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Effect of Ligand Substitution on the Interaction Between Anisotropic Dy(III) Ions and ^{57}Fe Nuclei in Fe_2Dy_2 Coordination Clusters

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Supporting Information

ABSTRACT: A series of $[Fe_2Dy_2(OH)_2(teaH)_2(RC_6H_4COO)_6]$ compounds has been synthesized and studied using Mössbauer spectroscopy. It is suggested that the local crystal field of the Dy^{III} centers and the external magnetic field can control their shape anisotropy and thus the interactions between the dysprosium and iron centers.

The magnetic anisotropy of many lanthanide ions can hinder reversal of the molecular magnetic moment, and in recent years there has been increasing interest in incorporating lanthanides in transition-metal magnetic materials in order to modulate their properties.[1] The dominant contribution to the anisotropy in magnetic materials containing lanthanides results from the effects of the crystal field on the rare earth's 4f wave function. Appropriate design of the ligand-field anisotropy makes it possible to design and control this magnetic anisotropy.[2] With angle-resolved single-crystal magnetometry, it is even possible to obtain the orientation of the principal axes of the magnetization of a Dy ion in a low-symmetry environment.[3]

Magnetic susceptibility studies of polycrystalline samples can give only averaged magnetic information regarding the spin orientation, making it necessary to have suitable single crystals available,[3] which is rarely feasible. For systems containing iron, however, the more sensitive technique of ^{57}Fe Mössbauer spectroscopy can be used. This gives information about the local moments at the iron nuclei and the spin-relaxation dynamics. More importantly, information concerning the anisotropy of not only the studied isotope but also elements interacting with this isotope, as well as the relative orientation of the local axes on the elements, can be gained.[4] Furthermore, this method has been shown to be valid for studying polynuclear coordination clusters and does not require single crystals.

In this work, we investigated how ligand substitution influences the direction of the magnetic anisotropy of Dy^{III} ions and how this affects the magnetic interaction between the Dy^{III} ions and the ^{57}Fe nuclei. We studied a family of coordination cluster molecules with different para-substituted benzoate ligands $[Fe_2Dy_2(OH)_2(teaH)_2(RC_6H_4COO)_6]$, where $teaH_3$ is triethanolamine and R = H (**1**), CH_3 (**2**), *t*-Bu (**3**), NO_2 (**4**), or CN (**5**). These compounds have a core motif similar to that of the reported Fe_2Ln_2 coordination clusters.[5] Complexes **1**−**5** crystallize in monoclinic (**1** and **3**) or triclinic (**2**, **4**, and **5**) space groups, with the central cores consisting of a planar Fe_2Dy_2 rhombus (Figure 1). Each Fe_2Dy trinuclear subunit is bridged by a μ_3-OH ion, one of which is above and the other below the plane. Each of the two $teaH^{2-}$ ligands binds in a tetradentate chelate fashion to Dy(1) or Dy(1′), with its protonated alcohol arm binding terminally to the Dy and each of its two deprotonated alkoxide arms bridging the Dy and an adjacent Fe atom. There is also a chelating benzoate group on each Dy atom, and ligation is completed by a syn,syn-bridging benzoate group across each of the four Dy−Fe edges of the rhombus. The Fe and Dy atoms are six- and nine-coordinate, respectively.

