

Optical Determination of the Single-Ion Zero-Field Splitting in Large Spin Clusters

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“Single-molecule magnets” (SMMs) represent the ultimate limit of miniaturization of magnetic data storage media.^{1,2} Quantum tunneling of magnetization effects^{3,4} also make SMMs candidates for quantum computing elements.⁵ The energy barrier DS^2 to loss of magnetization is provided by a large spin ground state, S , and its anisotropy due to a negative axial zero-field splitting (ZFS), D . Large S arises from ferri/ferromagnetic exchange in polymetallic transition metal complexes.¹ However, the factors that control D are poorly understood as there are many competing components including the single-ion ZFS and anisotropic and dipolar exchange. Here we demonstrate an optical method for determining the *single-ion* ZFS within clusters. We also show that the relative orientations of the local and cluster magnetic axes are *as important* as the sign of the single-ion ZFS in determining whether a cluster will be a SMM.

The ZFS of a spin state S that results from the vector coupling of two spins S_A and S_B is given by:

$$D_S = d_a D_A + d_b D_B + d_{ab} D_{AB} \quad (1)$$

where the d coefficients can be calculated given S , S_A , and S_B .⁶ D_A and D_B are the single-ion ZFS parameters, and D_{AB} is the ZFS due to exchange. This approach has been applied to dimers⁷ and also to larger clusters by successive coupling of spins.⁸ The ideal way to quantify the single-ion ZFS is by doping the paramagnetic ion of interest into a diamagnetic, isostructural host.⁷ However, this is often impossible because the diamagnetic analogue cannot be prepared. Some have worked “backwards” to estimate the single-ion ZFS from the experimentally determined cluster ZFS via the vector coupling approach.⁸ It would be far preferable to have a *direct measure* of the single-ion ZFS within the cluster.

The dodecametallic complex $[\text{Cr}_{12}\text{O}_9(\text{OH})_3(\text{O}_2\text{CCMe}_3)_{15}]$, $\{\text{Cr}_{12}\}$, has an $S = 6$ ground state with axial spin-Hamiltonian parameters of $D_{S=6} = +0.088 \text{ cm}^{-1}$, $g_{zz} = 1.965$, $g_{xy} = 1.960$ as shown by EPR spectroscopy.⁹ Frozen solution EPR proves the integrity of the cluster in solution. $\{\text{Cr}_{12}\}$ contains a pentacapped centered trigonal prism of Cr(III) ions (Figure 1) (each with six O-donor ligands) and has D_3 crystallographic symmetry such that there are only four independent Cr(III) sites. The axial EPR symmetry is consistent with the D_3 cluster symmetry.

The mechanism for ZFS in the 4A_2 ground state of the Cr(III) ion is mixing with excited states (both spin quartet and doublet) via spin-orbit coupling.¹⁰ Macfarlane has given analytical expressions for the ZFS of trigonally distorted Cr(III) ions in terms of the excited states arising from the d^3 configuration:¹¹

$$2D = \frac{4}{9} \left(\frac{1}{\delta_3^2} - \frac{1}{\delta_1^2} \right) \nu \zeta^2 + \left[\frac{4\sqrt{2}}{3\delta_1\delta_4} + \frac{2\sqrt{2}}{\delta_2\delta_3} + \frac{2\sqrt{2}}{3\delta_3\delta_4} + \frac{2\sqrt{2}}{\delta_2\delta_4} - \frac{16B}{\delta_1\delta_4\delta_5} - \frac{8\sqrt{2}B}{\delta_3\delta_4\delta_5} + \frac{9\sqrt{2}B}{\delta_2^2\delta_3} \right] \nu' \zeta^2 \quad (2)$$

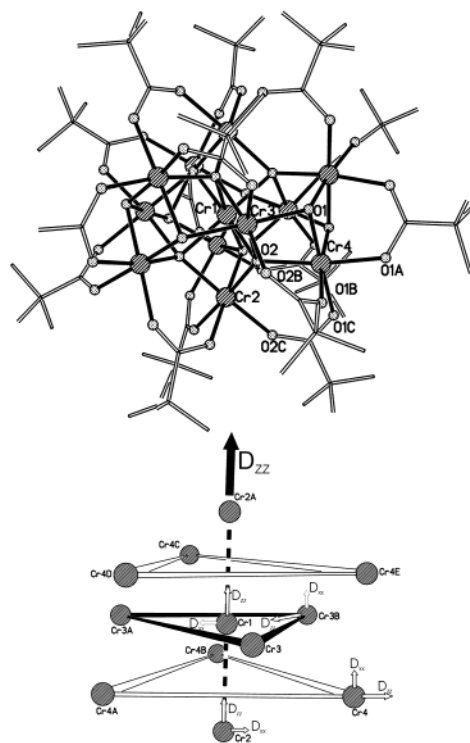


Figure 1. Molecular structure of $\{\text{Cr}_{12}\}$ (top), and scheme of the Cr_{12} skeleton and the relative orientations of the single-ion and cluster ZFS axes (bottom).

