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COMMUNICATION

Unprecedented Magnetic Relaxation via Fourth Excited State in Low-Coordinate Lanthanide Single-ion Magnets: A Theoretical Perspective

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Four low-coordinate SIMs have been studied to probe the relaxation dynamics using *ab initio* calculations. Our calculations reveal that both the symmetry and the equatorial ligand field play a key role in controlling the barrier heights in three coordinate $[\text{Ln}^{\text{III}}(\text{NSiMe}_3)_3]$ complexes (Ln=Dy/Er). This study unfolds an unprecedented blockade of magnetization up to three excited states for the Er(III) complex.

Mononuclear single-ion magnets (SIMs) have received perceivable interest in molecular magnetism, as many of them show large blocking temperature for magnetization reversal¹⁻³ and have potential applications in high-dense storage devices, spintronics and in quantum computing.⁴⁻⁷ Majority of the SIMs reported to date are lanthanide based compounds, however SIMs based on d-block and 5f-elements are also known.⁸⁻¹³ Many of the 4f-elements based SIMs hold record for the largest blocking temperature for magnetization reversal (U_{eff}) and thus are the popular choice for the experimental chemists.^{9,14-16} Unlike in transition metal chemistry, SIMs are attractive in lanthanide chemistry as larger lanthanide clusters possess weak exchange interaction which in turn leads to fast relaxation via quantum tunnelling of magnetization (QTM). At several occasions the relaxation of magnetization in polynuclear lanthanide clusters are found to be single-ion in origin. An illustrating example is the discovery of $\{\text{Dy}_3\}$ cluster which has a barrier height of more than 800 K, while the origin of the magnetic relaxation is found to be single-ion in nature.¹⁷ This revitalizes the lanthanide based SIMs as the barrier height can be controlled by the ligand field interaction.^{16,18}

Despite several lanthanide complexes possessing very large barrier height, only a few molecules exhibit the hysteretic behaviour at low temperatures due to rapid magnetization relaxation. This underlines the need to understand the mechanism of magnetic relaxation in these complexes to gain ground for future directions. The mechanism of magnetic relaxation has been probed via both experiment and theory and the following dominant processes are noticed in these complexes (i) Raman/Orbach¹⁹ process (ii) thermal assisted QTM between the excited state Kramers doublets (KDs) (iii) ground state QTM due to lack of axiality in the ground state KD.^{20,17} The presence of non-collinear structure of magnetic moment in low symmetry complexes activates multiple processes of magnetic relaxation. The competing nature of all these processes of magnetic

relaxation drastically reduces the effective energy barrier and apparently liquidates the Single Molecule Magnet (SMM) behaviour.

Large barrier heights in lanthanides based SIMs are attainable by fine tuning either the ligand field around the lanthanide ions or by inducing stronger metal-ligand interactions.²¹⁻²² An illustrating example for stronger metal-ligand interaction is $\{\text{Dy}_4\text{K}_2\}$ cluster where the coincidence of magnetic anisotropy led to suppression of the relaxation of magnetization reversal via the first excited KD yielding large U_{eff} values.¹⁷ The presence of large rotational symmetry axis in $[\text{Er}(\text{COT})_2]^-$ complex³ leads to second largest blocking temperature of 10K for magnetization reversal. Although high symmetry is desirable, lanthanide complexes often possess large coordination numbers (C.N.) and therefore maintaining the site symmetry is a challenging task. In this regard, low-coordinate lanthanide complexes are attractive as the symmetry around the lanthanide ions are to a certain extent controllable and hence can yield larger U_{eff} values.

