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First example of erbium triple-stranded helicate displaying SMM behaviour

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Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

www.rsc.org/

A series of isostructural C₃-symmetrical triple stranded dinuclear lanthanide $[Ln_2L_3](NO_3)_3$ molecules have been synthesized using subcomponent self-assembly of $Ln(NO_3)_3$ with 2-(methylhydrazino)benzimidazole and 4-tert-butyl-2,6-diformylphenol, where Ln = Tb(1), Dy(2), Ho(3), Er(4), Tm(5), Yb(6). The temperature dependent and field dependent magnetic properties of 1-6 were modeled using the van Vleck approximation including the crystal field term H_{CF} , the super-exchange term H_{SE} and the Zeeman term H_{ZE} . The ferromagnetic interaction were found in 1, 2, 4 and 6, while the antiferrmagnetic interaction were found in 3 and 5. The erbium analogue reveals the field induced SMM behaviour.

Introduction

The lanthanide helicates represent an important class of supramolecular compounds owing to the historical significance perceived with chemical and physical concepts of selfassembly control¹ as well as due to the rich practical applications inherently associated with *f*-block luminescent properties.² By contrast, relatively little attention has been given to slow magnetic relaxation properties, up to the pioneering works of Ishikawa and co-workers³ who showed unprecedented Single Molecule Magnet (SMM) behaviour of terbium(III) and dysprosium(III) phthalocyanine sandwich complexes. A new class of lanthanide single molecule magnets (Ln-SMMs) emerged and has been given particular attention due to a few important advantages in comparison to transition-metal-cluster SMMs. In order to form efficient molecular magnets *i.e.* such that exhibit significant energetic barrier for magnetization reversal (U_{eff}) one should aim for profound Ising-type magnetic anisotropy. To do so, scientists have focused on enhancing two parameters of their systems: axial zero-field splitting parameter D and the total spin of the molecule S.⁴ In fact, early accepted urge to go beyond higher energy barriers via synthesis of polynuclear clusters has been revisited⁵, since it is difficult to control the magnetic anisotropy of multiple metal centres and their easy axes of magnetization to generate large overall magnetic anisotropy.⁶

With inherent unsurpassed single-ion anisotropies resulting from electronic nature of lanthanides, Ln-SMMs display $U_{\rm eff}$ values that outperform so far any other metal systems.⁷ Additional advantages arise from actual possibility of surface decoration⁸ or quantum information processing⁹ which opens an avenue to molecular spintronics and solid-state devices.

After the first boom, chemists focused on the magnetostructural correlations and reached a conclusion that the symmetry and electronic configuration of the metal complex is somehow directly responsible for the significant changes in its magnetic behaviour, making the crystal field and spin-orbit coupling a major factors to investigate.¹⁰ It does not render preprogrammed syntheses any more facile, yet it necessitates the exploration of new isostructural systems that could shed light to the above rationale.¹¹

Up to date, there has been quite a number of mono-⁴ di-¹² and polinuclear Ln architectures⁶ that display SMM behaviour, with oblate Dy(III) ion out front.¹³ Interestingly, Ln-SMMs that employ prolate Er(III) are still relatively rare, with examples involving simple mononuclear systems¹⁴, organometallic complexes¹⁵, polyoxometallates¹⁶, radically-bridged dinuclear Er complexes¹⁷, and single illustrations of Er-SMMs of higher nuclearity *i.e.* tetranuclear cluster $[Er_4(salen)_6]^{18}$ where salen is N,N'-ethylenebis(salicylideneiminato) dianion, 1D coordination polymer¹⁹ and heteronuclar macrocyclic ErZn₃ species.²⁰

In fact, there have only been two reports²¹ of similar classes of compounds with ligands related to our studies, that deal with magnetism of lanthanides. 2,6-Diformyl-4-methylphenolato di(benzoyl)hydrazone ligands were reported to form helical complexes with Tb(III) and Dy(III) and only in the latter one just the onset of a slow relaxation of magnetization is observed under applied static magnetic field.^{21a} Very recently the use of N'-(2-hydroxy-3-methoxybenzylidene)-benzhydrazide) (H₂hmb) ligands led to

