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An Organoytterbium(III) Complex Exhibiting Field-Induced Single-Ion-Magnet Behavior

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Supporting Information

ABSTRACT: We present a new mononuclear half-sandwich complex, $[Cp^*Yb(DAD)(THF)]\cdot C_7H_8$ (**1**), based on a paramagnetic Yb^{III} ion coordinated by diamagnetic Cp* and enediamido$[2,6\text{-}Me_2C_6H_3NCH{=}CHNC_6H_3Me_2\text{-}2,6]^{2-}$ (DAD) ligands exhibiting field-induced single-ion-magnet behavior.

Organometallic chemistry of f elements involving neutral n- and/or π-bonded ligands offers a promising approach to achieving new molecular architectures with interesting physical or chemical properties and, particularly, to designing single-ion magnets (SIMs). These complexes, formed by a single paramagnetic ion and appropriated ligands, exhibit a slow relaxation of the magnetization and a memory effect arising from an anisotropy barrier that opposes the reversal of the magnetization at low temperature. For this reason, they present a growing interest for several applications including information storage and data processing.[1] Along this line of thought, several paramagnetic lanthanide ions exhibit tremendous magnetic properties because of a strong magnetic anisotropy combined with a large magnetic moment, which make them the ions of choice for SIM design. The magnetic behavior of the latter mainly depends on both the nature of the lanthanide ion and the symmetry/environment of the site dictated by the ligand nature.[2] Consequently, Kramers ions such as Dy^{3+}, Er^{3+}, and Yb^{3+} appear as the most promising lanthanide ions to design SIMs because they exhibit doubly degenerated $\pm m_J$ levels, one of the requisites to observe a slow relaxation of the magnetization, although non-Kramers ions such as Tb^{3+} can also exhibit doubly degenerated $\pm m_J$ levels in a highly symmetric environment. On the other hand, carbon-based anionic ligands traditionally used in organolanthanide chemistry and presenting an important steric hindrance are highly interesting to finely tune the coordination environment of the lanthanide ion[3] and therefore the slow relaxation of the magnetization. Their advantages are mainly due to (i) the particular geometry and the steric hindrance of these ligands, which may stabilize the f-electron density favorable to observing a SIM behavior and may also favor a high-symmetry environment of the final complex in order to minimize the quantum tunneling of the magnetization (QTM) induced by a transverse anisotropy component and (ii) the electronic effects due to the negative charge and donor strength of the ligands, which influence the electronic structure of the Stark sublevels in the complex. Recent examples have proven that organolanthanide complexes with tailored coordination environments exhibit large energy barriers and hysteresis effects.[4] For instance, the use of the cyclooctatetraene dianion[5] alone or in association with the pentamethylcyclopentadienide anion[6] allows the synthesis of SIMs based on Er^{3+} sandwich-type complexes with prominent uniaxial anisotropy, resulting in the appearance of a slow magnetic relaxation of the magnetization with relaxation barriers of 150 and 224 cm^{-1} respectively. Remarkably, QTM can be strongly reduced because of the high symmetry of the lanthanide site dictated by these planar π-delocalized ligands, allowing the observation of a magnetic hysteresis up to 10 K.[5a] Interestingly, among other similar complexes with paramagnetic lanthanides, only the Dy^{3+}-based one has revealed a SIM behavior.[7] To the best of our knowledge, no Yb^{3+}-based SIMs using an organolanthanide chemistry approach have been reported up to now.

