Luminescence-Driven Electronic Structure Determination in a Textbook Dimeric Dy$^\text{III}$-Based Single-Molecule Magnet


Abstract: A textbook dysprosium dinuclear complex based on acetylacetonate ligands, [Dy$_2$(acac)$_3$]$^2$O, has been synthesized and fully characterized. This simple dimer lanthanide complex shows well-resolved solid-state luminescence and behaves as a single-molecule magnet under zero DC field. A seminal crystal-field approach is used to marry both magnetism and luminescence in the frame of an energetic picture.

Introduction

Since the discovery of mononuclear-based single-molecule magnets (SMMs),[1] lanthanide ions are the cornerstone of a new generation of molecular magnets.[2–6] In particular, these molecular objects are promising for applications as single component in nanospin manipulation.[7–9] While their performances stagnated for a decade around 14 K,[10] a large step forward recently occurred with organometallic mononuclear-based compounds that store magnetic information around liquid nitrogen temperature.[11–13] These magnets are comprised of Ln$^\text{III}$ ions which possess large magnetic moment associated with a huge magnetic anisotropy. In parallel, lanthanides are well known to emit light from the UV to NIR range with characteristic emission bands.[14] This luminescence arises from formally Laporte-forbidden f–f transitions with long lifetime and a very weak absorption coefficient. To overcome this lack, suitable ligands are used as antennae to sensitize the emission.[15–17]

In a pioneering paper, van Vleck pointed out that crystal field splitting (CFS) is at the origin of both magnetism and luminescence and consequently both properties are strongly correlated.[18] Indeed, luminescence and magnetism both originate from crystal field of 4f orbitals. Some of us and other groups contributed to the revival of this old idea and in the beginning of the 2010s established correlation between magnetism and luminescence on Dy$^\text{III}$, and also Yb$^\text{III}$-based SMMs.[19–26] These results triggered a new interest into high-resolution luminescence measurements in order to experimentally establish the complete diagram of luminescent SMMs. Although classical, such determination can be quite tricky because of the presence of “extra-transitions” in the luminescence spectra, assigned sometimes too rapidly to “hot bands” or vibronic transitions[3, 27, 28] (see also ref. [29–31] for Dy$^\text{III}$).

On the magnetic aspects, one of the major issue with mononuclear SMMs is the presence of sizable quantum tunnelling of magnetization (QTM) at low temperature, which prevents the opening of the magnetic hysteresis loop.[5, 12, 33] This problem can be solved in minimizing the internal field through either dilution in a diamagnetic matrix or cancellation of the nuclear spin through isotopic enrichment.[7, 34–37] Another efficient possibility is to couple the magnetic centres (superexchange and/or dipolar interactions) within a polynuclear edifice.[38–46]

Recently, some of us developed synthetic strategies based on diketone moieties, which are well known ligands to coordinate lanthanide ions. Although these pincers can present several coordination modes, it is possible by controlling the synthesis parameters (pH, temperature, time, etc.) to isolate à la carte polynuclear complexes.[47–50] Herein, we report a textbook dysprosium dinuclear complex based on the acetylacetonate ligand (the simplest diketone). The goal of this work is to use seminal crystal field approach to marry magnetism and luminescence in the frame of an energetic picture.
Results and Discussion