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Electronic Supplementary Information (ESI) available: additional structural diagrams and magnetic data. See DOI: 10.1039/x0xx00000x

the series of dinuclear molecules with M_2O_3 (M = Y, Eu, Gd, Tb, Dy, Ho) and M_2O_2 (M= Er, Yb) cores showing the influence of the ionic radius decrease on the molecular structure and magnetic properties.^{21b} Up to our knowledge, dinuclear triple-stranded Er(III) helicates with $\{Er_2O_3\}^{3+}$ phenoxo core have not been previously published nor shown to display any SMM behaviour.

Here, we report a new family of six isomorphous benzimidazole-scaffolded triple-stranded lanthanide helicates, with the aim of ensuing detailed magnetostructural characterization in terms of SMM behaviour, particularly focusing on aspects of local ions symmetry and magnetic coupling.

Experimental section

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Materials and physical measurements

All manipulations were performed under aerobic conditions using solvents and chemicals as received unless otherwise stated. Microanalyses were performed using a Perkin-Elmer 2400 CHN microanalyser on fully desolvated samples (drying for 24 hours under vacuum). IR spectra were obtained with a Perkin-Elmer 580 spectrophotometer and

peak positions are reported in cm⁻¹. Magnetic measurements were performed using a Quantum Design MPMS-3 EVERCOOL magnetometer on ground crystalline samples evacuated for 24 hours prior to measurements and sealed in double-foil bags. The magnetic susceptibility data were corrected for the diamagnetic contribution of the sample holder and for the diamagnetic contribution of the sample itself. In the latter case the Pascal constants were used.²²

Synthesis of complexes

All lanthanide complexes were synthesized in a one-pot reaction from 2-(1-methylhydrazinyl)-1Htemplate benzo[d]imidazole (synthesized via slightly modified procedure adapted from Povstyanoi et al., yield: 90%),²³ 4-tert-butyl-2,6diformylphenol and $Ln(NO_3)_3 \cdot xH_2O$ (where Ln - Tb, Dy, Ho, Er, Tm, Yb and x - 5 or 6). To a 50 ml round bottom flask containing hydrazine derivative (53.3 mg, 0.33 mmol) and dialdehyde (33.9 mg, 0.16 mmol) dissolved in 10 ml of MeOH_{abs}, hydrated Ln(III) salt (0.11 mmol) and another 10 ml of MeOH_{abs} was added which resulted in formation of clear yellow solution. The reaction mixture was stirred at room temperature for 2 h, after which slight excess of triethylamine (30.0 μ l, 0.22 mmol) was added and further stirred for 22 h.

Compound	1	2	3	4	5	6
Formula	C ₈₄ H ₈₇ Tb₂N₂4O₃ ⋅3(NO₃)	C ₈₄ H ₈₇ Dy ₂ N ₂₄ O ₃ ·3(NO ₃)	C ₈₄ H ₈₇ Ho₂N₂4O₃ ⋅3(NO₃)	C ₈₄ H ₈₇ Er₂N₂4O₃· 3(NO₃)	C ₈₄ H ₈₇ Tm₂N₂4O₃·3 (NO₃)	C ₈₄ H ₈₇ Yb₂N₂4O ·3(NO₃)
Formula weight	1984.64	1991.80	1996.66	2001.32	2004.66	2012.88
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	R-3c	R-3c	R-3c	R-3c	R-3c	R-3c
a(Å)	26.2088(6)	26.1377(11)	26.1368(10)	26.1100(7)	26.1210(5)	25.9543(5)
c(Å)	48.2544(11)	47.2565(16)	48.150(2)	48.0953(13)	47.7029(13)	48.9988(13)
V(Å ³)	28705.3(17)	27959(3)	28486(2)	28395(2)	28187.4(15)	28584.8(13)
Z	12	12	12	12	12	12
D _x (g cm ⁻³)	1.38	1.42	1.40	1.40	1.42	1.40
F(000)	12072	12096	12120	12144	12168	12192
μ(mm⁻¹)	7.75	1.66	1.73	1.83	1.95	2.02
Reflections:						
collected	23031	17460	18209	17425	32539	60274
unique (R _{int})	6555 (0.025)	5460 (0.059)	5577 (0.061)	5547 (0.017)	5515 (0.037)	5595 (0.057)
with I>2ơ(I)	4491	3178	2877	4227	3653	3270
R(F) [I>2ơ(I)]	0.042	0.042	0.041	0.039	0.043	0.044
wR(F ²) [I>2σ(I)]	0.139	0.0916	0.086	0.152	0.137	0.101
R(F) [all data]	0.063	0.089	0.105	0.056	0.075	0.085
wR(F ²) [all data]	0.155	0.106	0.098	0.166	0.158	0.111
Goodness of fit	1.14	1.02	0.94	1.29	1.11	1.43
max/min $\Delta \rho$ (e·Å ⁻³)	0.54/-1.04	1.56/-1.02	0.87/-0.46	1.05/-1.20	1.64/-1.71	1.98/-1.17