Recently Tang and co-workers have reported low-coordinate Er(III) and Dy(III) complexes to probe the role of ligand field in the design of SMMs.²³ The first set comprises tri-coordinate $[\text{Ln}^{\text{III}}(\text{N}(\text{SiMe}_3)_2)_3]$ (where Ln=Er (**1a**), Dy(**1b**)) complexes where Ln(III) is located slightly above the trigonal plane of the donor atoms (out-of-plane-shift τ is 0.53 Å). These complexes possess a C_{3v} local symmetry around Ln(III) ion. The second set comprises $[\text{Ln}^{\text{III}}(\text{NHPhPr}_2)_3(\text{THF})_2]$ (where Ln=Er (**2a**), Dy(**2b**)) complexes possessing trigonal bipyramidal geometry with two tetrahydrofuran ligands coordinated on the axial positions.²⁴ Complex **1a** is the first example where zero-field SMM behaviour ($U_{\text{eff}}=85 \text{ cm}^{-1}$) was noted for an equatorially coordinated Er(III) complex. On the other hand complex **1b** lacks SMM behaviour. In the other set, complex **2b** is a zero-field SMM with U_{eff} of 23 cm^{-1} while complex **2a** lacks zero-field SMM behaviour. A butterfly shaped magnetic hysteresis loop has been reported for both **1a** and **2b** confirming the SMM behaviour. Although these sets of four complexes illustrate the importance of coordination geometry around the lanthanide ions, reasons behind the presence/absence of SMM behaviour and the mechanism of magnetic relaxations are not clearly resolved. Here we aim to achieve this by probing the magnetic anisotropy and the mechanism of magnetic relaxation pathways associated with these complexes using *ab initio* CASSCF+RASSI calculations on the X-ray structures²⁴⁻²⁸ using MOLCAS 7.8 code (see ESI for computational details).

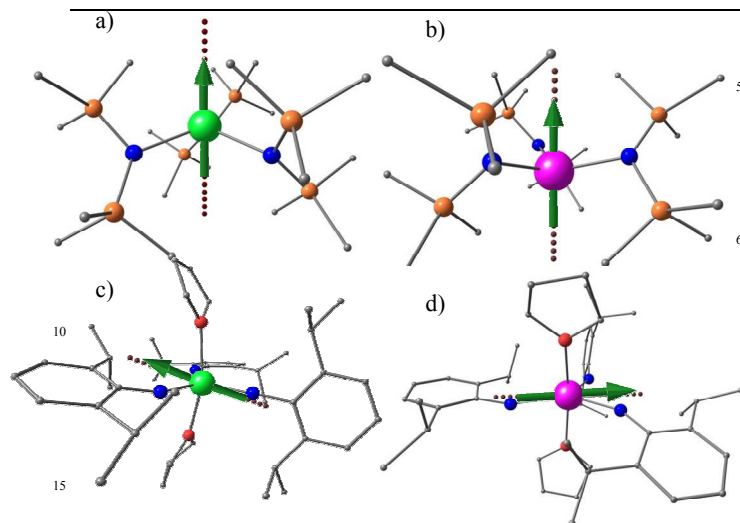


Fig. 1. *Ab initio* computed orientation of principal magnetization axis of the ground state KDs for complexes a) **1a**, b) **1b**, c) **2a** and d) **2b** plotted on top of the X-ray structure. Color Code: green (Er), pink (Dy), blue (N), red (O), orange (Si), grey for (C). The hydrogens are omitted for clarity.

The atomic ground state for Er(III) and Dy(III) are $^4I_{15/2}$ and $^6H_{15/2}$ respectively possessing eight ground state KDs for which the g-tensors are estimated (see ESI Table S5,S6,S7 and S8). The computed orientations of the g-tensors for ground state KD in all four complexes are shown in Figure 1 (see ESI Figure S1 for orientation of g-tensors of other excited KDs). The computed energy spectrum of eight KDs spanned up to 539 cm^{-1} and 1337 cm^{-1} for complexes **1a** and **1b** respectively. The computed g-tensor for complex **1a** is found to be purely axial in nature, ($g_{xx}=0.0000$, $g_{yy}=0.0005$ and $g_{zz}=17.8770$) and stabilizes $m_J=\pm 15/2$ as the ground state. On the other hand in case of complex **1b**, a reverse trend has been noted with stabilization of $m_J=\pm 1/2$ as the ground state. This state naturally possesses high transverse g-components ($g_{xx}=10.9845$, $g_{yy}=10.3215$ and $g_{zz}=1.3844$). The stabilization of $m_J=\pm 1/2$ as the ground state has been noted also earlier in $[\text{Dy}(\text{COT})_2]^-$ sandwich complex.²⁹ The principal magnetization axis of the ground state KD is oriented along the C_3 axis for both the complexes **1a** and **1b**. This is in agreement with the expected orientation based on the electro-static potential.^{18, 30} Presence of C_3 symmetry around the metal ion leads to collinearity of principal magnetization axes up to third excited KDs (*c.a.* <2 degree deviation; see ESI Table S5 and S6) and this sets the theoretical barrier height to 331 cm^{-1} for **1a** (vide infra). Table 1. *Ab initio* computed principal values of ground state g-tensors for all four complexes.