Synthesis and crystal structure

Acetylacetone (Hacac, 1 equiv.) and Et₃N (1.5 equiv.) were added dropwise to a methanolic solution of DyCl₃·6H₂O (0.5 equiv.) after 10 min. of stirring, the clear colourless mixture was filtered, and the filtrate was left undisturbed at room temperature. After two days of slow evaporation of the solvent, single crystals of [Dy₂(acac)₉(μ₂-acac)(H₂O)₂] Dy₂, suitable for single-crystal X-ray analysis, were obtained (43 % yield) (Table S1 in Supporting Information). The centrosymmetrical dimer is constituted by six deprotonated acac ligands, two coordinated water molecules and two Dy⁴⁺ cations. The latter are located in a (O₃) environment where five oxygen atoms (O31, O37, O27, O17, O11) belong to three terminal acac ligands, and one oxygen atom (O1) to a coordinated water molecule. The bridging acac ligands (O27, O21) binding in a μ₁,κ₁,κ₁-acac-O,Odime complete the coordination sphere of the lanthanide cation (Figure 1). The oxygen atom O21 bridges the two Dy⁴⁺ ions with intermolecular Dy–Dy distances equal to 4.0363(4) Å (Table S2). SHAPE analysis reveals that the Dy⁴⁺ ions seat in an almost perfect square antiprism environment (Table S3). The Dy–O bond lengths involving the water molecule and terminal acac ligands (2.361(3) Å and ≈ 2.332 Å) are slightly shorter than those for oxygen atoms involved in the Ln-O-Ln symmetrical double bridge (≈ 2.465 Å). All these bonds lengths are in good agreement with those usually observed for Ln⁶⁺ dimers with a fully oxygenated coordination sphere.¹⁴ An intramolecular hydrogen bond involves a coordinated water molecule and the oxygen atom of one acac, with O–O distance equal to 2.646 Å. A hydrogen bond (intramolecular) involves the other hydrogen atom of the water molecule and the oxygen atom of one acac of the neighbouring molecule. These intermolecular hydrogen bonds create chains of dimers along the a-axis. The shortest inter-dimer Dy–Dy distance is equal to 6.0816(7) Å. Sample purity was checked by powder X-ray diffraction experiment comparing the experimental diagram to the theoretical one obtained from the crystal structure (Figure S1).

Photophysical properties

Photophysical measurements were performed on a polycrystalline sample at room and low temperatures. Upon direct excitation of the lanthanide at 363 nm, classical luminescence of Dy⁴⁺ was observed with three main sharp bands localized in the visible at 482, 576 and 662 nm corresponding to 4f–4f transitions from the ⁴F₉/₂ excited level to the ⁴H₁₅/₂, ⁴H₁₃/₂ and ⁴H₁₁/₂ levels, respectively (Figure 2).

High-resolution excitation and emission spectra were obtained at 77 K revealing the sub-level splitting (crystal field splitting) of ⁴F₉/₂ and ⁴H₁₅/₂ levels, respectively (Figure 2). The excitation spectrum clearly shows five main transitions (474.8, 472.8, 471.2, 468.4 and 466.8 nm) as expected for the ⁴F₉/₂ level, giving a clear and complete spectroscopic picture of the excited state. The analysis of the ground state sub-level splitting is more complicated with overlap of the expected eight transitions. However, the band at 474.6 nm matches perfectly well with the lowest energy transition of the excitation spectrum and therefore can be unambiguously assigned to a "zero-phonon" transition (transition between the lowest m sub-levels). It is worth noting that emission generally occurs from the lowest energy excited state and particularly from its lowest crystal field sub-levels. However, due to thermal effects, excited m states can be populated according to a classical Boltzmann distribution that can be calculated from the splitting of the excited state (Figure 3). The details of the calculations are given in Supporting Information. They indicate that all m excited states are populated at room temperature and will all contribute to the emission spectrum through the so-called "hot bands" (5 × 8 = 40 expected transitions). Decreasing the temperature will depopulate the m excited states and considerably simplify the emission spectrum. Therefore, variable temperature emission spectra were recorded between 200 and 7 K (Figure 3) and the excited m state population is compiled in Table S5.

At 200 K, the theoretical Boltzmann distribution indicated that all the m excited states are populated with three major contributions N₀, N₁ and N₂ (Table S5). Their contributions to the emission spectrum are clearly evidenced by the presence of two transitions (noted h₁ and h₂, Figure 3) at higher energy compared to the zero phonon one (noted 0 on Figure 3), and match perfectly with the excitation bands. On cooling, the hot band h₁ disappears at a higher temperature (75 K) than h₂ (25 K). These observations are in good accordance with the calculated Boltzmann distribution (Table S5). Therefore, below 15 K, no hot bands are visible anymore. Considering the unresolved two contributions merged in the rounded band at 477.8 nm, the emission spectrum is unambiguously composed of seven clear transitions. The additional shoulder observed at

Figure 1. Top: view of Dy₂ dimer with major labels and intra-hydrogen bonds (orange dashed lines). Bottom: chains of [Dy₂] dimers running along the a-axis of the unit cell with inter-hydrogen bonds. For clarity, hydrogen atoms not involved in hydrogen bonds have been omitted.
473.4 nm leads to the complete eight-level energy diagram expected for the $^6\text{H}_{15/2}$ level in relatively low symmetry environment (474.2, 477.6, 478.0, 479.8, 481.0, 482.2, 483.4(s) and 487.4 nm). The last small band observed at lower energy ($\nu_1$) is assigned to a vibronic contribution. Overall, this study enables us to determine the complete CFS energy diagram of the ground level $^6\text{H}_{15/2}$ (0, 150, 168, 246, 298, 354, 384, 571 cm$^{-1}$) and particularly the $D$ value, corresponding to the energy gap between the two first $m_1$ states of the $^6\text{H}_{15/2}$ level of 150 cm$^{-1}$.