Previously we published the synthesis of a series of mixed-ligand Yb^{3+} complexes coordinated by cyclopentadienyl and dianionic 1,4-diaza-1,3-butadienyl (DAD) ligands [CpYb(DAD)(THF)] (Cp = C_5Me_5, C_5Me_4H; DAD = 2,6-$R'_2C_6H_3NC(R'')C(R'')NC_6H_3R'_2$-2,6, where R″ = H, Me and R′ = Me, *i*Pr; THF = tetrahydrofuran) featuring heteroleptic sandwich structures[8,9] reminiscent of that of [Cp*Er(COT)].[5] However, they did not display a slow relaxation of the magnetization.[9] Because the sandwich-type ligand field was shown to stabilize the prolate $m_J = {}^{15}/_2$ state of Er^{3+},[5a] we were curious to check whether the complexes containing the prolate $m_J = \pm{}^7/_2$ state of the Yb^{3+} ion[2] coordinated by cyclic aromatic Cp* and dianionic noncyclic enediamido ligand exhibit magnet-like behavior. The choice of these ligands is based on their steric hindrance, which allows the isolation of strictly mononuclear molecular organolanthanide species. Additionally, the modulation of the ligands' substituents can tune their donor strength as well as the geometry of the complex. Employing π-delocalized hard donor Cp* may promote an equatorial ligand field suitable for the stabilization of the prolate electron density of the m_J =

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$\pm^7/_2$ state of Yb^{3+}. The lone electron pairs of N atoms and the π electrons of the C═C bond allow the enediamido ligand to act as both n- and π-electron donors,[10] creating a coordination environment for the Ln^{3+} ion strikingly different from that in [Cp*Ln(COT)]. We show in this Communication that careful modulation of the enediamido ligand leads to the occurrence of a field-induced slow magnetic relaxation of the magnetization in a Yb^{3+} organometallic complex.

The reaction of $[Cp^*_2Yb(THF)_2]$ with $2,6\text{-}Me_2C_6H_3N{=}CHCH{=}NC_6H_3Me_2\text{-}2,6$ (DAD) was carried out in toluene at 60 °C (Scheme S1, Supporting Information, SI). Similarly to the previously published results obtained with the bulkier $2,6\text{-}i\text{Pr}_2C_6H_3N{=}CHCH{=}NC_6H_3i\text{Pr}_2\text{-}2,6$ ligand,[9] this reaction results in the oxidation of Yb^{2+} to Yb^{3+} and the cleavage of one Yb−Cp* bond, affording the heteroleptic complex $[Cp^*Yb(DAD)(THF)]\cdot C_7H_8$ (**1**), which contains a dianionic DAD^{2-} ligand (64% yield). The compound crystallizes as a solvate with one molecule of toluene. The molecular structure of the complex is depicted in Figure 1. The single-crystal X-ray structure determination revealed that the coordination environment of the Yb^{3+} ion is set up by a η^5-coordinated Cp* ligand, a $2\sigma{:}\eta^2$-coordinated DAD^{2-} dianion, and one THF molecule. The average Yb−C(Cp*) bond length in **1** (2.611 Å) is much shorter than the corresponding value in the parent Yb^{2+} complex (for comparison, see $Cp^*_2Yb(py)_2$; 2.74 Å)[11] and clearly indicates oxidation of the Yb ion during the reaction. The Yb−N distances in **1** [2.142(3) Å] are slightly shorter than those measured in known eight-coordinate Yb^{3+} complexes [2.193(1)−2.286(7) Å].[12] The lengths of N−C [1.414(4) Å] and C−C [1.364(5) Å] bonds within the NCCN fragment are consistent with its dianionic character.[13] The C═C bond of a doubly reduced enediamido NCCN moiety also contributes in metal−ligand bonding: η^2 coordination of the C═C bond of the enediamido moiety to the Yb^{3+} ion results in the short Yb−C contacts [2.604(3) and 2.610(3) Å]. The five-membered metallocycle is not planar; the value of the dihedral angle between the NCCN and YbNN planes is 131.2°, and the value of the $Cp^*_{\text{Centr.}}$−Yb−$NCCN_{\text{Centr.}}$ angle is 142.5°. Analysis of the crystal packing reveals that the complexes are well isolated with a shortest intermolecular Yb−Yb distance equal to 8.977(2) Å (Figure S1, SI). The UV−vis spectrum of **1** displays an intense absorption band at 285 nm, close to the value observed for Li_2DAD, giving thus further evidence for the dianionic state of the DAD ligand (Figure S2, SI).