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Complex was isolated as large, needle like crystals by concentration of reaction mixture, precipitation with Et_2O and recrystallization of yellow solid residue by slow diffusion methods from diethyl, diisopropyl, tert-butylmethyl ether or toluene into MeOH/MeCN (1:1 v:v) system at lowered temperature (*cf.* crystallographic data).

[Tb₂(L-H)₃](NO₃)₃ (1): Yield: 65.5 mg, 60.3 %. Elemental analysis calc. for $[C_{84}H_{37}N_{27}O_{12}Tb_2]$ (1) (1984.61): C, 50.84; H, 4.42; N, 19.06; found: C, 51.07; H, 4.82; N, 18.66 %. Selected IR (KBr, cm⁻¹): vN-H 3415(m); v(C-H)_{ar} 3131(m), 3098(m), 3053(m); v_{as}(CH₃) 2953(s); v_s(CH₃) 2870(m); v(C=C)_{ar}, v(C=N) 1630(s), 1614(s), 1602(s), 1575(vs), 1490(m), 1470(s), 1431(m); 1368(s), 1319(s), 1266(s), 1244(s), v(NO₃⁻) 1384(s); γ(C-H)_{ar} 1081(m), 1037(s) ρ(C-H)_{ar} 1008(m), 950(m), 830(m), 750(s).

[Ho₂(L-H)₃](NO₃)₃ (3): Yield: 76.7 mg, 70.1 %. Elemental analysis calc. for $[C_{84}H_{87}N_{27}O_{12}Ho_2]$ (1) (1996.62): C, 50.53; H, 4.39; N, 18.94; found: C, 50.80; H, 4.75; N, 18.46 %. Selected IR (KBr, cm⁻¹): vN-H 3415(m); v(C-H)_{ar} 3130(m), 3098(m), 3053(m); v_{as}(CH₃) 2953(s); v_s(CH₃) 2869(m); v(C=C)_{ar}, v(C=N) 1627(s), 1614(s), 1601(s), 1575(vs), 1490(m), 1469(s), 1430(m); 1368(s), 1319(s), 1266(s), 1242(s), v(NO₃⁻) 1384(s); γ(C-H)_{ar} 1081(m), 1037(s) ρ(C-H)_{ar} 1005(m), 950(m), 830(m), 750(s).

