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Mononuclear Lanthanide Single-Molecule Magnets Based on Polyoxometalates

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Due to their nanometric size, quantum effects on their magnetic properties, and extremely long magnetic relaxation times, single-molecule magnets (SMMs)¹ have been considered as promising candidates for the development of high-density magnetic memories, molecular spintronic applications,² and quantum computing devices.³ Although most SMMs are polynuclear transition-metal complexes with high-spin ground states and axial magnetic anisotropy,⁴ the possibility of constructing nanomagnets using a single lanthanide ion was demonstrated experimentally on phthalocyaninato–lanthanide complexes.⁵ In these nanomagnets, the magnetic anisotropy required for observing slow relaxation of the magnetization arises from the zero-field splitting of the lanthanide ion J ground state when it is placed in a ligand field (LF). For certain LF symmetries, such splitting can stabilize sublevels with a large $|J_z|$ value, thus achieving an easy axis of the magnetization.⁶ Still, few studies on mononuclear lanthanide-based complexes exhibiting SMM behavior, apart from phthalocyaninato–lanthanide complexes, have been reported.

Owing to the ability of polyoxometalates (POMs) to encapsulate lanthanides with coordination geometries similar to those of bis(phthalocyaninato)lanthanide complexes, it seemed to us of interest to study the magnetic properties of this sort of compound. Here we report the structure and magnetic properties of the sodium salt of the $[\text{ErW}_{10}\text{O}_{36}]^{9-}$ polyanion (**1**).⁷ This lanthanide complex represents the first example of a POM exhibiting SMM behavior.

The compound was prepared by following a previously described procedure.⁸ DC static magnetic measurements follow a Curie–Weiss law in the high-temperature regime with a Curie constant $C = 11.4 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, in good agreement with that expected for a paramagnetic Er^{3+} ion in the $^4I_{15/2}$ ground state ($11.43 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$), and a Weiss constant $\Theta = -10.5 \text{ K}$ (Supporting Information).

Low-temperature AC magnetic susceptibility measurements reveal the typical features associated with the SMM behavior (Figure 1). Thus, both the in-phase (χ_M') and out-of-phase (χ_M'') signals show strong frequency dependences; χ_M' shows a maximum and starts to decrease in the 5.5–7.5 K range, while χ_M'' defines a maximum between 5 (1000 Hz) and 6.2 K (10 000 Hz). Analyses of the frequency dependence of the χ_M'' peaks through an Arrhenius plot permit estimation of the magnetization–relaxation parameters in this system (Figure 1b). Best fitting ($R = 0.999$) afforded a barrier height (U_{eff}/k_B) of 55.2 K with a pre-exponential factor (τ_0) of $1.6 \times 10^{-8} \text{ s}$. The existence of a single relaxation process is supported by the representation of the normalized χ_M' vs χ_M'' at 5.5 K in the Cole–Cole plot (Figure 1b; χ_T = isothermal susceptibility, χ_S =

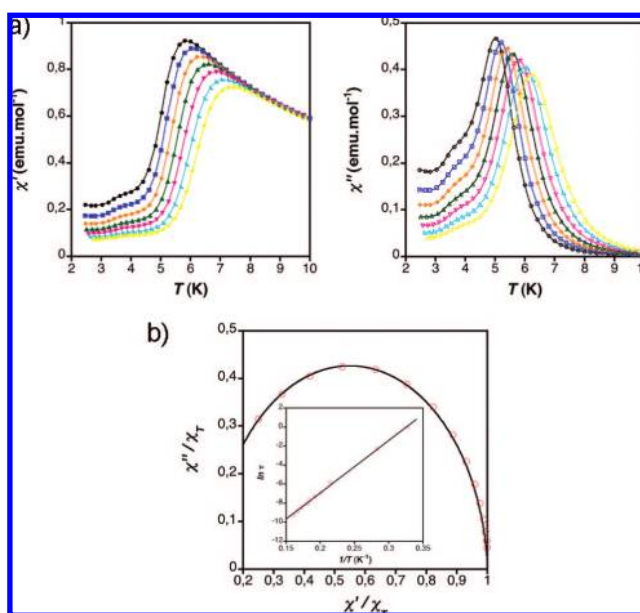


Figure 1. (a) In-phase and out-of-phase dynamic susceptibility of **1**. From left to right: 1000, 1500, 2200, 3200, 4600, 6800, and 10 000 Hz. Solid lines are eye guides. (b) Cole–Cole plot at 5.5 K. Lines represent the best fitting of the experimental data to a Debye model providing $\alpha = 0.03$. Inset: relaxation time fitting to the Arrhenius law in the 1–10 000 Hz interval.