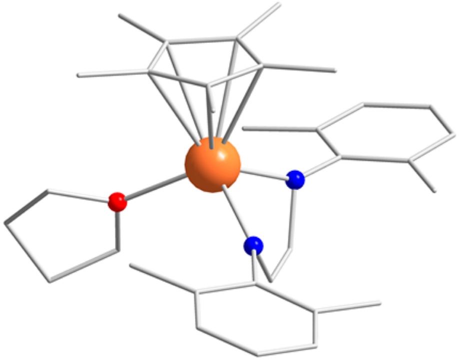

Figure 1. Molecular structure of complex **1**. Color code: orange, Yb; red, O; blue, N; gray, C.

The magnetic properties of **1** were investigated by using a SQUID MPMS-XL magnetometer working in the 1.8−300 K temperature range up to 7 T. The room temperature χT value of $2.27\ cm^3\cdot K\cdot mol^{-1}$ is close to the theoretical value of $2.57\ cm^3\cdot K\cdot mol^{-1}$ expected for one Yb^{3+} ion ($^2F_{7/2}$, $S = {}^1/_2$, $L = 3$, $g = {}^8/_7$; Figure S3, SI). Upon cooling, a decrease of χT occurs because of thermal depopulation of the Stark sublevels to reach the value of $1.15\ cm^3\cdot K\cdot mol^{-1}$ at 1.8 K. The field dependence of the magnetization at 1.8 K reaches values of 1.76 μ_B at 7 T (inset of Figure S3, SI) without a clear saturation.

Alternating-current (ac) measurements were performed at low temperature in order to evidence the occurrence of a slow relaxation of the magnetization arising from a SIM behavior. The frequency dependence of the alternative susceptibilities with frequency ranging from 1 to 1488 Hz under a zero direct-current (dc) field at 1.8 K reveals the absence of a significant component of an out-of-phase susceptibility, χ''. This is frequently observed for 4f SIMs and more particularly for Yb^{3+} complexes because of the fast QTM. However, applying dc fields (300−3000 Oe) leads to the appearance of an out-of-phase component (Figure S4, SI) with a clear maximum for dc fields larger than 300 Oe. The optimum field of 1500 Oe, which corresponds to the field at which the relaxation time is higher (lowest frequency of the maximum; Figure S5, SI), is found to be 1500 Oe. The frequency dependence of the in-phase and out-of-phase components of the ac susceptibility as a function of the temperature was performed under this optimum field of 1500 Oe and reveals a single frequency-dependent peak associated with a slow relaxation of the magnetization (Figures 2 and S6, SI). The maxima of the peaks of χ'' shift to higher frequency with increasing temperature, from 133 Hz at 1.80 K to 1250 Hz at 4.20 K. The anisotropic energy barrier, U_{eff}, can be estimated considering an Orbach process [$\tau = \tau_0 \exp(U_{\text{eff}}/kT)$] in the high-temperature region. A clear deviation from the Arrhenius law appears in the low-temperature range (Figure S7, SI), reflecting the appearance of additional relaxation pathways such as Raman and/or direct processes. A fitting of the temperature dependence of the relaxation time was performed using the model recently updated by Long et al.[14] and the following equation: $\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/kT) + CT^m + AT^n$. In this equation, the first term accounts for an Orbach process, while the second and third ones stand for two-phonon Raman and direct relaxation processes, respectively. The best parameters (Table S2, SI) are obtained by fixing $m = 5, 7$, or 9 and $n = 1$ (usually found for the direct process). The best-fit parameters are obtained with a value of $m = 9$, which is the value usually found for Kramers ions such as Yb^{3+}.[14] The energy barrier is found to be $U_{\text{eff}} = 14 \pm 2\ cm^{-1}$ with the value $\tau_0 = 1.74 \times 10^{-6}$ s, characteristic for superparamagnetic systems. Although small in

