



Cite this: *Chem. Commun.*, 2016, 52, 7168

Received 12th April 2016,
Accepted 5th May 2016

DOI: 10.1039/c6cc03066a

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An unprecedented zero field neodymium(III) single-ion magnet based on a phosphonic diamide†

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The axial ligation by the –P=O group of a phosphonic diamide in an air-stable Nd(III) complex ensures a pseudo- D_{5h} symmetry leading to the stabilization of the $m_j = |\pm 9/2\rangle$ state; this in turn is responsible for the observed SIM behaviour at zero field and the slow relaxation of magnetization up to 8.0 K.

The tremendous growth in the area of 4f based single-molecule magnets (SMMs) in the last decade has been driven by their interesting quantum physical phenomena and macroscopic magnet-like behaviour displayed in the molecular regime.¹ The active research on SMMs has further been encouraged by their potential futuristic technological application in high density data storage devices, molecular spintronics and quantum computing devices.² As the 4f wave functions are more localized, they feebly interact with the ligand orbitals and result in a large unquenched orbital angular momentum with large spin-orbit coupling in the ground state. Furthermore the high anisotropic electronic charge distribution of 4f orbitals offers a high single-ion anisotropy for 4f ions. Despite the fact that the crystal field (CF) splitting in the case of 4f ions is very weak, it has been proven beyond doubt that the CF and the local symmetry around the central 4f ion play important roles in fine-tuning the properties of SMMs.³

In order to understand the slow relaxation dynamics and further fine-tune the properties of SMMs, the focus has shifted in recent times to single-ion magnets (SIMs), especially to the heavier lanthanides *viz.* as Dy(III), Tb(III) and Er(III).^{4–6} On the other hand, the strongest magnets that are employed in the industry are based on lighter lanthanide elements, such as SmCo₅ and Nd₂Fe₁₄B.⁷ The rare abundance of the critical elements and rising costs further make the heavier rare-earth based research on SMM expensive and unsustainable in the long run. In particular, isolation of SMMs based on the lighter lanthanides

is rare as the spin-orbit coupling is not strong enough compared to those of the heavier lanthanide analogues.^{8,9} Although recently few SMMs and SCMs (single-chain magnets) based on more abundant non-critical lighter lanthanides have been reported in the literature, the area of lighter lanthanide based SMMs is still less explored.^{8,9} In the case of Nd(III), a slow relaxation of magnetization has recently been observed in few field induced Nd(III)-based SMMs and carboxylate based SCMs but Nd(III)-based zero-field SMMs is still out-of-sight.⁹ One of the important challenges in obtaining SMMs in lanthanides such as Nd(III) lies in the design of a favourable ligand field. Being an oblate ion, stronger axial and weaker equatorial ligation is likely to help building SMMs with larger U_{eff} values as stated earlier.^{3,10} We have recently demonstrated how symmetry and the nature of the CF with stronger axial interactions can be exploited to increase the anisotropy barrier and blocking temperature in a Dy(III) SIM.¹¹

In a quest to further explore the viability of lighter lanthanide ions for the synthesis of SIMs, herein we present a simple seven coordinate air-stable Nd(III) complex derived from a phosphonic diamide, with a pseudo- D_{5h} symmetry.¹¹ To the best of our knowledge, the molecule reported here is the first example of an Nd(III)-based zero field SIM (Table 1).

