Inorganic Chemistry

Functionalized Trigonal Lanthanide Complexes: A New Family of 4f Single-Ion Magnets

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prepared through a one-pot synthesis where, first, the ligand H_{3L} was synthesized *in situ* through a Schiff base reaction of tris(2-aminoethyl)amine with 2,6-diformyl-*p*-cresol. Following addition of $Ln(OTf)_3 \cdot xH_2O$ and base, LnL was obtained. Powder X-ray diffraction confirms that all complexes are isostructural. LnL contain pendant, noncoordinating carbonyl functions that are reactive and represent direct anchoring points to appropriately functionalized surfaces. Furthermore, these reactive carbonyl functions can be used to postfunctionalize LnL: for example,



with aromatic π systems. We present herein the Schiff base condensation of 7 with benzylamine to yield 9 as well as the characterization and magnetic properties of 9. Our study establishes LnL as a truly versatile module for the surface deposition of Ln-based single-ion magnets.

INTRODUCTION

Lanthanide (Ln) coordination complexes have emerged as an exciting class of molecular magnetic materials because of the plethora of quantum phenomena that they display both at the macroscopic and single-molecule levels. The discovery, almost 20 years ago now, by Ishikawa et al. that Ln(III) phthalocyanine double-decker complexes¹⁻⁴ displayed single-molecule-magnet (SMM) behavior,^{5,6} sparked an intense renewed interest in the synthesis and magnetic properties of Ln-based coordination complexes. In the following years, new Ln complexes offered improved blocking temperatures^{7–9} over the previously developed transition-metal-based SMMs.^{10–12} In particular, mononuclear Ln-based coordination complexes displaying SMM behavior were termed single-ion magnets (SIMs).¹³ Recently, blocking temperatures of dysprocenium SIMs have reached the liquid nitrogen regime.^{14–16}

SMMs and SIMs have been proposed for applications in quantum information processing (QIP).^{17–38} For example, Gd(III) complexes have been proposed as quantum bits (qubits)^{39–41} and atomic clock transitions of a Ho(III) qubit were used to enhance its phase memory time.³⁶ Logic gates, such as CNOT and SWAP, have been implemented in two-qubit systems^{19,27} and proposed for three-qubit systems.⁴² In recent groundbreaking work, the four-level nuclear spin of Tb(III) was exploited by Balestro et al. to implement Grover's quantum algorithm.⁴³ Integration of SMMs and SIMs in QIP devices requires controlled surface deposition of the complexes.⁴⁴ The readout of surface-deposited SIMs has

been performed both on ensembles⁴⁵ and at the singlemolecule level.^{46,47} Ln-based complexes have been studied on several surfaces such as graphite,⁴⁸ graphene,^{45,49} carbon nanotubes,⁴⁶ silicon,⁵⁰ gold,⁵¹ and metal oxides.⁵² The majority of these studies have been performed on lanthanide phthalocyanine double-decker complexes.

We, and others, have previously studied the Ln(trensal) complexes (with H₃trensal = 2,2',2''-tris(salicylideneimino)-triethylamine).⁵³⁻⁶² In particular, we have recently demonstrated that Yb(trensal)⁶¹ is an excellent electronic qubit³⁰ and that it also acts as a prototypical coupled electron qubit–nuclear qudit where intrinsic implementation of quantum error corrections is possible.⁶³ Ln(trensal) is a family of complexes with trigonal symmetry around the lanthanide ion.⁵⁸ H₃trensal does not contain any surface anchoring or reactive groups that can be used for surface deposition. However, a key criterion for surface contains chemical functions that offer the possibility to establish a relatively strong interaction with the surface on which the molecule is to be deposited upon. This led us to

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Figure 1. Comparison of H₃L with H₃trensal and other H₃trensal derivatives.

Scheme 1. LnL Reacts Readily with Primary Amines, for Instance Benzylamine, to Form LnL*



synthesize and study lanthanide complexes of the ligand tris(((3-formyl-5-methylsalicylidene)amino)ethyl)amine (H_3L , Figure 1).