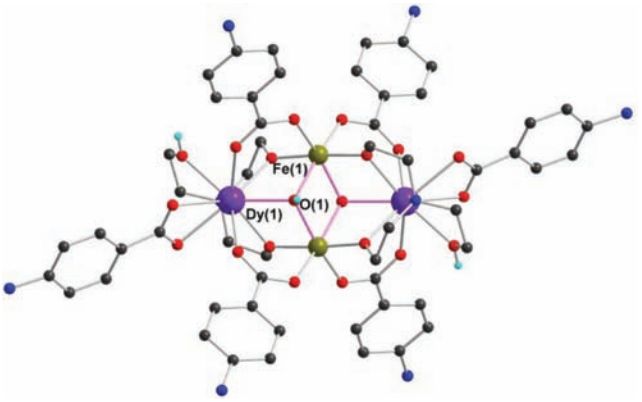

Figure 1. Molecular structure of $[Fe_2Dy_2(OH)_2(teaH)_2(R\text{-}C_6H_4COO)_6]$ (organic H atoms have been omitted for clarity; Dy, violet; Fe, green; O, red; N, blue; C, black, H, turquoise). The blue substituents at the para positions of the benzoic rings are H (**1**), CH_3 (**2**), $C(CH_3)_3$ (**3**), NO_2 (**4**), and CN (**5**). Relevant ranges of distances and angles: Fe(1)−Fe(1′), 3.20−3.27 Å; Fe(1)−O(1), 2.04−2.07 Å; Fe(1)−O(1)−Fe(1′), 102.46−104.26°.

The Mössbauer spectra of polycrystalline compounds **1**−**5** at 3 K are typical of the crossover from intermediate to slow relaxation, exhibiting magnetic hyperfine lines developing below 5 K superimposed on a broad absorption doublet (Γ = 0.57−0.60 mm/s) at the center of the spectrum (Figure 2) with ΔE_Q = 0.95−1.06 mm/s and δ = 0.46−0.48 mm/s (relative to Fe metal at 298 K). The parameters for the central doublet are very similar to those obtained for spectra at higher temperatures (25 or 50 K) (Figure S-4 in the Supporting Information) and those observed for the antiferromagnetically coupled diiron(III) sites of iron−oxo proteins and relevant model compounds.[6] Along the series we observed that the hyperfine field determined from the magnetic onset is not constant but varies from compound to compound from 5.9 to 19.9 T (Figure 2). Analysis of bond lengths and angles around the iron and dysprosium ions gave very similar values for all of the compounds. Moreover, the polyhedral environments of the

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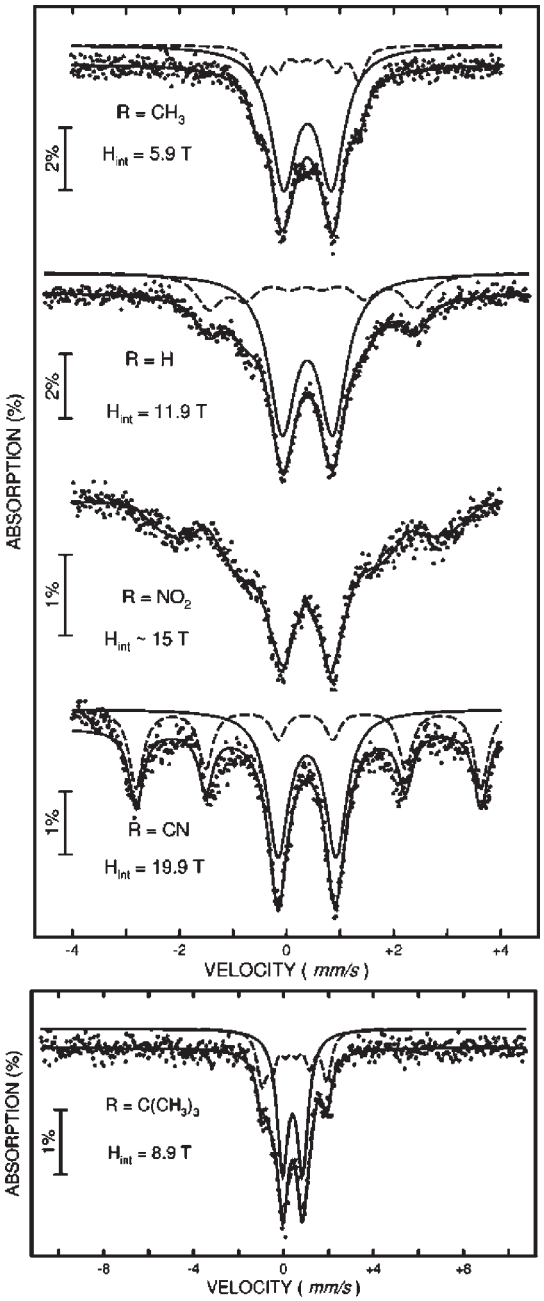

