedra (Figures 1 and S1 in the SI). The shortest intermetallic Er···W distances within the layer are 5.6920(1) and 5.6934(1) Å, respectively, while all remaining intermetallic distances among identical polyhedra are the length of either the *a* or *b* axis of the unit cell. The structural feature ultimately permits the existence of strong and highly directional O−H···N hydrogen bonds between layers mediating the crystal packing of the compound. In contrast with the high disorder observed in the previously reported $Ln(H_2O)_5[M(CN)_8]$ materials in which the lanthanide center is nonacoordinated, we believe that this robust structural pattern can explain the absence of disorder in $Er(H_2O)_4[W(CN)_8]$ because these hydrogen bonds are (i) bifurcated in nature, (ii) very strong, and (iii) highly directional [$d_{O\cdots N}$ is 2.8397(19) Å, while the interaction angle is greater than 170° (Tables S2 and S4 in the SI)]. Ultimately, there are no degrees of freedom for thermal disorder. This close packing between adjacent layers promotes relatively short intermetallic distances across the layers: the Er···W and W···W (or Er···Er) distances are 7.6113(2) and 7.77690(10) Å. Even though this compound shares identical general structural features with $Er(H_2O)_4[W(CN)_8]$ reported by Kepert et al.,[11] we note that our determination clearly shows no evidence for the existence of structural disorder associated with the terminal cyanide ligands. Powder X-ray diffraction and elemental analysis confirm that only one single phase is obtained during the synthesis (Figure S2 in the SI).

Received: November 21, 2011
Published: May 31, 2012

dx.doi.org/10.1021/ic2024988 | *Inorg. Chem.* 2012, 51, 6425−6427

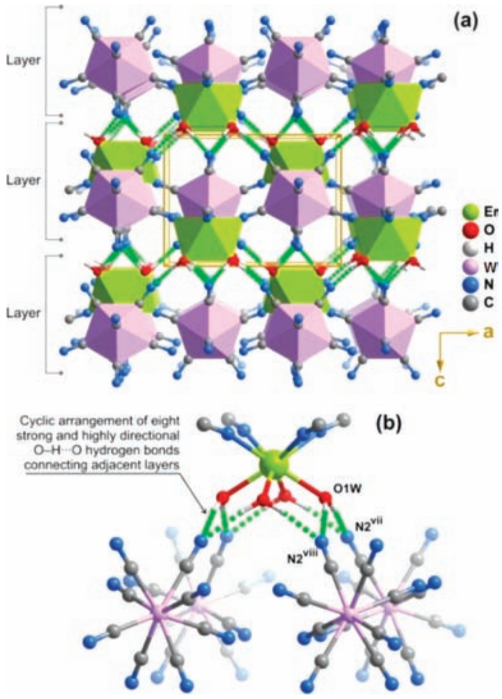

Figure 1. (a) Mixed polyhedral and ball-and-stick representation of the crystal packing of $Er(H_2O)_4[W(CN)_8]$ viewed in perspective along the [010] direction of the unit cell. $O_{water}-H\cdots N_{terminal\ CN}$ hydrogen-bonding interactions connecting adjacent layers are represented as dashed green lines. (b) Portion of the crystal packing emphasizing the eight symmetry-related O−H···N hydrogen bonds.

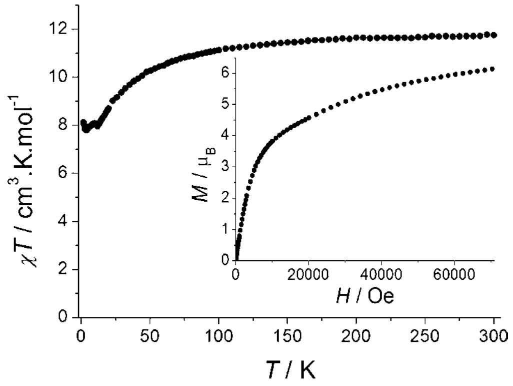

Figure 2. χT vs T plot for $Er(H_2O)_4[W(CN)_8]$ performed under a magnetic field of 1000 Oe. Inset: Field dependence of magnetization performed at 1.8 K.