adiabatic susceptibility).⁹ The fit of the data to a general Debye model provides almost an ideal semicircle with $\alpha = 0.03$ ($\alpha = 0$ for an infinitely narrow distribution of relaxation times). This value is among the lowest reported for SMMs and single-chain magnets.

Given the good insulation of Er^{3+} ions provided by the polyoxowolframate frame (the shortest Er–Er distance in the crystal structure is 11.225 Å), the slow relaxation phenomena exhibited by **1** should be considered as a single-molecule property.

As the SMM behavior observed in mononuclear lanthanide-based magnets is strongly dependent on the exact coordination geometry around the metal, the crystal structure of **1** was determined. The POM complex is formed by two anionic $[\text{W}_5\text{O}_{18}]^{6-}$ moieties sandwiching the Er^{3+} ion (Figure 2). These anionic clusters are surrounded by sodium cations, to balance the charge, which are octahedrally coordinated by water molecules. Consequently, a large amount of solvent molecules are present in the solid state.¹⁰ Each anionic $[\text{W}_5\text{O}_{18}]^{6-}$ moiety is twisted 44.2° with respect to the other. This skew angle is very close to that expected for an ideal D_{4d} symmetry ($\Phi = 45^\circ$). Therefore, the coordination site can be described as slightly distorted square-antiprismatic (Figure 2). Er–O distances also support this minor distortion, ranging from 2.339(3)

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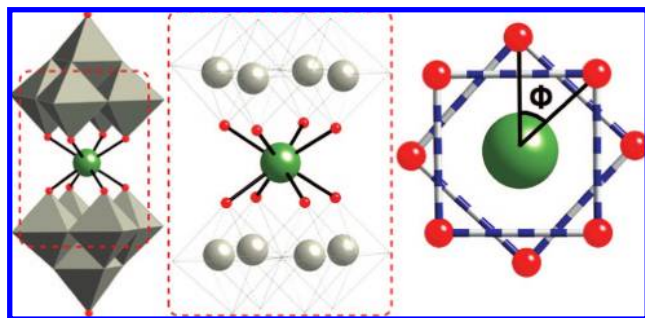


Figure 2. Structure of the $[\text{ErW}_{10}\text{O}_{36}]^{9-}$ POM and projection showing the Er^{3+} ion square-antiprismatic coordination site.

to 2.387(3) Å (average 2.367(7) Å). This geometry corresponds to an approximate D_{4d} LF symmetry, as also exhibited by the series of “double-decker” phthalocyanine complexes. However, in the former case, the geometry around the Er^{3+} ion is more distorted with a skew angle of 41.4°. In addition, in **1**, the 2.47(1) Å interplanar distance, calculated as the distance between the upper and lower planes containing the four oxygen atoms, and the average 2.86(5) Å distance between the four neighboring oxygen atoms placed in each plane are indicative of a certain axial compression of the square-antiprism built up by the 8-fold coordinated Er^{3+} ion (Figure 2). In contrast, axial elongation is observed for the phthalocyaninato complexes.¹¹ These geometrical differences in the crystal fields, although small, seem to be sufficient to completely change the magnetic relaxation properties of these lanthanide-based complexes. In fact, no slow relaxation phenomenon was observed for the Er-containing phthalocyanine complex but only for the Tb, Dy, and Ho derivatives.⁵ In turn, preliminary data obtained for the other members of the $[\text{Ln}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-}$ series ($\text{Ln}^{\text{III}} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Yb}$) indicate that only the Ho derivative shows SMM-like behavior around 2 K.