Complexes	1a	1b	2a	2b
g_{xx}	0.0000	10.9845	0.0383	0.0075
g_{yy}	0.0005	10.3215	0.6381	0.0128
g_{zz}	17.8770	1.3844	16.1980	19.6742

In case of complexes **2a** and **2b**, the computed energy spectrum of eight KDs spanned up to 372 cm^{-1} and 790 cm^{-1} respectively. The computed g-tensors for both these complexes show a general pattern observed for low-symmetry complexes (see ESI Table S7 and S8).³¹⁻³² The computed g-tensor for ground state KD of complex **2a** shows axiality ($g_{xx}=0.0383$, $g_{yy}=0.6381$ and $g_{zz}=$

16.1980) but it lacks the pure Ising nature. The first excited KD possesses high transverse anisotropy ($g_{xx}=3.56$, $g_{yy}=5.49$ and $g_{zz}=9.97$) and lies 76 cm^{-1} far from the ground state. The corresponding principal magnetization axis is tilted by 55.39 degrees from ground state KD for complex **2a**. On the other hand, the computed g-tensor for ground state KD of complex **2b** reflects higher degree of axiality ($g_{xx}=0.0074$, $g_{yy}=0.0128$ and $g_{zz}=19.6742$) compared to complex **2a**. The first excited state is 199 cm^{-1} higher in energy from the ground state KD with an 18.67 degrees tilt with respect to the ground state KD. The presence of two oxygen donor ligands on the axial positions provides the desired ligand field for the oblate Dy(III) ion and thus leads to a larger barrier height compared to its Er(III) analogue. The computed magnetic susceptibility data are in good agreement to the experiments for all four complexes (see Figure S3 in ESI).

In the next step we have computed the transversal magnetic moments between the connecting pairs to probe the mechanism of magnetic relaxation in these complexes. The spin-phonon relaxations are related to the square of the transversal magnetic moment.³³ To attain an insight in the mechanism of magnetic relaxation, here we have computed the mean absolute values of transversal magnetic moments between the connecting pairs of opposite magnetization for all four complexes to (see Figure 2). The best SIM among the four studied complex is **1a** with an U_{eff} of 85 cm^{-1} . For complex **1a** the transversal magnetic moments between the ground state KD is negligible (*ca.* $10^{-4} \mu_B$), which suggest that the QTM is quenched at the ground state. Due to the presence of symmetry, the major relaxation is found to proceed via the 4th excited KD .i.e. it follows $[-1 \rightarrow -2 \rightarrow -3 \rightarrow -4 \rightarrow -5] \rightarrow [+5 \rightarrow +4 \rightarrow +3 \rightarrow +2 \rightarrow +1]$ path (see Figure 2a). However the transversal magnetic moments between the excited KDs are moderate in **1a** (*ca.* $10^{-1} \mu_B$) and suggest partial TA-QTM being operative through all the four excited KDs. Besides, the off-diagonal terms of transversal magnetic moments (*ca.* $10^{-1} \mu_B$) between the ground state and excited state of opposite magnetization related to Orbach process is also moderate and opens up further relaxation paths in **1a**. Although theoretical estimate of barrier is 331 cm^{-1} , these multiple relaxation paths TA-QTM and Orbach process which are weakly operational and reduce the U_{eff} value. However our calculations predict a perceivable magnetization blockade up to three excited states and relaxation via fourth excited KDs and this phenomenon is unprecedented among lanthanide based magnets. This suggests that complex **1a** possesses a large U_{eff} value and dilution experiments with diamagnetic analogues could raise the barrier beyond the observed experimental U_{eff} values (Note beyond the single-ion relaxation mechanism discussed, intermolecular interactions also lead to a significant relaxation, this is expected to be significant especially when the intermolecular Er(III)...Er(III) distances are as short as 7.34 Å found in complex **1a**). Due these effects one-to-one comparison of U_{eff} values between theory and experiment is not straight forward.