The mononuclear seven coordinate Nd(III) complex, [L₂Nd(H₂O)₅][I₃·L₂·(H₂O)] (**1**), is readily synthesized in good yields from the

Table 1 Comparison of **1** with reported Nd(III)-based SIMs/SCMs

Complex	U_{eff}/K	H_{dc}/Oe	Ref.
1	16.08, 24.69	0	This work
1	39.21	2000	This work
NdTp ₃	4.08	100	9a
[Li(DME) ₃][Nd(COT ^{''}) ₂]	21	1000	9b
Na ₉ [Nd(W ₅ O ₁₈) ₂ ·32H ₂ O]	73.95	1000	9c
{[Ln ₂ (CNCH ₂ COO) ₆ (H ₂ O) ₄]·2H ₂ O} _n	26.6	1500	9d
{[Nd(μ ₂ -L1) ₃ (H ₂ O) ₂]·C ₂ H ₃ N ₃] _n	27	2000	9e
[Nd(μ ₂ -L2)(L2)(CH ₃ COO)(H ₂ O) ₂] _n	29	3500	9e

H_{dc} = applied dc field; Tp[−] = trispyrazolylborate; L1 = 3,5-dinitrobenzoic acid; L2 = 2,4-dinitrobenzoic acid; COT^{''} = bis(trimethylsilyl)cyclo-octatetraenyl dianion.

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† Electronic supplementary information (ESI) available: Synthetic details, crystallographic details, magnetic studies and quantum mechanical calculations. CCDC 1451543. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc03066a

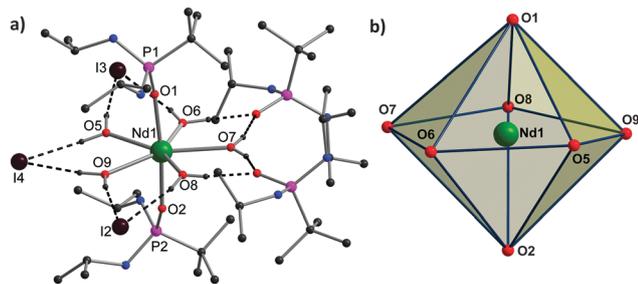


Fig. 1 (a) Molecular structure of **1**. Only water hydrogens are shown for the clarity. The H-atoms of the water molecules are weakly hydrogen bonded to the three iodine anions and two lattice phosphonic diamide ligands. (b) Polyhedron showing the pseudo- D_{5h} symmetry around the Nd(III) ion.

reaction of neodymium iodide hydrate and the phosphonic diamide ligand, 12 t -BuPO(NH i Pr) $_2$ (**L**), under ambient conditions. Complex **1** has been fully characterized by both analytical and spectroscopic techniques. Single crystal X-ray structure analysis of the pale yellow block shaped crystal reveals that **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric part of the unit cell contains a seven coordinate Nd(III) ion in a pseudo- D_{5h} symmetry. The five equatorial coordination sites around the metal are occupied by water molecules, while phosphonic diamide ligands coordinate to the metal through the phosphoryl oxygen (P=O) along the two axial coordination sites (Fig. 1). The axial Nd–O(P) distances (2.285 and 2.294 Å) are considerably shorter than the average equatorial Nd–O(aqua) distances (2.4414 Å), indicating the tighter binding of phosphonamide ligands compared to water molecules. The axial O1–Nd–O2 angle (*trans*) of 174.43 (8) $^\circ$ and the average *cis* O(w)–Nd–O(w) angle of 72.09 $^\circ$ indicate a nearly ideal pentagonal bipyramidal geometry around the central metal ion (Table S2, ESI †). The standard symmetry analysis using SHAPE suggests an almost ideal D_{5h} symmetry with a deviation of 0.286 (Table S3, ESI †).¹³ The nearest Nd–Nd distance in the lattice is 10.738 Å.