$$\begin{split} & [\text{Er}_2(\text{L-H})_3](\text{NO}_3)_3 \ (4): \ \text{Yield:} \ 64.0 \ \text{mg}, \ 58.4 \ \%. \ \text{Elemental analysis} \\ & \text{calc. for} \ [C_{84}H_{87}N_{27}O_{12}\text{Er}_2] \ (1) \ (2001.28): \ \text{C}, \ 50.41; \ \text{H}, \ 4.38; \ \text{N}, \\ & 18.90; \ \text{found:} \ \text{C}, \ 50.72; \ \text{H}, \ 4.76; \ \text{N}, \ 18.51 \ \%. \ \text{Selected IR} \ (\text{KBr}, \\ & \text{cm}^{-1}): \ \text{vN-H} \ 3415(\text{m}); \ \text{v}(\text{C-H})_{ar} \ \ 3133(\text{m}), \ 3098(\text{m}), \ 3052(\text{m}); \\ & \text{v}_{as}(\text{CH}_3) \ \ 2952(\text{s}); \ v_{s}(\text{CH}_3) \ \ 2869(\text{m}); \ \text{v}(\text{C=C})_{ar}, \ \text{v}(\text{C=N}) \ \ 1629(\text{s}), \\ & 1616(\text{s}), \ 1602(\text{s}), \ 1575(\text{vs}), \ 1490(\text{m}), \ 1469(\text{s}), \ 1431(\text{m}); \ 1367(\text{s}), \\ & 1319(\text{s}), \ \ 1266(\text{s}), \ 1244(\text{s}), \ \text{v}(\text{NO}_3^{-}) \ \ 1384(\text{s}); \ \gamma(\text{C-H})_{ar} \ \ 1081(\text{m}), \\ & 1037(\text{s}) \ \rho(\text{C-H})_{ar} \ \ 1007(\text{m}), \ 950(\text{m}), \ 830(\text{m}), \ 748(\text{s}). \end{split}$$

[Tm₂(L-H)₃](NO₃)₃ (5): Yield: 58.2 mg, 53.0 %. Elemental analysis calc. for $[C_{84}H_{87}N_{27}O_{12}Tm_2]$ (1) (2004.28): C, 50.33; H, 4.37; N, 18.87; found: C, 50.53; H, 4.70; N, 18.50 %. Selected IR (KBr, cm⁻¹): vN-H 3415(m); v(C-H)_{ar} 3131(m), 3098(m), 3051(m); v_{as}(CH₃) 2952(s); v_s(CH₃) 2870(m); v(C=C)_{ar}, v(C=N) 1630(s), 1615(s), 1602(s), 1576(vs), 1490(m), 1469(s), 1431(m); 1367(s), 1319(s), 1266(s), 1244(s), v(NO₃⁻) 1384(s); γ(C-H)_{ar} 1080(m), 1037(s) ρ(C-H)_{ar} 1008(m), 949(m), 830(m), 750(s).

[Yb₂(L-H)₃](NO₃)₃ (6): Yield: 82.9 mg, 75.2 %. Elemental analysis calc. for $[C_{84}H_{87}N_{27}O_{12}Yb_2]$ (1) (2012.87): C, 50.12; H, 4.36; N, 18.79; found: C, 50.43; H, 4.72; N, 18.26 %. Selected IR (KBr, cm⁻¹): vN-H 3413(m); v(C-H)_{ar} 3131(m), 3098(m), 3053(m); v_{as}(CH₃) 2953(s); v_s(CH₃) 2870(m); v(C=C)_{ar}, v(C=N) 1630(s), 1613(s), 1601(s), 1575(vs), 1490(m), 1470(s), 1431(m); 1368(s), 1319(s), 1267(s), 1244(s), v(NO₃⁻) 1384(s); γ(C-H)_{ar} 1081(m), 1038(s) ρ(C-H)_{ar} 1007(m), 950(m), 829(m), 750(s).

Crystallographic studies

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Pale-yellow crystals, appropriate for X-ray diffraction data collection were obtained by vial to vial diffusion methods from methanol/acetonitrile and organic ethers (1-6). Data were collected at 100(1) K (2, 4) or at room temperature (1, 3, 5, 6) by the ω -scan technique on the Agilent Technologies SuperNova four-circle diffractometer (Atlas CCD detector, Nova microfocus CuK_{α} radiation source, λ = 1.54178 Å, compound 1) or XCalibur four-circle diffractometer (Eos CCD detector with graphite-monochromatized MoK_{α} radiation source, λ =0.71073 Å, compounds **2** - **6**). The data were corrected for Lorentz-polarization and absorption (multiscan method) effects.²⁴ Accurate unit-cell parameters were determined by a least-squares fit of 8867 (1), 5316 (2), 2769 (3), 8313 (4), 7858 (4a), 14499 (5), and 19815 (6) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92²⁵ and refined with the fullmatrix least-squares procedure on F² by SHELXL-2013.²⁶ Hydrogen atoms were placed in the calculated positions, and refined as 'riding model' with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for appropriate non-hydrogen atom. The crystal structure contained relatively large voids filled with disordered solvent molecules of ca. 5400 Å³ per unit cell (ca. 20% of the unit cell volume); The attempts to refine the solvent molecules were unsuccessful, so the SQUEEZE procedure was applied.²⁷ Relevant crystal data are listed in Table 1, together with the refinement details. In some cases restraints were used in order to avoid the eccentric shapes of the thermal ellipsoids (ISOR