Figure 2. ^{57}Fe Mössbauer spectra of **1** (R = H), **2** (R = CH_3), **3** [R = $C(CH_3)_3$], **4** (R = NO_2), and **5** (R = CN) in zero applied field at 3.0 K. On left-hand side of each spectrum, the value of the internal hyperfine field H_{int} determined from the sextet is given. For compound **4**, the distribution of probability for the magnetic hyperfine field was used.

dysprosium ions, which play an important role in controlling the direction of the magnetic anisotropy, are similar for all of the compounds.

Mössbauer spectroscopy senses the hyperfine interactions present at the nucleus of the Mössbauer isotope. The internal hyperfine field H_{int} is determined by four contributions: H_{fc} (Fermi contact), H_{ls} (orbital moment), H_{dd} (dipole field), and H_{latt} (lattice). In the case of **1**−**5**, the first three contributions are zero because of zero electronic spin density on the nuclei. H_{latt} is very small even in paramagnetic systems. Therefore, the only contribution to the internal hyperfine field at the iron nuclei in

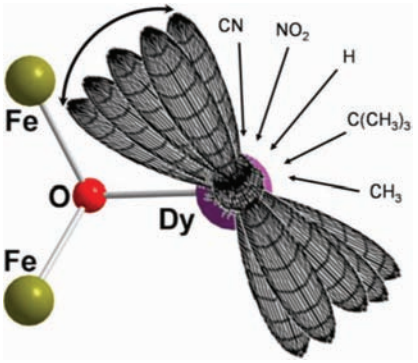

Figure 3. Schematic arrangements of the local magnetic moments (anisotropic axes) of a Dy ion relative to the Fe_2 unit.

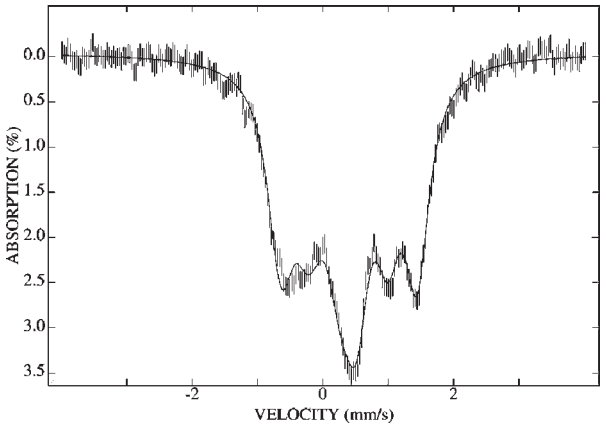

Figure 4. Mössbauer spectrum of polycrystalline **5** (R = CN) recorded at 3 K in a perpendicular applied field of 4.0 T. The solid line is a spectral simulation for ΔE_Q = 1.09 mm/s, δ = 0.50 mm/s, H_{eff} = 4.0 T, and η = 1.0, assuming an isolated ground state with S = 0.

these compounds results from the magnetic interaction with the anisotropic Dy^{III} ions. Since the exchange interaction between Dy^{III} and Fe^{III} is expected to be negligible because the 4f electrons of the dysprosium ions are well-shielded by their 5s and 5p electrons, any observed interaction could be essentially magnetic-dipolar, which is unlikely because it should be very small. More likely it arises from the transferred field or else is due to polarization of the Fe^{III} electron clouds by the magnetic Dy ions.

This raises the question of why the internal field felt by the iron nuclei differs so much from sample to sample. One possible explanation is that the orientations of the easy axes of magnetization (or magnetic flux density) of the dysprosium ions are different in the different compounds presented here. If we imagine that every Dy ion corresponds to a dipole, the orientation of this dipole will be dictated by the local crystal field and ground state of the Dy ion (Figure 3).