The magnetic susceptibility measurements of **1** carried out in an applied dc field of 1000 Oe shows a $\chi_M T$ value of 1.58 cm 3 K mol $^{-1}$ at 300 K (Fig. 2), which is close to the expected value of 1.63 cm 3 K mol $^{-1}$ for an isolated Nd(III) ion (ground state = $^4I_{9/2}$). The $\chi_M T$ value linearly decreases upon cooling and reaches a value of 1.17 cm 3 K mol $^{-1}$ at 2.0 K. The M vs. H curve (Fig. 2 inset) shows a sharp increase in magnetization at a lower field before reaching 1.45 μ_B at 7.0 T. AC susceptibility measurements carried out to understand the slow relaxation dynamics at zero dc field at an oscillating ac field show two maxima for the out-of-phase susceptibility component χ_M'' (Fig. 3 and Fig. S3, ESI †), one each at the higher and lower frequency (temperature) range. The tailing at the lower temperature region clearly indicates the presence of the quantum tunnelling pathway being operative at zero field. Fitting of the magnetic relaxation time (τ) to the Arrhenius equation, $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ (Fig. 3 inset) results in an anisotropic energy barrier of $U_{\text{eff}} = 16.08$ K and $\tau_0 = 2.64 \times 10^{-4}$ s and $U_{\text{eff}} = 24.69$ K and $\tau_0 = 5.03 \times 10^{-6}$ s for the fast and slow relaxation processes, respectively. The slow relaxation process becomes temperature-independent below 4 K (Fig. 3), confirming the

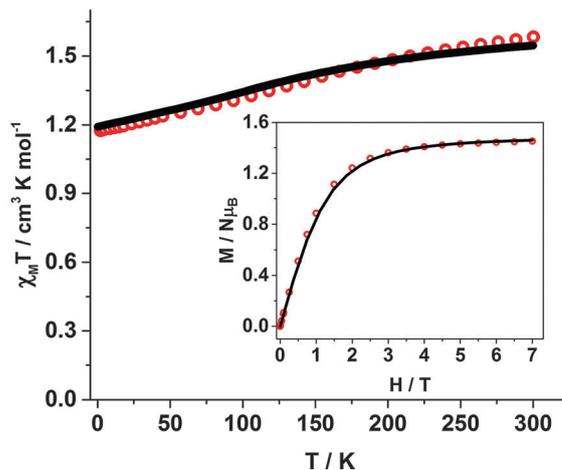


Fig. 2 Experimental and *ab initio* CASSCF computed temperature dependence of the $\chi_M T$ product at 1000 Oe. Inset: Field dependence of magnetisation. Red hollow circles correspond to the experimental data and the solid lines are the computed data. The *ab initio* data is scaled down by 0.963 to reproduce the experimental values.

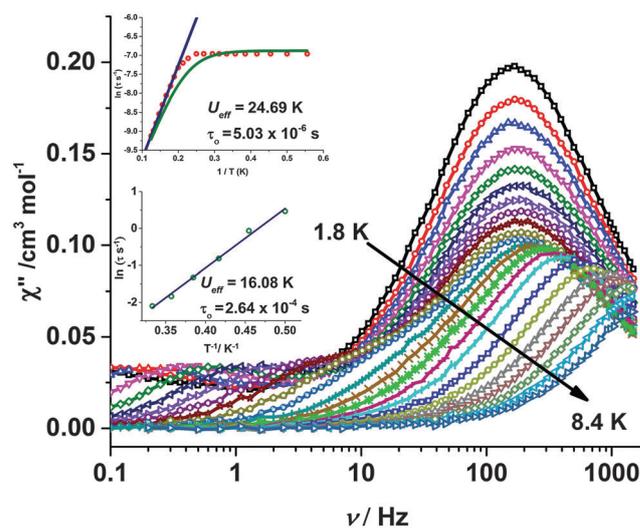


Fig. 3 Out-of-phase (χ_M'') component of the frequency dependent ac susceptibility measured in an oscillating ac field of 1 Oe and zero applied dc field for **1**. Inset: Plot of the relaxation time τ (logarithmic scale) versus T^{-1} obtained; the solid blue line corresponds to the fitting of the Arrhenius law and the green line to the multiple relaxation pathway.