Figure 1. Schematic representation of subcomponent self-assembly of amine with dialdehyde in the presence of lanthanide nitrate as exemplified on erbium(III) analogue **4**: a) *in situ* formed Schiff-base ligand HL in its preorganized, dual-pocket form; b) crystal structure of $[Er_2L_3]^{3+}$ cation. (i): MeOH, triethylamine.

for three methyl carbon atoms: C17D, C10A and C21A in **1** and C17D in **3**) and rigid bond restraints for tBu fragments in **3**, **5** and **6**). Crystallographic data were deposited with the Cambridge Crystallographic Data Centre^{‡.}

Results and discussion

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Crystal structures

Subcomponent self-assembly^{23,28} of hydrated Ln(NO₃)₃ salt with 2-(methylhydrazino)benzimidazole and 4-tert-butyl-2,6-diformylphenol in 2:6:3 molar ratio in the presence of triethylamine leads to isolation of yellow crystals of the following formula: $[Ln_2L_3](NO_3)_3$ where Ln – Tb(1), Dy(2), Ho(3), Er(4), Tm(5), Yb(6) (Figure 1). X-Ray crystal data of 4 is shown as a representative one, since all compounds were found to be isostructural – which is notable taking into consideration the lanthanide contraction. (Figure 1, Table 1).²⁸

The $[Er_2L_3]^{3+}$ cation is C_3 -symmetrical - two erbium centres lie on crystallographic threefold axis. Metal-to-ligand ratio is 2:3 and each symmetry-generated ligand wraps around both erbium ions by two nitrogen atoms - from hydrazone and benzimidazole groups - and by bridging phenolate oxygen atom (Figure 1b, Figure 2), resulting from deprotonation of HL

Fable 2. Rele Er ₂ L ₃](NO ₃) ₃	evant dista complex	nces, angles and	l dihedral a	ngles present in the	2
Distances [Å]		Angles	[°]	Dihedral angles [°]	
N1-Er1	2.464	N1-Er1-N11	62.95	N1-C2-N10- N11	2.19
N11-Er1	2.649	N11-Er1- 014	64.71	N11-C12-C14- 014	15.2 0
014-Er1	2.311	N22-Er2- N20	62.45	N22-C23-N21- N20	7.20
N22-Er2	2.508	N20-Er2- 014	65.48	N20-C19-C14- O14	16.6 5
N20-Er2	2.674	Er1-014- Er2	98.95	Er1-C13-C15- Er2	45.3 4
014-Er2	2.309				
Er1-Er2	3.512				

Schiff-base ligand. In consequence Er(III) ions are ninecoordinated, in a face-sharing distorted tricapped trigonal prismatic geometry. The ligand molecules are significantly folded, in order to coordinate two relatively close metal centres (Er…Er distance is 3.512 Å) thus forming dinuclear triple-stranded helicates with dihedral angle between terminal ring systems being 61.03(7)°. Other relevant structural data that concerns immediate vicinity of erbium(III) cations is listed in Table 2.

The charge is balanced by three NO_3^- anions of which one is symmetry-independent and the others are generated by threefold axis. Benzimidazole amine proton did not dissociate, therefore N-H···O and relatively short and linear C-H···O hydrogen bonds can be found, which join both cations and anions, thus resulting in creation of a highly-symmetrical three-dimensional supramolecular network (Figure 3).

It must be noted that lanthanide complexes of structurally related Robson type ligands (hydrazides of substituted 2,6-diformylphenols)^{21a,29,30} exhibited only pseudo-C₃-symmetric environment and crystallized in monoclinic space groups,



Figure 2. Asymmetric unit of $C_{3^{-}}$ symmetrical cation; ellipsoids are drawn at 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.