Crystal-field and static magnetic properties

Taking the advantage of the previous photo-physical analysis and of the almost perfect $D_{4h}$ coordination sphere around the Dy$^{3+}$ ion, an attempt at determining the electronic structure and the magnetic properties of Dy$_2$ was performed by using crystal-field (CF) theory. Indeed, the CF Hamiltonian [Eq. 1] of a 4f ion placed in a $D_{4h}$ environment can be written as follows:

$$\hat{H}^\text{CF} = \alpha_J \hat{B}_J^0 \hat{O}^0_J (J) + \beta_J \hat{B}_J^2 \hat{O}^2_J (J) + \gamma_J \hat{B}_J^4 \hat{O}^4_J (J)$$

(1)

where the $\alpha_J$, $\beta_J$, and $\gamma_J$ are parameters obtained using the Wigner–Eckard theorem and depend on the considered $J$-manifold (here $J = 15/2$ and $\alpha_J$, $\beta_J$, and $\gamma_J$ coefficients are equal to $-2/315$, $-8/135135$ and $4/3864861$, respectively), the $\hat{O}^0_J$ are the Stevens operators, and the $B_J^q$ terms are the CF parameters.

Assuming that the ground multiplet $^4\text{H}_{15/2}$ is well separated from the other excited multiplets, the matrix elements $(J, M_J, \hat{O}^q_J (J), M_{J'})$ can be then simply determined by using the values originally tabulated by Stevens.$^{122}$ The 16-fold degeneracy of the $^4\text{H}_{15/2}$ multiplet is released, but without any admixture between the $m_1$ states.

The CF parameters were therefore determined with a least-squares procedure by fitting the energies determined from the analyses of the emission spectra. The resulting determined en-
energies, calculated with $B_{zz}^0 = -60 \text{ cm}^{-1}$, $B_{zz}^0 = -118 \text{ cm}^{-1}$ and $B_{zz}^0 = +150 \text{ cm}^{-1}$, are given in Table 1. A relatively good agreement was obtained between the fitted and experimentally observed energies (root mean square deviation of the fitted energies equal to 19.61). The fitted CF parameters lead to a ground state (GS) corresponding to $m_s = \pm 13/2$, whereas the highest $m_s$ state ($\pm 15/2$) is found at $562 \text{ cm}^{-1}$ above the GS.

In order to confirm this electronic structure, static magnetic susceptibility measurements were performed on polycrystalline sample. The $\chi_{MT}T$ versus $T$ curve is shown in Figure 4. The room temperature value of the $\chi_{MT}T$ is $26.7 \text{ cm}^3 \text{K}^{-1} \text{mol}^{-1}$, which is very close to the expected value $(28.34 \text{ cm}^3 \text{K}^{-1} \text{mol}^{-1})$ for two isolated Dy$^{3+}$ ions. $\chi_{MT}T$ decreases continuously on cooling because of the combined effect of the thermal depopulation of the CF states of the $^8S_{15/2}$ level and the interaction between magnetic centres within the dimer (Figure 4). Meanwhile, magnetization at 2 K does not saturate at high field and does not reach 5.00 $\text{N}\mu$ per Dy$^{3+}$ (inset, Figure 4) as would be expected for the stabilization of the single components $m_s = \pm 15/2$ of the GS multiplet (9.3 instead of 10.0 $\text{N}\mu$ at 50 kOe). The $\chi_{MT}T$ versus $T$ curve was then fitted over the whole temperature range by using the following total Hamiltonian [Eq. 2]:

$$\hat{H} = \hat{H}^\text{CF} + \beta g_I \left(\hat{J}_1 + \hat{J}_2\right) \cdot \hat{H} + \hat{J}_1 \cdot D \cdot \hat{J}_2$$