presence of QTM in the ground state Kramers doublet (KD). The fitting to the Arrhenius law in the case of the slow relaxation process deviates from linearity below 4.7 K and indicates the presence of QTM along with Orbach process as a dominant relaxation pathway (see the ESI †). The Cole–Cole plots (χ_M'' vs. χ_M') also indicate the presence of two relaxations and fitting the data to a generalized Debye model indicates the presence of a wide distribution of relaxation times ($0.02 < \alpha_1 < 0.209$ and $0 < \alpha_2 < 0.237$) (Fig. S4, ESI †).¹⁴ The presence of such multiple relaxation processes has been previously observed in SIMs.^{6f,15}

In order to lift the degeneracy and to quench the QTM, ac susceptibility measurements were carried out at an applied

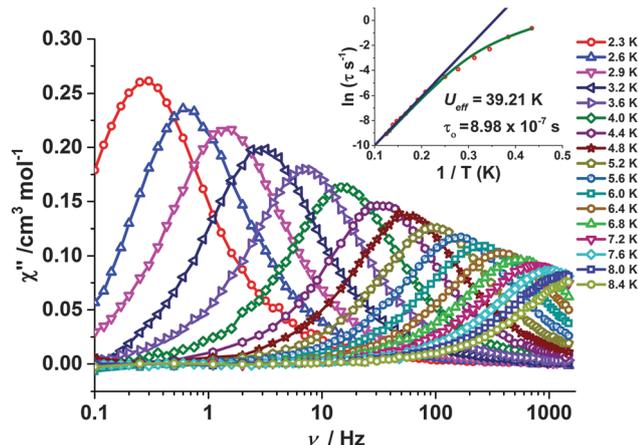


Fig. 4 Out-of-phase (χ_M'') component of the frequency dependent ac susceptibility measured in an oscillating ac field of 1 Oe and applied dc field of 2000 Oe for **1**. Inset: Plot of the relaxation time τ (logarithmic scale) versus T^{-1} obtained; the solid blue line corresponds to the fitting of the Arrhenius law and the green line to the multiple relaxation pathway.

dc field of 2000 Oe (Fig. 4 and Fig. S5 and S8, ESI[†]). This results in a single relaxation process with an anisotropy barrier of $U_{\text{eff}} = 39.21$ K and $\tau_0 = 8.98 \times 10^{-7}$ s. The application of dc field quenches the QTM relaxation pathway observed in the low temperature regime at zero dc field (see above). The fitting of the Cole–Cole plots (χ_M'' vs. χ_M') with the generalized Debye model results in semi-circles (Fig. S9, ESI[†]) with a narrow distribution of the relaxation times ($0.07 < \alpha_1 < 0.02$) indicating the presence of a single relaxation process with Orbach and Raman as the dominant relaxation pathways (Fig. 4 (inset) and Fig. S11, ESI[†]).

In order to unravel the factors that result in the slow relaxation dynamics of **1**, we have performed *ab initio* calculations (CASSCF/RASSI/SINGLE_ANISO) using the MOLCAS.^{16–18} All the calculations have been performed on the final refined single crystal X-ray structure of **1** by excluding the lattice water molecule. The computed five KDs belonging to the $^4I_{9/2}$ ground state of the Nd(III) ion spans up to 599.1 K (Table S4, ESI[†]) suggesting significant electrostatic interaction exerted by the ligands. The g tensors of ground state KDs are found to be strongly axial ($g_{xx} = 0.02$, $g_{yy} = 0.02$ and $g_{zz} = 6.30$) with very small transverse components. The wave functional analysis shows that ground state is found to be solely in the $m_J = \pm 9/2$ ($|\pm 9/2\rangle$; 0.99) state (Table S5, ESI[†]).

The g_{zz} axis of the ground state is found to lie close to the oxygen (O=P) atom of the phosphonic amide ligand (along the C_5 axis tilted by $\sim 5^\circ$). The g tensors of the first excited state KDs possess large transverse terms ($g_{xx} = 0.10$, $g_{yy} = 0.42$ and $g_{zz} = 5.10$), revealing the possibility of relaxation *via* the first excited state. The angle between the g_{zz} axis of first excited KDs and the ground state KDs is 69.39° , affirming relaxation *via* the first excited KDs. The first excited state is estimated to be an admixture of $m_J = |\pm 5/2\rangle$ and $m_J = |\pm 1/2\rangle$ states.