The magnetic properties of this compound were investigated by using a SQUID magnetometer. Figure 2 shows the temperature dependences of χT performed with an applied field of 1000 Oe. The χT value at room temperature of 11.75 $cm^3 \cdot K \cdot mol^{-1}$ corresponds to the calculated value for noninteracting Er^{3+} ($S = {}^3/_2$, $L = 6$, $g = {}^6/_5$, $C = 11.48$ $cm^3 \cdot K \cdot mol^{-1}$)[17] and W^{5+} ($S = {}^1/_2$, $g = 2.0$, $C = 0.375$ $cm^3 \cdot K \cdot mol^{-1}$) ions. The χT curve decreases as the temperature decreases, reaches a minimum, then abruptly increases, and shows a peak below 12 K. The presence of a minimum may be attributed to the thermal depopulation of the Stark sublevels of the Er^{3+} $^4I_{15/2}$ ground state. The field dependence of magnetization performed at 1.8 K shows a rapid increase of magnetization with the field with a magnetization value of 6.14 μ_B at 70 kOe (Figure 2), corresponding well to the expected one of 6.40 μ_B calculated for ferromagnetic interactions between W^{5+} ($S = {}^1/_2$, $g = 2.0$) and Er^{3+} (5.40 μ_B) ions.[12,13] The $M = f(H)$ curve shows also a hysteretic behavior with a coercive field of 25 Oe at 1.8 K (Figure S3 in the SI). The nature of the magnetic transition in this compound was further investigated by using alternating-current (ac) measurements. The temperature dependence of the in-phase susceptibility, χ', performed at 1 Hz shows an abrupt increase below 12 K, while the out-of-phase component, χ'', increases from zero below 12 K and presents a nonsymmetrical peak with a maximum at 2.42 K (Figure 3).

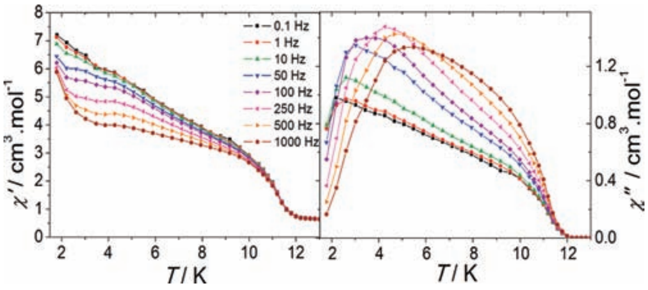

Figure 3. Temperature dependence of the in-phase, χ', and out-of-phase, χ'', components of the ac susceptibility at different frequencies varying from 0.1 to 1000 Hz.

Despite their asymmetric shape, both χ' and χ'' curves present a frequency dependence in its low-temperature part that may be fitted with an Arrhenius law, $\tau = \tau_0 \exp(E_a/k_BT)$ (where τ_0 is the preexponential factor and E_a is the energy barrier) with $\tau_0 = 3.99 \times 10^{-5}$ s and $E_a/k_B = 10.77$ K (Figure S4 in the SI). The obtained τ_0 value is relatively high in comparison with the classical superparamagnetic systems exhibiting slow relaxation of magnetization (10^{-8}–10^{-12} s).[14] Fitting the Cole–Cole plot (χ'' vs χ'; Figure S5 in the SI) yields an α parameter with a relatively high value, 0.237 at 1.8 K, showing that no single relaxation is observed.[15]

The magnetic characterization of the molybdenum analogue, $Er(H_2O)_4[Mo(CN)_8]$, does not indicate similar behavior (Figure S6 in the SI) and therefore rules out the possibility of a single-ion relaxation arising from Er^{3+}. X-ray diffraction measurements on single crystals of $Er(H_2O)_4[W(CN)_8]$ clearly show that no structural disorder can be evidenced in this compound. Thus, the observed frequency dependence may rather be explained by the presence of a noncolinearity of spins or a magnetic disorder at a short distance in the network. However, the hypothesis of spin-glass behavior induced by different sizes of crystallites, surface effects, or an orientation of coherent domains cannot be totally excluded.