To understand the sharp difference observed in the magnetic relaxation properties of these two series, we performed a preliminary determination of the LF parameters using the susceptibility data of four members of the $[\text{Ln}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-}$ family (Tb, Dy, Ho, and Er derivatives, Supporting Information). From the best simultaneous fitting, the following LF parameters for the Er derivative have been extracted: $A_0^2\langle r^2 \rangle = -409 \text{ cm}^{-1}$, $A_0^4\langle r^4 \rangle = -273 \text{ cm}^{-1}$, and $A_0^6\langle r^6 \rangle = 62 \text{ cm}^{-1}$. These parameters indicate the presence of a Kramers doublet ground state for the Er compound with $m_j = \pm 13/2$ and two excited states with $m_j = \pm 1/2$ and $\pm 15/2$, separated from this ground state by energies of 3 and 18 cm^{-1} , respectively. The rest of the states are at energies higher than 100 cm^{-1} . In contrast, for the Er bis(phthalocyaninato)lanthanide complex, the ground state was determined to be the $m_j = \pm 1/2$ doublet, being the first excited doublet at more than 100 cm^{-1} .¹² Such a difference in the energy levels scheme, which mainly arises from the change of sign of the $A_0^2\langle r^2 \rangle$ parameter, seems to be associated with the different axial distortion (compression vs elongation) of the Er coordination site in these two complexes and accounts for the SMM behavior observed in the title compound.

In conclusion, we have shown that POM chemistry can provide ideal examples of lanthanide single-ion SMMs. Up to now, the interest in this kind of complex mainly focused on their photo- and electroluminescent properties.¹³ This novel feature adds interest to these inorganic molecules in molecular magnetism¹⁴ and quantum computing,¹⁵ as a plethora of new series of SMMs can be foreseen

by suitable choice of POM ligands. Compared with the double-decker phthalocyanine SMMs, POM complexes present several advantages: From the chemical point of view, they are much more stable, keeping their structures in solution. At the same time, the POM framework guarantees magnetic insulation of the lanthanide. Finally, attending to their composition, they can be prepared as nuclear spin-free systems. This requirement is of great importance to permit the use of these molecular magnets in quantum computing, as nuclear spins are a main source of quantum decoherence at low temperature.¹⁶

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Supporting Information Available: Crystal structure file, detailed experimental procedure, temperature dependence of the static susceptibility and Curie–Weiss fitting, experimental dc magnetic susceptibility and theoretical fitting for the LnW_{10} family ($\text{Ln} = \text{Ho}, \text{Dy}, \text{Tb}$ and Er) employed in the estimation of the LF parameters, FT-IR spectrum, and crystal packing in the solid state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Crystal data for **1**: A needle-like pink crystal of **1** was mounted on a Nonius-Kappa CCD single crystal diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ nm}$) at 120 K. Data collection and reduction were performed using the programs Collect, Denzo, and Scalepack. Crystal structure was solved by direct methods using the program SIR97, followed by Fourier synthesis and refined on F^2 with Shelxl-97. Anisotropic least-squares refinement of non-H atoms was performed. All hydrogen atoms were located geometrically. $\text{H}_7\text{OErNa}_9\text{O}_7\text{W}_{10}$, $M_w = 3348.67$, triclinic, $P\bar{1}$, $a = 12.744(3) \text{ \AA}$, $b = 13.071(3) \text{ \AA}$, $c = 20.470(4) \text{ \AA}$, $\alpha = 82.89(3)^\circ$, $\beta = 74.53(3)^\circ$, $\gamma = 88.80(3)^\circ$, $V = 3260.8(11) \text{ \AA}^3$, $T = 120(2) \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 3.411 \text{ g/cm}^3$, $F(000) = 2950$, $\rho = 1.025 \text{ mm}^{-1}$, 33760 reflections, 18853 unique ($R_{\text{int}} = 0.077$), $2\theta_{\text{max}} = 60.18^\circ$, $R(F) = 0.0714$ and $R_w(F^2) = 0.1742$ for 18853 reflections [$I > 2\sigma(I)$].
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