Figure 3. Crystal packing of $[{\rm Er}_2L_3]({\rm NO}_3)_3$ complex as seen along threefold axis (z-direction)



Figure 4. Capped stick representations of Λ (above) and Δ (bottom) helicates found in the crystal lattice as seen along (left) and perpendicular (right) to C₃ axis.

whereas our system crystallizes in truly symmetric trigonal R-3c space group.

Such lanthanide helical species may display inherent chirality,³¹ and we have found our complexes to crystallize as a racemic compound, where both enantiomers are present in one lattice in the *meso* relation (Figure 4). The unit cell of **4** is *ca.* 28000 Å³ and consists of twelve independent helical



(red; Dy), **3** (green; Ho), **4** (blue; Er), **5** (magenta; Tm) and **6** (orange; Yb).

species that are equally distributed between Δ and Λ isomers, nevertheless they form adjacently displaced quartets in dublets of isomers (i.e. $\Delta\Delta\Lambda\Lambda$ are formed instead of $\Delta\Lambda\Delta\Lambda$ when perceived along Ln-Ln axis; Figure S1 in the Electronic Supplementary Information)

Magnetic properties

Direct current (DC) magnetic measurements including $\chi T(T)$, M(H) and M(H/T) data for **1-6** are presented in Figure 5 and Figures S2-S8 in the Electronic Supplementary Information. The χT values at 300 K are close to those expected for the respective free ions (Table S1 in the Electronic Supplementary Information). The trends in $\chi T(T)$ curves at 1 kOe (Figure 5a) observed with decreasing



Figure 6. a) Frequency dependence of the out-of-phase AC magnetic susceptibility for **4** at various temperatures (from 1.8 to 2.1 K; H_{AC} = 3 Oe; H_{DC} = 1500 Oe) and b) The Cole-Cole plot for **4**. The solid lines represent the best fit to the generalized Debye model (Eq. 1).

Table 3. The selected parameters obtained by fitting the Cole-Cole plots of **4** using the modified generalized Debye model (Eq. 1)

Т/К	τ/ ms	α	
1.8 K	0.2026	0.142	
1.9 K	0.1665	0.115	
2.0 K	0.1436	0.117	
2.1 K	0.0993	0.225	

temperature are indicative of the depopulation of the excited m_J states in the 25-300 K range, combined with the zero-field splitting effects and the intramolecular super-exchange magnetic coupling J_{LnLn} through the phenoxo-bridges at low temperature: definitely ferromagnetic for **1**, **2**, **4** and **6** and antiferromagnetic for **3** and **5**. Intermolecular interactions do not play significant role in **1-6**. The tendency of the respective M(H) curves at 1.8 K confirm the ferromagnetic for **5** (Figure 5b). The isofield lines in the reduced magnetization plots in **1-5** are non-superimposable indicating significant magnetic anisotropy in these compounds (Figures S3-S7 in the Electronic Supplementary Information). The full set of magnetic data including $\chi T(T)$, M(H) and M(H/T) were reproduced well within the van Vleck approximation only when the fitting procedure

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fully included the crystal field term H_{CF} , the super-exchange term H_{SE} and the Zeeman term H_{ZE} (Figure S2-S8, Table S2).³² Despite the overparametrization of the crystal field term, the fits confirm the type of intramolecular interactions: ferromagnetic for **1**, **2**, **4** and **6** and antiferromagnetic for **3** and **5** and suggest significant magnetic anisotropy in **1**-**5** (see Electronic Supplementay Information for detailed description of the fitting procedure and the fitting results).