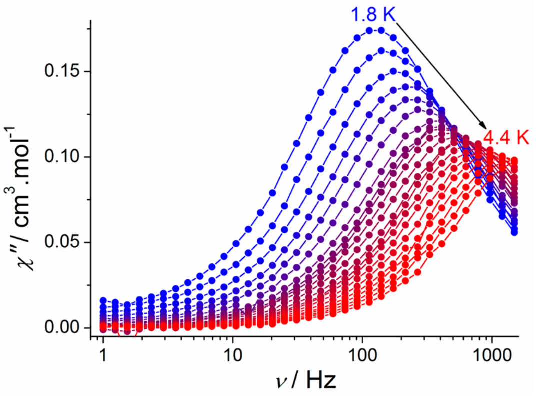

Figure 2. Frequency dependence of the out-of-phase susceptibility, χ'', performed under a 1500 Oe dc field.

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comparison with Dy^{3+}- or Tb^{3+}-based Single-Molecule Magnets/SIMs, the energy barrier found appears to be one of the highest reported for Yb^{3+} systems.[15] Additionally, the high value of the A parameter indicates a strong contribution from the direct process at low temperature. Plotting χ'' versus χ' (Cole−Cole plots) in the temperature range 1.8−4.2 K gives well-defined semicircles, confirming the occurrence of a single relaxation process in the high-temperature range (Figure S8, SI). The data can be fitted using a generalized Debye model, giving an α value of 0.282 at 1.8 K, which strongly decreases to 0.00069 at 4.2 K (Table S3, SI). This low value of α at high temperature (Orbach process) indicates a narrow distribution of the relaxation time.[16]

The need to use a static dc field to observe a slow relaxation of the magnetization directly reflects the presence of a strong QTM that arises from a direct process between the quasi-degenerate Kramers ground doublet. Such a process may be induced by various factors such as a deviation from high symmetry, inducing a mixing of the $\pm m_J$ states, the presence of dipolar interactions, or hyperfine coupling.[17] Unfortunately, any attempts to chemically dilute the complex in a diamagnetic matrix of Y^{3+} or Lu^{3+} were unsuccessful, precluding an in-depth analysis of the dipolar interactions role. Nevertheless, the symmetry of the Yb site could also be responsible for such QTM. In contrast to Dy^{3+} and Er^{3+} ions, Yb^{3+} has a complicated energy splitting that is directly correlated to the shape of the 4f charge density of the m_J states. Indeed, a strong angular dependence leads to an almost oblate density for $m_J = \pm{}^5/_2$, while a prolate density for $m_J = \pm{}^7/_2$ is observed.[2] To our knowledge, only one example of a Yb^{3+}-based system displaying a zero-dc-field slow relaxation of the magnetization has been reported in a polyoxometallate complex where a strictly square-antiprismatic coordination environment is imposed, leading to the stabilization of the oblate $m_J = \pm{}^5/_2$ ground state.[18] In contrast, the Yb^{3+} ion in **1** lies in a low-symmetry environment that could stabilize neither the oblate $m_J = \pm{}^5/_2$ or the prolate $m_J = \pm{}^7/_2$ ground states[2] despite the use of bulky ligands, explaining the need of a static dc field to shortcut the QTM.

In summary, a new heteroleptic Yb^{3+} half-sandwich complex **1** has been synthesized from a Yb^{II} complex. Unlike the previously reported related complexes coordinated by other DAD-based ligands,[8,9] this compound behaves as a field-induced SIM with a single relaxation process and constitutes the first example of an organoytterbium system exhibiting such a property. To gain further insights into the origin of such slow relaxation of the magnetization, the preparation of a series of neutral and ionic Yb^{3+} complexes coordinated by DAD^{2-} and $DAD^{\bullet -}$ ligands is pursued now in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01318.

Experimental details, a crystallographic table, and detailed magnetic data (PDF)

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Notes

The authors declare no competing financial interest.

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