Analysis of CASSCF charges on the oxygen atoms attached to the Nd(III) ion reveals that the oxygen atoms at the axial positions possess pronounced negative charge compared to the non-axial oxygen atoms leading to the stabilization of the $m_J = |\pm 9/2\rangle$ state

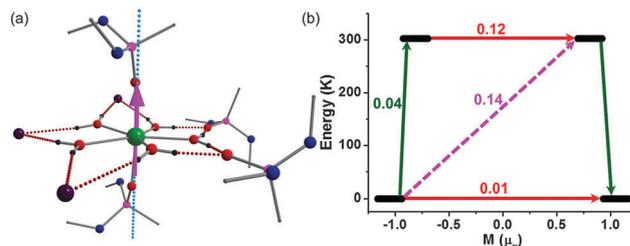


Fig. 5 Electronic structures and energy levels for **1**. (a) CASSCF computed g_{zz} orientation of the ground state KD of complex **1** (methyl groups and most H-atoms have been omitted from the figure for clarity) and (b) possible relaxation pathways in **1**. The black line indicates the KDs as a function of magnetic moments. Red lines represent QTM *via* ground state KDs/TA-QTM *via* the first excited state. Pink dashed lines show a possible Orbach process.

as the ground state (Table S6, ESI[†]). Thus, this is the first instance where stabilization of the maximum m_J ($m_J = |\pm 9/2\rangle$) has been achieved as the ground state for any of the Nd(III) complexes reported to date.⁹

In order to understand the overall mechanism of the relaxation process, we have computed the transverse magnetic moments that connect the opposite pairs of magnetization. Possible relaxation pathways arising out of these calculations are pictorially depicted in Fig. 5. The prominent transverse magnetic moments between the ground state KDs and the first excited state KDs suggest the operation of QTM ($0.01 \mu_B$) and TA-QTM ($0.12 \mu_B$), resulting in two relaxation processes as experimentally observed.

The calculated magnetic data are in agreement with the experimental data adding confidence to our methodology. However, the calculated relaxation barrier height (U_{cal} is 302 K) is overestimated. This is essentially due to the fact that the U_{cal} estimated ignores the ground state QTM effects which are found to be non-negligible for complex **1**. Besides, other effects such as intermolecular interactions or possible non-Orbach relaxation channels also contribute to the observed differences. This overestimation of U_{cal} compared to U_{eff} is particularly prominent in lighter lanthanide elements as also reported elsewhere.^{8e,9d,e}

In summary this study highlights the importance of symmetry and fine-tuning of the CF by an appropriate ligand design to obtain first zero field SIM among Nd(III)-based complexes. Theoretical studies suggest the stabilization of the $m_J = |\pm 9/2\rangle$ state as the ground state with smaller transverse terms leading to the realization of unprecedented zero-field SIM. Studies to fine-tune the ligand environment to further enhance the barrier heights are currently underway in our laboratory.

This work was supported by the DST Nanomission (SR/NM/NS-1119/2011), SERB, New Delhi and IIT-Bombay. R. M. thanks DAE-BRNS for the Outstanding Investigator Award and SERB (SB/S2/JCB-85/2014), New Delhi for J. C. Bose Fellowship. G. R. thanks SERB (EMR/2014/000247) for financial support. We acknowledge Dr L. Ungur and Prof. L. F. Chibotaru, Belgium for additional MOLCAS routines. S. K. G. thanks UGC, New Delhi and IRCC, IIT Bombay for research fellowship and T. R. thanks CSIR for a research fellowship. We are grateful for the availability

of the Institute Central Facility (SVSM) in the Department of Physics, Indian Institute of Technology Bombay.

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