For complex **1b** on the other hand, the $m_J=\pm 1/2$ is stabilized as the ground state followed by other higher m_J excited states resulting in a barrier less potential well. This difference in behaviour between **1a** and **1b** is visible in the DFT computed spin density plots (see ESI Figure S2). The computed transversal magnetic

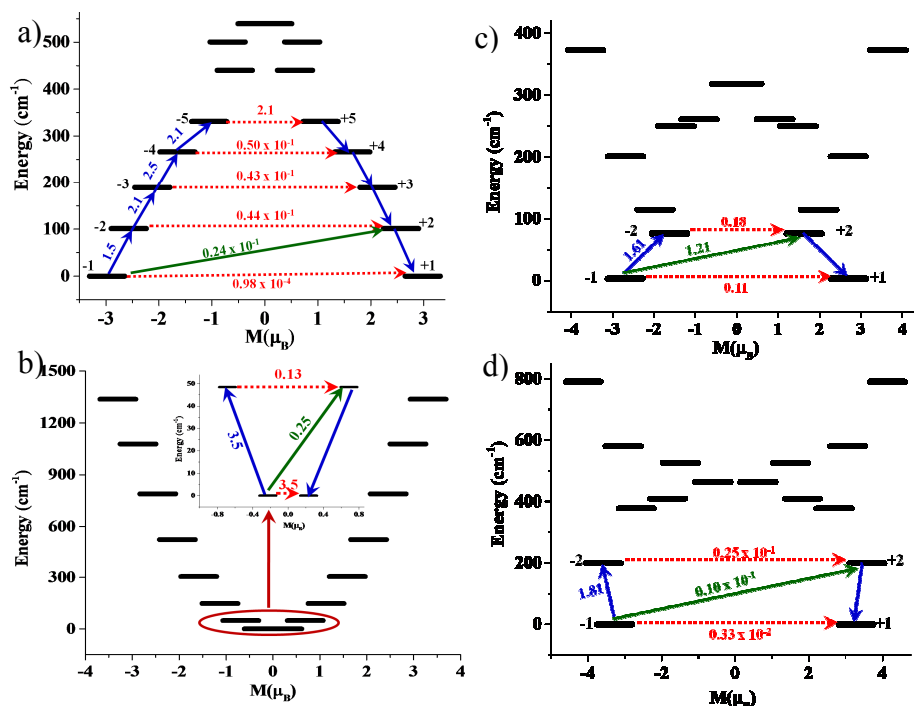


Fig. 2. The *ab initio* computed magnetization blocking barrier for all the four complexes. a) **1a** b) **1b** c) **2a** and d) **2b**. The thick black line indicates the Kramers Doublets (KDs) as a function of magnetic moment. The green lines show the possible pathway of the Orbach process. The blue lines show the most probable relaxation pathways for magnetization reversal. The dotted red lines represent the presence of QTM/TA-QTM between the connecting pairs. The numbers provided at each arrow are the mean absolute value for the corresponding matrix element of the transition magnetic moment.

moments shown in Figure 2b (subset), clearly suggest that ground state QTM is the major relaxation pathway for this complex and this wipes out the SMM behaviour.

In case of complex **2a** and **2b**, the relaxation of magnetization occurs through the first excited state via Orbach/TA-QTM processes due to non-collinear magnetic moments. The computed transversal magnetic moments between the ground state KDs clearly suggest the presence of significant QTM ($0.11\mu_B$) in case of complex **2a**, while it is weak (*ca.* $10^{-2}\mu_B$) in case of complex **2b**. Due to these reasons, **2b** is a zero-field SMM while **2a** is a field induced SMM. Quite interestingly the axial coordination of THF ligands dramatically changes the energies of the KDs and thus the magnetic properties (see Figure 2c and 2d). The presence of axial ligands stabilize $m_J = \pm 15/2$ as the ground state for both the species, however collinearity of the magnetization axes are lost resulting in the relaxation via the first excited KDs in both the cases. Besides the wavefunction of the ground state KD of **2b** is almost pure $m_J = \pm 15/2$ state with negligible contributions from other m_J projections while the wavefunction of the **2a** has significant contributions from other m_J projections leading to smaller gap between the ground state and first excited state KD for **2a** compared to **2b**.