Alternating current (AC) magnetic measurements ($H_{AC} = 1$ Oe) were performed at low temperature in the 0 - 2 kOe DC field range. In the absence of a DC field only compound 4 exhibited a very weak signal of the out-of-phase magnetic susceptibility with a clear frequency-dependent "tail". Frequency dependent peaks could be observed by applying static DC field (Figure 6a). H_{dc} = 1500 Oe has been found to be the optimum field determined from the χ'' maximum vs. field plot. The χ'' vs. v dependence of **4** showed one clear maximum indicating a slow magnetic relaxation in 4 (Figure 6a). The Cole-Cole plots in the 1.8-2.1 K range are semi-circle shaped with the onset of an additional semi-circle at low-frequency, below 1 Hz (Figure 6b). The magnetic relaxation times τ and α factors, which account for the distribution of the relaxation time of the large semi-circle, were obtained by fitting the Cole-Cole plots using the linear combination of two modified generalized Debye models as shown in Eq. 1:

$$\chi(\omega) = \chi_{S} + (\chi_{T} - \chi_{S})(\frac{f_{A}}{1 + (i\omega\tau_{A})^{1-\alpha_{A}}} + \frac{1 - f_{A}}{1 + (i\omega\tau_{B})^{1-\alpha_{B}}}) \quad \text{Eq. 1}$$

Table 3 summarizes the results obtained from fitting the Cole-Cole plot. Only parameters for the large semi-circle are given. The anisotropic energy barrier U_{eff} was obtained by fitting the 1.8-2.1 K range to the Arrhenius law $\tau = \tau_0 \exp(U_{eff}/k_BT)$, (τ relaxation time) and U_{eff}/k_B and τ_0 were determined to be 9.5 K, and 1.08×10^{-6} s, respectively (Figure 6a inset). The slow magnetic relaxation in **4** seems to be thermally activated (Orbach mechanism). However, the larger value of the τ_0 parameter compared to the $10^{-7} - 10^{-9}$ s typical for the thermally activated SMM behaviour indicate that other relaxation mechanisms (direct or Raman) might also play an important role. Nevertheless, the slow magnetic relaxation in **4** is quite typical for Ln-SMMs. Our compound is one of the very few examples of Er^{III}- based SMMs^{14,15} and represents the first dinuclear one of a helical character.

Conclusions

Synthesis of a new family of C₃-symmetrical triple-stranded dinuclear helicates that employ benzimidazole-scaffolded Schiff-base ligand is reported together with their magnetic and structural characterization. Erbium analogue **4** displays DC field induced SMM behaviour and is the first reported representative example of C₃-symmetric family with the $\{Er_2O_3\}^{3+}$ phenoxo core. Surprisingly, the Dysprosium analogue **2** does not exhibit slow magnetic relaxation above T = 1.8 K which is in contradiction to the well-established fact that most Dy-based molecular magnets exhibit SMM behavior. This can be rationalized in terms of prolate/oblate shapes of lanthanide

based on "prolate lanthanide ions". We further aim to investigate presented system with respect to the effect of lanthanide contraction and different counterions on its solution behaviour and photophysical studies. We also plan to exploit the latent potential of presented helical structure towards the synthesis of pure enantiomeric forms *via* the tools of supramolecular chiral resolution.

architectures that display single-molecule magnet properties

Acknowledgements

This research was carried out as a part of the Polish Ministry of Science and Higher Education project: Grant No. 0111/DIA/2012/41 in the frame of "Diamond Grant" programme. Magnetic measurements were performed at the Jagiellonian University, Faculty of Chemistry using the equipment purchased from the Large Research Infrastructure Fund of the Polish Ministry of Science and Higher Education (decision no. 6350/IA/158/2013.1)

Notes and references

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre. CCDC numbers: 1038101 (Tb - 1), 1038102 (Dy - 2), 1038103 (Ho - 3), No. CCDC-1038936 (Er - 4), 1038105 (Tm - 5), 1038106 (Yb - 6). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk/data_request/cif.

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Table of contents entry:

First example of erbium triple-stranded helicate displaying SMM behaviour

Adam Gorczyński, Maciej Kubicki, Dawid Pinkowicz,* Robert Pełka, Violetta Patroniak* and Robert Podgajny*

Subcomponent self-assembly gives a new family of the triple-stranded helicates of $\{Ln^{III}_{2}O_{3}\}^{3-}$ core (Ln = Tb, Dy, Ho, Er, Tm and Yb) yielding the erbium congener revealing field-induced SMM characteristics.





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