We present herein the synthesis, characterization, and magnetic properties of eight novel complexes LnL with Ln = Gd (1), Tb (2), Dy (3), Ho (4), Er (5), Tm (6), Yb (7), Lu (8). The static and dynamic magnetic properties of 1–7 are compared to those of the corresponding Ln(trensal) complexes. The eight LnL complexes retain similar symmetries and coordination environments of the lanthanide ions as for the Ln(trensal) complexes. These new complexes present pendant, noncoordinating carbonyl functions that are reactive and represent direct anchoring points to appropriately functionalized surfaces. Furthermore, these reactive carbonyl functions can be used to attach by postfunctionalization novel functions to LnL: for example, aromatic π systems. We present herein the Schiff base condensation of LnL with benzylamine to yield LnL* (Scheme 1 and Figure 3) as well as the characterization and magnetic properties of LnL*. The aromatic π systems introduced to LnL by postfunctionalization act themselves as anchoring groups to surfaces that are not compatible with the initial carbonyl functions, making LnL a truly versatile module for the surface deposition of Ln-based SIMs with relevance to QIP.

EXPERIMENTAL SECTION

Materials and Physical Measurements. All solvents and reagents were purchased commercially and used as received. No attempts were made to exclude moisture and oxygen during the syntheses. In addition, no instability of the complexes has been observed when they were stored for months at room temperature. $Ln(OTf)_3 \cdot xH_2O$ was prepared by refluxing an aqueous suspension of Ln_2O_3 with trifluoromethanesulfonic (triflic) acid overnight. $Ln(OTf)_3 \cdot xH_2O$ was then isolated by evaporation of the solvent. In the case of Tb(OTf)_3 ·9H_2O, aqueous H_2O_2 was added to the suspension of the oxide before refluxing. This was done to reduce Tb(IV) to Tb(III). The water content of $Ln(OTf)_3 \cdot xH_2O$ was determined by an EDTA titration using xylenol orange as an indicator.

Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer. Positive-ion mode MALDI mass spectrometry was performed on a Bruker Solarix XR 7T ESI/MALDI FT-ICR MS instrument at The Department of Chemistry, University of Copenhagen. Elemental (C, H, and N) analyses were carried out on a FlashEA 1112 instrument at The Microanalytical Laboratory at The Department of Chemistry, University of Copenhagen. Powder Xray diffraction (PXRD) was measured on a Bruker D8 ADVANCE powder diffractometer using a Cu K α radiation (λ = 1.5418 Å) source. ¹H and ¹³C NMR spectra were recorded on a Bruker 500 MHz instrument equipped with a cryoprobe. For both ¹H and ¹³C NMR calibration was done against solvent signals from the deuterated solvent. Direct current (dc) and alternating current (ac) magnetic susceptibility measurements were performed on polycrystalline samples fixated in n-hexadecane using a Quantum Design MPMS-XL SQUID magnetometer. The χT products obtained from the measurements were corrected for the diamagnetism of *n*-hexadecane and of the sample using Pascal's constants. X-band electron paramagnetic resonance (EPR) spectra were obtained using a Bruker Elexsys E500 instrument. Luminescence spectra were recorded using a Horiba-Jobin Yvon Fluorolog fluorimeter with an InGaAs nearinfrared (NIR) detector.

Crystal Structure Determination. Single-crystal X-ray diffraction was performed at 120 K on a Bruker D8 VENTURE diffractometer equipped with a Mo K α high-brilliance I μ S S3 radiation source ($\lambda = 0.71073$ Å), a PHOTON 100 CMOS detector, and an Oxford Cryosystems cooling system. The setup was controlled using the APEX2 software package. Data reduction was performed using SAINT,⁶⁴ and absorption corrections were made with SADABS.⁶⁵ The structures were solved using intrinsic phasing with SHELXT⁶⁶ and refined using SHELXL (least squares).^{67,68} The OLEX2 program package was used to visualize the structures during refinement.^{69,70} Other than hydrogen, all atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using the "Add H" command in OLEX2. In the crystal structure of 9 in addition to the complex there is some diffuse electron density stemming from cocrystallized solvent. This could not be assigned to a given lattice solvent, and the solvent mask (SQUEEZE) in OLEX2 was hence used. The solvent mask found an electron density corresponding to 80 e⁻, which roughly corresponds to three methanol molecules, which were included in the formula.

Synthesis. 2,6-Diformyl-p-cresol (DFMP). DFMP was synthesized according to a literature procedure. 71

Anal. Calcd for C₉H₈O₃: C, 65.85; H, 4.91. Found: C, 65.66; H, 4.90. ¹H NMR (500 MHz, CDCl₃): δ /ppm 11.45 (s, 1 H), 10.21 (s, 2 H), 7.77 (s, 2H), and 2.39 (s, 3H) (Figure S1). ¹³C NMR (125.74 MHz, CDCl₃): δ /ppm 192.4, 161.9, 138.2, 129.7, 123.1, and 20.2 (Figure S2).