(2)

where the first and second part of the Hamiltonian correspond to the CF and Zeeman interactions, respectively, acting on the full $J = 15/2$ manifold, whereas the third part of the Hamiltonian corresponds to the magnetic interaction between the two Dy$^{3+}$ centres. The experimental curve was fitted with only one free parameter: the interaction $D$. CF parameters $B_{zz}^0$, $B_{zz}^0$ and $B_{zz}^0$ are set and fixed from spectroscopy (see above). The fitted $\chi_{MT}T$ versus $T$ curve is represented on Figure 4. It properly reproduces the experimental data with $D = -8.31 \times 10^{-3} \text{ cm}^{-1}$ and an agreement factor $R^2 = 1.57 \times 10^{-4}$. The $M$ versus $H$ curve at 2 K is then simulated with the same set of parameters and matches well the experimental curve.

Single-crystal magnetometry performed at very low temperature provides a unique tool to probe 1) the magnetic anisotropy of the ground state and 2) the orientation of the principal magnetic axes, always in the ground state. However, such a technique is subject to crystallographic restrictions. Indeed, if the interaction between magnetic centres is weak with respect to thermal energy, the quantitative analysis is restricted to one crystallographic site. Furthermore, since the measurement is averaged over all the magnetic moments in a single-crystal, only one orientation is tolerated which restricts the application domain to P1 and P1 space groups, as is for the present Dy$_3$ structure. In the effective spin framework, each Dy$^{3+}$ ion can be viewed as a spin $1/2$ with the principal $g$-values $g_{xx} = 5.03$, $g_{yy} = 5.59$ and $g_{zz} = 12.98$ (Figure S2 and S3 in Supporting Information). Clearly, the magnetic anisotropy is not purely axial and the Dy$^{3+}$ magnetic moment cannot be considered as Ising. The error induced on susceptibility measurements by the application of a moderate field of 1 kOe for a single-crystal measurement, which might induce saturation effect as well as decoupling of the two magnetic moments, is not significant (Figure S3) with less than 2% difference between low field (13.88 $\text{cm}^3 \text{K}^{-1} \text{mol}^{-1}$ at 200 Oe) and 1 kOe (13.66 $\text{cm}^3 \text{K}^{-1} \text{mol}^{-1}$) at 2 K. The orientation of the $g$-tensor is given in Figure 5. The most magnetic axis is clearly oriented along the two aac-moieties and is perpendicular to Dy–O(water) direction. The determination of the orientation of the magnetic axes gives the possibility to calculate the dipolar contribution, $J_{\text{dip}}$ to the interaction between the two Dy$^{3+}$ ions. $J_{\text{dip}}$ is calculated equal to $-0.008 \text{ cm}^{-1}$ and matches almost perfectly with the estimated $D$ value from the $\chi_{MT}T$ versus $T$ curve. This suggests that the interaction is entirely of dipolar origin.

![Figure 4. Temperature dependence of $\chi_{MT}$ of Dy$_3$. Inset: field dependence of the magnetization for Dy$_3$ measured at 2 K. Red lines are best fitted curves.](image_url)
Dynamic magnetic susceptibility

Both in-phase, $\chi_M'$, and out-of-phase, $\chi_M''$, components of the ac susceptibility show frequency dependence below 6 K with the frequency of the ac magnetic field (Figure 6) in the absence of an external dc magnetic field. These are characteristic of the presence of slow relaxation of the magnetic moment of the dimer and the signature of a SMM. The ac data can be quantitatively analysed with an extended Debye model (see Supporting Information, Table S6 and Figure S4). In this frame, the distribution of the relaxation time is relatively narrow with the empiric parameter $\alpha$ falling between 0.06 and 0.12. In addition, the non-relaxing fraction of the magnetic moment, defined as the percentage between the high and low frequency limits of the susceptibility, is relatively constant close to 13% (Table S6). This shows that most of the magnetic moment relaxes at a single frequency. The temperature dependence of the relaxation time is represented in Figure 7. It can be analysed with the following equation [Eq. 3]:

$$\tau^{-1} = \tau_0^{-1} \exp \left( \frac{\Delta}{T} \right) + \frac{B_1}{1 + \frac{B_2}{T} H} + \frac{A T h^n}{\text{Direct}}$$