This demonstrates that ligand field around the metal ions needs to be carefully tailored towards SMM behaviour with the observation that equatorial ligand field favours Er(III) ions while axial ligand field favours Dy(III) ions. The change is particularly dramatic for Dy(III) ion where the ground state and the magnetic properties switched completely as we move from **1b** to **2b**.

However such changes are marginal as we move from **1a** to **2a** and the difference in magnetic properties observed are essentially due to lower m_J levels mixing brought in by the axial ligands.

To gain further insights, we have also computed the crystal field parameters for all the four complexes which provide a better picture of the QTM process.^{27, 28} The computed axial B_0^2 terms are quite high for **1a** and **1b** compared to their non-axial terms (see ESI Table S9). In case of complexes **1a** and **1b** the B_0^2 and the B_0^4 parameters are found to have opposite signs which support the observed change in the energy level pattern.²¹ On the other hand, same sign of the axial terms are observed for both **2a** and **2b** leading to similar energy pattern. A large QTM in case of **2a** is expected due to large non-axial B_2^2 term while axial terms are dominant in complex **2b**.

To seek larger U_{eff} value for complex **1b**, we have developed a magneto-structural correlation for the out-of-plane-shift parameter (τ parameter) where the Er(III) ion is moved to the plane of the ligands gradually (see Figure 3, ESI Figure S4 and Table S10). Significant increases in the U_{eff} values are observed with maximum U_{eff} being achieved for the planar structure (i.e. when the $\tau=0$ Å).

Besides for the planar structure, all the principal magnetization axes of all the KDs are collinear leading to relaxation via the 7th excited state. This leads to very large barrier height (>750 cm⁻¹) for the planar structure. This highlights importance of coordination number and the symmetry in enhancing the barrier heights in lanthanide based SMMs.

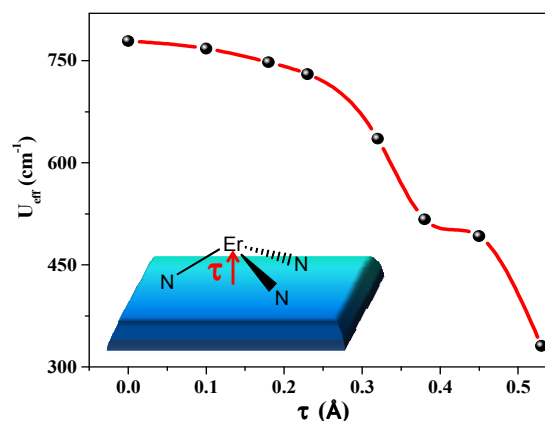


Fig.3. Magneto-structural correlations performed to observe the effect of out of plane shift (τ parameter) on the computed U_{eff} value.

To this end using *ab initio* calculations we have probed the mechanism of magnetic relaxation in four low-coordinate lanthanide complexes and our study unfolds an unprecedented magnetization blockade for three coordinate Er(III) complex up to

third excited state. Developed magneto-structural correlation reveals that even minuscule changes can drastically increase the U_{eff} values – a strategy that can be adapted by the experimentalists to fine tune the barrier height. The combined experimental and theoretical work is in progress currently in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [CASSCF+RASSI computed spin free states, spin orbit states, energies of the low-lying Kramers Doublet, magnetic susceptibility along with g-tensor orientations for all four complexes. DFT computed spin densities and details of developed magneto-structural correlations]. See DOI: 10.1039/b000000x/