GdL (1). DFMP (335 mg; 2.0 mmol) was dissolved in hot (around 60 °C) acetonitrile (10 mL). To this was added a solution of tris(2-aminoethyl)amine (tren, 100 mg; 0.68 mmol) in methanol (3 mL) dropwise. To the resulting orange solution was added Gd(OTf)₃· 9H₂O (524 mg; 0.68 mmol), and the solution was heated to boiling. Over 15 min the volume was reduced to approximately 6 mL. Then Et₃N (0.4 mL; 3 mmol) in acetonitrile (2 mL) was added slowly and the solution was stirred at boiling until a yellow precipitate formed.

Yield: 194 mg (39%). Anal. Calcd for $C_{33}H_{33}N_4O_6Gd: C, 53.64; H, 4.50; N, 7.58. Found: C, 53.54; H, 4.57; N, 7.52. MALDI-MS in positive ion mode: [GdLH]⁺ <math>m/z$ 740.17, [GdLNa]⁺ m/z 760.15 (Figure S5). IR (cm⁻¹): 1669 (s, carbonyl stretch), 1624 (s, imine stretch) (Figure S14).

TbL (2). DFMP (362 mg; 2.2 mmol) was dissolved in hot (around 60 °C) acetonitrile (50 mL). Then a solution of tren (0.11 mL; 0.73 mmol) in methanol (25 mL) was added dropwise over 1 h, whereby the solution turned orange. It should be pointed out here that if the temperature of the DFMP in acetonitrile solution is above 70 °C, the solution turns red upon addition of tren, resulting in a less pure product. Thus, the resulting solution after addition of tren should always be orange. The orange solution was refluxed for 1 h, and then Tb(OTf)₃·9H₂O (561 mg; 0.73 mmol) in acetonitrile (10 mL) was added. The solution turned darker and was boiled for 45 min, whereby the volume was reduced to 50 mL. Then Et₃N (0.5 mL; 3.6 mmol) in acetonitrile (10 mL) was slowly added, yielding a yellow precipitate, which was isolated and washed with 3 × 20 mL of ethanol and 3 × 20 mL of diethyl ether.

Yield: 284 mg (53%). Anal. Calcd for $C_{33}H_{33}N_4O_6Tb$: C, 53.52; H, 4.49; N, 7.57. Found: C, 52.78; H, 4.47; N, 7.47. MALDI-MS in positive ion mode: $[TbLH]^+ m/z$ 741.18, $[TbLNa]^+ m/z$ 763.16, m/z $[TbLNa]^+$ (Figure S6). IR (cm⁻¹): 1669 (s, carbonyl stretch), 1624 (s, imine stretch) (Figure S15).

The remaining LnL complexes 3-8 were synthesized analogously to 2.

DyL (3). Yield: 301 mg (55%). Anal. Calcd for $C_{33}H_{33}N_4O_6Dy$: C, 53.26; H, 4.47; N, 7.53. Found: C, 53.47; H, 4.74; N, 7.57. MALDI-MS in positive ion mode: [DyLH]⁺ m/z 746.18, [DyLNa]⁺ m/z 768.17 (Figure S7). IR (cm⁻¹): 1668 (s, carbonyl stretch), 1624 (s, imine stretch) (Figure S16).

HoL (4). Yield: 354 mg (65%). Anal. Calcd for $C_{33}H_{33}N_4O_6$ Ho: C, 53.09; H, 4.46; N, 7.50. Found: C, 52.74; H, 4.44; N, 7.53. MALDI-MS in positive ion mode: [HoLH]⁺ m/z 747.18, [HoLNa]⁺ m/z 769.16 (Figure S8). IR (cm⁻¹): 1668 (s, carbonyl stretch), 1624 (s, imine stretch) (Figure S17).

ErL (5). Yield: 337 mg (62%). Anal. Calcd for $C_{33}H_{33}N_4O_6Er: C$, 52.93; H, 4.44; N, 7.48. Found: C, 52.81; H, 4.57; 7.44. MALDI-MS in positive ion mode: [ErLH]⁺ m/z ,750.18, [ErLNa]⁺ m/z 772.16 (Figure S9). IR (cm⁻¹): 1668 (s, carbonyl stretch), 1624 (s, imine stretch) (Figure S18).