The compound also presents an unusual field-dependent behavior. For this reason, the dependence of the in-phase component of the ac susceptibility, which is the first derivative of magnetization, was performed as a function of an applied magnetic field at 1.8 K (500 Hz; Figure 4). This curve shows low- and high-field peaks. The former is the temperature-independent peak at 5 Oe; its intensity decreases as the temperature increases and completely vanishes above 12 K. Such behavior points out the presence of a field-induced spin reorientation. The second high-field peak appears at 1800 Oe; its intensity decreases with the temperature and vanishes at around 5 K. Regarding these results, the temperature dependence of the ac susceptibility has been performed with

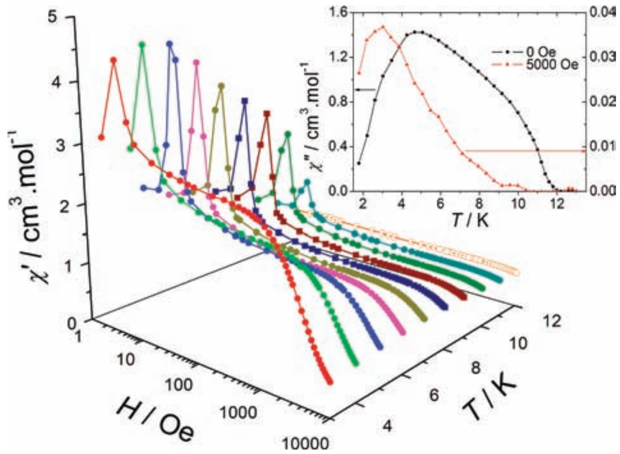

Figure 4. Field dependence of the in-phase, χ', component of the ac susceptibility performed at different temperatures varying from 1.8 to 12 K. Inset: Temperature dependence of the out-of-phase, χ'', ac susceptibility performed at 500 Hz with different fields.

different magnetic fields (inset of Figure 4). The intensities of the χ' and χ'' peaks observed in zero magnetic field decrease as the field increases (from 5 Oe), and the magnetic transition at 12 K completely disappears around 15 Oe. Simultaneously, a new transition at 3.5 K appears with an applied magnetic field higher than 1800 Oe (Figure S7 in the SI). Note that this new field-induced transition is frequency-independent and therefore reflects the presence of long-range magnetic ordering below 3.5 K.

To summarize, the obtained new cyano-bridged coordination network $Er(H_2O)_4[W(CN)_8]$ presents a two-dimensional gridlike structure. In contrast with the compounds $Ln(H_2O)_5[M(CN)_8]$ (Ln^{3+} = Tb, Gd, Eu, Sm), reducing the lanthanide coordination number from 9 to 8 induces a modification of the general packing arrangement, resulting in a strongly hydrogen-bonded three-dimensional network with an increase of the interplane distance. $Er(H_2O)_4[W(CN)_8]$ presents a magnetic transition below 12 K. This is the second highest magnetic transition among the Prussian Blue analogues incorporating lanthanides. The dynamic magnetic properties and the visible absence of structural disorder indicate the presence of a short-range magnetic ordering transition probably originating from magnetic disorder, which may be overcome by applying a relatively small magnetic field. Classical long-range magnetic ordering below 3.5 K appears for higher field. Note that such field-dependent magnetic behavior has never been observed for such a family of compounds. The intrinsic origin of the observed disorder is an interesting open problem that is currently being investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on the synthesis, magnetic properties, and crystallographic studies of $Er(H_2O)_4[W(CN)_8]$ and $Er(H_2O)_4[Mo(CN)_8]$ (technical section detailing the structure solution and refinement procedures, tabulated geometrical data for the metallic coordination environments, and hydrogen-bonding interactions) and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank C. Rebeil (PAC ICGM, France) for magnetic measurements. We are grateful to the University of Montpellier II, CNRS, Fundação para a Ciência e a Tecnologia (FCT, Portugal), for financial support through the R&D Project PDTC/QUI-QUI/098098/2008 (FCOMP-01-0124-FEDER-010785).

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