where ν and ν' are related to the splitting of the 4T_2 and 4T_1 states due to a trigonal distortion,¹² B is the Racah parameter, ζ is the spin-orbit coupling constant (273 cm^{-1}), and δ_i are the optical ground state-excited state energies as defined in Table 1.

Optical spectra of $\{\text{Cr}_{12}\}$ resemble those of single-ion $\{\text{CrO}_6\}$ species (Figure 2) and can be assigned analogously (Table 1; note that we have used term symbols appropriate to a monomer). A magnetic circular dichroism (MCD) spectrum resolves many of the bands in the UV/vis spectrum (as observed previously for clusters¹³), e.g. the $^4A_2 \rightarrow ^4T_2$ transition is split into two bands consistent with D_3 symmetry, and also enhances the sharp spin-forbidden transitions.¹⁴ We have analyzed these data to determine the *mean single-ion* Cr(III) ZFS in the cluster. Although there are four independent Cr(III) sites in $\{\text{Cr}_{12}\}$, their metrical parameters do not differ dramatically, and the differences are not resolved in optical experiments. Using eq 2 we calculate the single-ion ZFS for the Cr(III) ions, $|D| = 1.035 \text{ cm}^{-1}$. Although Solomon has demonstrated the importance of anisotropic covalency in related calculations on $[\text{FeCl}_4]^-$,¹⁵ it has been shown that this can be neglected for $\{\text{CrO}_6\}$ species.¹⁶

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Table 1. Optical Data for {Cr₁₂}

UV/vis/cm ⁻¹ ^a	MCD/cm ⁻¹ ^b	assignment ^c	energy ^d	label ^e
<i>e</i>	14085	⁴ A ₂ → ² E	9B+3C	
–	ca. 15150	⁴ A ₂ → ² T ₁	9B+3C	
16475	15673	⁴ A ₂ → ⁴ T ₂	Δ	δ ₁
–	16502	(⁴ E + ⁴ A ₁)		
–	20000	⁴ A ₂ → a ² T ₂	15B+4C	δ ₂
22883	21598 ^f	⁴ A ₂ → a ⁴ T ₁	Δ+12B	δ ₄
–	24154	(⁴ E + ⁴ A ₂)		
–	27933	⁴ A ₂ → b ² T ₂	Δ+9B+3C	δ ₃
(35000) ^g	–	⁴ A ₂ → b ⁴ T ₁	2Δ+3B	δ ₅

^a 300 K UV/vis. ^b 1.8 K MCD. ^c Assignment and nomenclature from Macfarlane.^{11,12} ^d Excited-state energies in terms of crystal field splitting (Δ) and Racah parameters (B, C). These data give Δ = 16475 cm⁻¹, B = 534 cm⁻¹, C ≈ 3000 cm⁻¹, and trigonal splitting parameters^{11,12} ν = 1658 cm⁻¹, ν' = ca. 1700 cm⁻¹. ^e Blank implies not observed. ^f Splitting of a⁴T₁ state determined by simultaneous Gaussian fitting to UV/vis and MCD. ^g Not observed, calculated from Δ, B, and C.

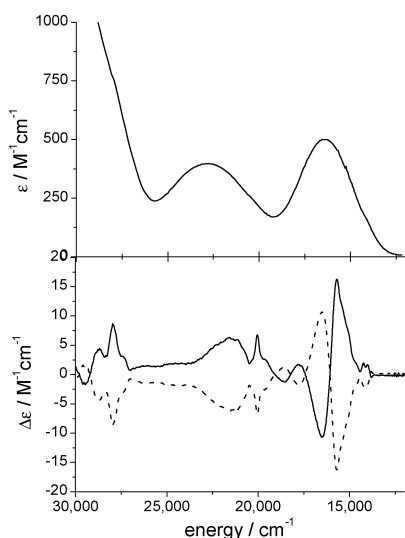


Figure 2. (a) Room-temperature UV/vis spectrum, and (b) 1.8 K MCD spectra in magnetic fields of +5 T (solid line) and -5 T (dashed line), of {Cr₁₂} in CHCl₃/toluene (1:1 v/v) solution.