which features four different processes that depend or not on temperature and external dc magnetic field. In our case, the external magnetic field is not involved so the direct process is not considered, and the QTM becomes temperature independent. The Orbach process involves an energy barrier that can be considered as the gap between the ground and the first excited state which is set at 150 cm$^{-1}$. Compared to experimental data, the Orbach process, even in considering an extremely fast and very unrealistic intrinsic relaxation time $\tau_0 = 10^{-20}$ s, is much too slow to be considered (vertical green line in Figure 7) with $\Delta = 216$ K (150 cm$^{-1}$). In this frame, the temperature dependence of the relaxation time is fitted with only Raman and QTM processes (Figure 7). The best fitted curve is obtained with $C = 3.34\text{ s}^{-1}\text{ K}^{-n}$, $n = 5.044$ and $r_{\text{QTM}} = 4.66 \times 10^{-4}$ s (Figure 7).

Conclusions

This paper focused on a textbook example of Dy$^{III}$ dimer behaving as a luminescent single-molecule magnet in zero external dc field. Boltzmann statistics applied to solid-state variable temperature luminescence coupled with excitation spectroscopy at liquid nitrogen temperature allows the unambiguous extraction of the low-lying ($^7\text{H}_{15/2}$ manifold) energy diagram. Seminal Stevens theory applied to this energy picture provides crystal-field parameters that can be injected in the simulation of the magnetic susceptibility with only the magnetic interaction between Dy$^{III}$ ions as a free parameter. These investigations emphasize that optical spectroscopies and magnetism work hand-in-hand to give a complete view of the ground state multiplet splitting. Standing on this experimental evidence we demonstrate that the Orbach process (relaxation through the first excited state) is not involved in the dynamics of the magnetization.

Experimental Section

Single-crystal X-ray diffraction

This was carried out by using a Gemini diffractometer and the related software. An absorption correction based on the crystal faces

Figure 6. Frequency dependence of the in-phase, $\chi_M'$, and out-of-phase, $\chi_M''$, components of the ac susceptibility measured in zero external dc field for Dy$_2$.

Figure 7. Temperature dependence of the relaxation time of the magnetic moment of Dy$_2$ (black dots) with the best fitted curve with Raman + QTM processes (red line). The Orbach process with $\Delta = 150$ cm$^{-1}$ is represented as green line. The separated contributions from Raman (blue line) and QTM (orange line) are also represented.
was applied to the data sets (analytical). The structure was solved by direct methods using the SHELXT program,[13] and then refined with full-matrix least-square methods based on $F^2$ (SHELXL-97).[14] All non-hydrogen atoms were refined with anisotropic displacement parameters, except for hydrogen atoms of water molecules that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. All atomic displacement parameters for non-hydrogen atoms were refined with anisotropic terms.

CCDC 1970193 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

**Magnetic measurements**

Magnetic susceptibility data (2–300 K) were collected on powdered polycrystalline samples on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetic field of 0.02 T below 20 K, 0.2 T between 20 and 80 K and finally 1 T above 80 K, using a pelletized sample in Teflon tape to prevent orientation within the magnetic field. Alternating current (ac) measurements were performed in the 2–6 K range in zero external dc field in 1–1000 Hz range. The magnetization isotherm was collected at 2 K. All data were corrected for the contribution of the sample holder and the diamagnetism estimated from Pascal’s constants.

**Photophysical measurements**

Solid-state emission and excitation spectra were measured using a Horiba Jobin Yvon Fluorolog-3$^\text{rd}$ spectrofluorimeter, equipped with a three slit double grating excitation and emission monochromator with dispersion of 2.1 nm mm$^{-1}$ (1200 grooves mm$^{-1}$). The steady-state luminescence was excited by unpolared light from a 450 W xenon CW lamp and detected at an angle of 90° by a Hamamatsu R928 photomultiplier tube (200–900 nm). Spectra were reference corrected for both the excitation intensity variation and the emission spectral response. Solid sample was placed in a 0.5 mm diameter quartz tube that was cool down either in liquid nitrogen dewar (77 K) or set into an Oxford Instrument cryostat (Optistat CF2) insert directly in the sample chamber of the spectrofluorimeter. The interference signals due to scattered excitation light were suppressed by a 400 nm high pass filter placed at the entry of emission monochromator. Luminescence decay plots were obtained by pulsed excitation using a FL-1040 UP xenon lamp and lifetimes were obtained by an exponential least-squares fitting using Origin$^\text{®}$.

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**Conflict of interest**

The authors declare no conflict of interest.

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