- H. L. C. Feltham and S. Brooker, *Coord. Chem. Rev.*, 2014, **276**, 1-33.
- D. N. Woodruff, R. E. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110-5148.
- K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2013, **135**, 17952-17957.
- M. N. Leuenberger and D. Loss, *Nature*, 2001, **410**, 789-793.
- R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141-143.
- P. Totaro, L. Poggini, A. Favre, M. Mannini, P. Sainctavit, A. Cornia, A. Magnani and R. Sessoli, *Langmuir*, 2014, DOI: 10.1021/la500846a.
- M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M. A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia and R. Sessoli, *Nature*, 2010, **468**, 417-421.
- K. R. Meihaus, S. G. Minasian, W. W. Lukens, S. A. Kozimor, D. K. Shuh, T. Tylliszczak and J. R. Long, *J. Am. Chem. Soc.*, 2014, **136**, 6056-6068.
- E. Lucaccini, L. Sorace, M. Perfetti, J.-P. Costes and R. Sessoli, *Chem. Commun.*, 2014, **50**, 1648-1651.
- J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat Chem*, 2013, **5**, 577-581.
- J. D. Rinehart and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 12558-12559.
- M. A. Antunes, L. C. J. Pereira, I. C. Santos, M. Mazzanti, J. Marçalo and M. Almeida, *Inorg. Chem.*, 2011, **50**, 9915-9917.
- J. M. Zadrozny and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 20732-20734.
- L. Sorace, C. Benelli and D. Gatteschi, *Chem.Soc.Rev.*, 2011, **40**, 3092-3104.
- J.-L. Liu, Y.-C. Chen, Y.-Z. Zheng, W.-Q. Lin, L. Ungur, W. Wernsdorfer, L. F. Chibotaru and M.-L. Tong, *Chem. Sci.*, 2013, **4**, 3310-3316.
- J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078-2085.
- R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru and R. E. P. Winpenny, *Nat. Chem.*, 2013, **5**, 673-678.
- N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny and A. Soncini, *Nat Commun*, 2013, **4**, doi:10.1038/ncomms3551.
- R. Orbach, *Proc. R. Soc. Lond. A.*, 1961, **264**, 485-495.
- Y.-N. Guo, L. Ungur, G. E. Granroth, A. K. Powell, C. Wu, S. E. Nagler, J. Tang, L. F. Chibotaru and D. Cui, *Sci. Rep.*, 2014, **4**, doi:10.1038/srep05471.
- L. Ungur, J. J. Le Roy, I. Korobkov, M. Murugesu and L. F. Chibotaru, *Angew. Chem.Int.Ed.*, 2014, **53**, 4413-4417.
- K. S. Pedersen, L. Ungur, M. Sigrist, A. Sundt, M. Schau-Magnussen, V. Vieru, H. Mutka, S. Rols, H. Weihe, O. Waldmann, L. F. Chibotaru, J. Bendix and J. Dreiser, *Chem. Sci.*, 2014, **5**, 1650-1660.
- P. Zhang, L. Zhang, C. Wang, S. Xue, S.-Y. Lin and J. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 4484-4487.
- W. J. Evans, M. A. Ansari, J. W. Ziller and S. I. Khan, *Inorg. Chem.*, 1996, **35**, 5435-5444.
- D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Chem. Commun.*, 1972, 349-350.
- W. A. Herrmann, R. Anwender, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber and G. R. J. Artus, *Z. Naturforsch., B:Chem.Sci.*, 1994, **49**, 1789-1797.
- S. Jank, H. D. Amberger and N. M. Edelstein, *Spectrochim. Acta, Part A*, 1998, **54**, 1645-1650.
- S. Jank, H. Reddmann and H. D. Amberger, *Inorg. Chim. Acta*, 2008, **361**, 2154-2158.
- J. J. Le Roy, M. Jeletic, S. I. Gorelsky, I. Korobkov, L. Ungur, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2013, **135**, 3502-3510.
- D. Aravena and E. Ruiz, *Inorg. Chem.*, 2013, **52**, 13770-13778.
- J. Ruiz, A. J. Mota, A. Rodriguez-Dieguez, S. Titos, J. M. Herrera, E. Ruiz, E. Cremades, J. P. Costes and E. Colacio, *Chem. Commun.*, 2012, **48**, 7916-7918.
- L. Ungur and L. F. Chibotaru, *Phys.Chem. Chem. Phys.*, 2011, **13**, 20086-20090.
- D. A. Garanin and E. M. Chudnovsky, *Phys. Rev. B*, 1997, **56**, 11102-11118.