We can use this measured single-ion ZFS to calculate the cluster ground-state ZFS, using vector coupling. However, because *D* is a tensor quantity related to its diagonal elements by

$$D = D_{zz} - \frac{D_{xx} + D_{yy}}{2} \quad \text{with} \quad D_{xx} + D_{yy} + D_{zz} = 0 \quad (3)$$

the relative orientations of the principal distortion axes of the four Cr(III) sites (*x*, *y*, *z*) relative to the cluster axes (*X*, *Y*, *Z*) must be considered. The cluster axes are defined by symmetry: *D*_{ZZ} must be collinear with the *C*₃ axis. The central ion, Cr(1), and the trigonal face caps, Cr(2) and Cr(2a), lie on the *C*₃ axis, and their local *z*-axes are required to be coincident with the *C*₃ (Figure 1b), and therefore their *D*_{zz} components project directly onto the cluster *D*_{ZZ}. The rectangular face caps, Cr(3) and symmetry equivalents, lie on the *C*₂ axes (perpendicular to *C*₃), and if we assume local axial symmetry, then these define the *z*-axes for these sites and their local *D*_{xx} components project onto *D*_{ZZ}. The fourth site, Cr(4) and symmetry equivalents, are in general positions. There is a slight tetragonal elongation of the octahedral coordination geometry along the O(1A)–Cr(4)–O(2) direction: the O(1A)⋯O(2) vector is almost perpendicular (93°) to the *C*₃ axis. Therefore, the local *D*_{xx} components project onto the cluster *D*_{ZZ}.

The only logical explanation from symmetry considerations for an *S* = 6 ground state in {Cr₁₂} is if the spins on the four Cr(III)

ions at the center of the cage [Cr(1), Cr(3), Cr(3a), and Cr(3b)] are aligned antiparallel with the remaining spins. We can couple the spins within the cluster in several ways to achieve this, and we give the results for one such scheme here.¹⁷ Finally, we make the assumption that the cluster ZFS is entirely single-ion in origin (*D*_{AB} = 0). Using the vector coupling approach we have:

$$D_{ZZ} = 0.279D_{xx} + 0.052D_{zz} \quad (4)$$

From the optical data and eqs 3 we have *D*_{zz} = ∓0.693 cm⁻¹ and *D*_{xx} = ±0.347 cm⁻¹. Equation 4 gives *D*_{ZZ} = ±0.061 cm⁻¹ and hence the ground-state ZFS of {Cr₁₂} is calculated as *D*_{S=6} = ±0.091 cm⁻¹. This is in remarkable agreement with the measured value of +0.088 cm⁻¹ and implies that the ground state ZFS originates almost exclusively from the single-ion ZFS. The measured value of *D*_{S=6} is positive, which implies the single-ion ZFS is negative; this is consistent with the sign for trigonally distorted {CrO₆} centers such as in ruby.¹⁰ A vector coupling approach also reproduces the cluster *g*-values.

For future work in SMMs, these results have important implications: (i) optical data can allow *measurement* of single-ion ZFS parameters; (ii) the relative orientations of the distortion axes of the single-ions is crucial; (iii) even though a negative ZFS is a requirement for SMM behavior, it is not vital that the component single-ion *D* is negative: here if the single-ion *D*-value were *positive*, {Cr₁₂} would be a SMM. Very large positive single-ion ZFSs could result in a large negative cluster ZFS if the relative orientation of local and global axes can be controlled.

Acknowledgment. We thank the EPSRC for funding.

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- (17) For example, the Cr(III) ions on the *C*₃ axis are connected by three single-atom bridges, and we expect them to be strongly anti-ferromagnetically coupled to give *S* = ³/₂. We then couple the three rectangular face caps to give *S* = ¹/₂. We couple pairs of vertices of the trigonal prism ferromagnetically to give *S* = 3 pairs and then couple these together to give *S* = 9. This is then coupled anti-ferromagnetically with the spin of the rectangular caps, to give *S* = ⁹/₂; finally, this is combined ferromagnetically with the *S* = ³/₂ on the central spine to give *S* = 6. Other coupling schemes give slight variations in the calculated *D*_{S=6}, but all are very close to the measured value.

JA029003X