The central $\{Fe_2(OH)_2\}$ unit is antiferromagnetically coupled and thus has an S = 0 ground state, as determined on the Y^{III} analogue of **1** (see Figure S-1). This allows us to establish the dependence on the orientation of the magnetic dipolar anisotropy with respect to that of the central diamagnetic Fe_2 unit and shows that the magnetic interactions between the Fe and Dy ions have different strengths in the five compounds. The five clusters are very closely isostructural, differing only in the para substituent

on the phenyl rings. This means that the electron-withdrawing/electron-donating effects of these substituents change the degree of communication between the 5s and 5p electrons of dysprosium and the 2p electrons of the oxygen atoms. This in turn affects the degree of asphericity of the 4f shell and thus the direction of the magnetic dipolar anisotropy of the Dy^{III} ions.

When we applied an external magnetic field, the magnetic insets in the spectra of **1**−**5** vanished with increasing field (e.g., see the spectra for **5** shown in Figure S-5), and the Mössbauer spectra at high fields exhibited patterns typical of diamagnetic complexes. The experimental spectrum of **5** obtained at H_{appl} = 4.0 T is shown in Figure 4.

The simulation parameters were the field at the nucleus H_{eff} = 4.0 T, ΔE_Q = 1.09 mm/s, δ = 0.50 mm/s, and the asymmetry parameter η = 1.0. The experimental data fit very well with $H_{eff} = H_{appl}$. In other words, there was no detectable contribution from magnetic hyperfine interactions other than the applied field and therefore no residual paramagnetism at 3.0 K. One possible explanation for such behavior in an external applied magnetic field might be that under the influence of the benzene substituents, there is magnetic reversal of the Dy^{III} Ising moments that give rise to spin reorientation (i.e., canting) on the Fe sites, correspondingly changing the exchange interaction energy and producing a weak ferromagnetic moment. Upon application of an external magnetic field, it appears that the applied field affects the ground state of Dy^{III} by a slight mixing of the excited state wave functions into the ground state, lowering the energy of the system and resulting in a change in its direction of polarization. Thus, the Fe^{III} and Dy^{III} spin systems may become decoupled, and the Fe^{III} spins may recover their low-energy (diamagnetic) configuration, driven by the inherent Fe^{III} anisotropy. Another potential reason is that although the 4f charge distribution is aspherical whenever it carries net orbital angular momentum, the anisotropy can be modulated by quenching of the orbital moment by the crystalline field. Applying an external field of 4−5 T results in either a further quenching of the orbital momentum (but now by the applied field) or reorientation of the magnetic dipolar anisotropy or spins. The second assumption is more trustworthy, because in magnetic materials, rare-earth metal ions require stronger applied fields to overcome the anisotropic forces, in comparison with fields of a few kilooersteds for a transition element such as iron.[7]

A reasonable further experiment would be to perform Mössbauer studies of these compounds in solution to test whether any of the magnetic sextets (or features) can be attributed to solid-state effects, such as interactions between dimers, the distance between molecules is in the range 10−12 Å. Since the Fe−Dy distances within the molecules are ∼3.5 Å, it is unlikely that intermolecular interactions are significant, rendering such experiments unnecessary.

Overall, this study has shown that the local crystal field can vary slightly with minor changes of electronegativity in the ligand sphere and that the external magnetic field and donor−acceptor nature of the ligands may sufficiently control the asphericity of the 4f shell of lanthanide ions and their shape anisotropy and thus the interaction between lanthanides and other magnetic centers. Although the concept of using Mössbauer spectroscopy to determine the orientation of the principal axes of the magnetization of anisotropic lanthanide ions is not yet a precise quantitative notion, the simple approximation used in this communication already provides a consistent and logical model interpretation. Current studies of isostructural complexes with other lanthanides are underway.

■ ASSOCIATED CONTENT

Supporting Information. Experimental section, CIFs, and additional Mössbauer spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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