TmL (6). Yield: 314 mg (57%). Anal. Calcd for $C_{33}H_{33}N_4O_6Tm: C$, 52.81; H, 4.43; N, 7.46. Found: C, 52.14; H, 4.49; N, 7.53. MALDI-MS in positive ion mode: [TmLH]⁺ m/z 751.18, [TmLNa]⁺ m/z 773.17 (Figure S10). IR (cm⁻¹): 1668 (s, carbonyl stretch), 1625 (s, imine stretch) (Figure S19).

YbL (7). Yield: 343 mg (62%). Anal. Calcd for $C_{33}H_{33}N_4O_6$ Yb: C, 52.52; H, 4.41; N, 7.42. Found: C, 52.69; H, 4.23; N, 7.70. MALDI-MS in positive ion mode: [YbLH]⁺ m/z 756.19, [YbLNa]⁺ m/z 778.17 (Figure S11). IR (cm⁻¹): 1668 (s, carbonyl stretch), 1625 (s, imine stretch) (Figure S20).

LuL (8). Yield: 350 mg (63%). Anal. Calcd for $C_{33}H_{33}N_4O_6Lu: C$, 52.39; H, 4.40; N, 7.41. Found: C, 52.09; H, 3.90; N, 7.51. MALDI-MS in positive ion mode: [LuLH]⁺ m/z 757.19, [LuLNa]⁺ m/z 779.17 (Figure S12). IR (cm⁻¹): 1667 (s, carbonyl stretch), 1625 (s, imine stretch) (Figure S21). ¹H NMR (500 MHz, DMSO- d_6) δ /ppm 9.86 (s, 3 H), 8.22 (s, 3 H), 7.32 (d, 3 H, J = 2.6 Hz), 7.28 (d, 3 H, J = 2.7 Hz), 3.83 (t, 6 H, J = 6.0 Hz), 3.09 (t, 6 H, J = 5.9 Hz), and 2.13 (s, 9 H) (Figure S3). ¹³C NMR (125.74 MHz, DMSO- d_6) δ /ppm 190.5, 168.9, 166.6, 141.8, 131.5, 125.4, 125.2, 120.2, 58.9, 58.2, and 19.6 (Figure S4).

YbL*.3MeOH (9). 7 (60 mg; 0.080 mmol) was suspended in a 1:1 mixture of MeOH and $CHCl_3$ (10 mL). Benzylamine (0.3 mL; 2.7 mmol) was added to the solution, which was then refluxed for 30 min. The solution was filtered and left at 50 °C to evaporate. When the volume was reduced to around 2 mL, crystals formed. These were isolated and washed with diethyl ether.

Yield: 66 mg (74%). Anal. Calcd for $C_{57}H_{66}N_7O_6Yb$: C, 61.22; H, 5.95; N, 8.77. Found: C, 61.2; H, 5.20; N, 9.10. MALDI-MS in positive ion mode: [YbL*H]⁺ m/z 1023.38 (Figure S13). IR (cm⁻¹): 1619 (s, imine stretch) (Figure S22).

Solid-state dilute samples of 1-7 (1'-7', respectively) were obtained following the same procedure as specified for 2. 1' was prepared using molar ratios of 5% and 95% of Gd(OTf)₃·9H₂O and Y(OTf)₃·9H₂O, respectively. 2'-7' were prepared using molar ratios of 1% of Tb-Yb(OTf)₃·9H₂O and 99% of Y(OTf)₃·9H₂O for 2'-4' or 99% of Lu(OTf)₃·9H₂O for 5'-7', respectively. 1'-7' were obtained with yields similar to those for 1-8. The elemental analysis results are given in Table 1. Furthermore, PXRD confirms that the dilute samples are isostructural and have the same structures as the parent compounds (Figure S26).

Table 1. Elemental Analysis for Solid-State Dilution of 1-7 (1'-7', Respectively)

	1′	2′	3′	4′	5′	6′	7'
% calcd	$C_{33}H_{33}N_4O_6Y$				$C_{33}H_{33}N_4O_6Lu$		
С	59.1				52.4		
Н	4.96				4.40		
Ν	8.36				7.41		
% found							
С	60.0	58.7	58.8	58.7	51.90	52.10	52.29
Н	5.58	4.94	4.95	4.94	4.58	4.58	4.83
Ν	8.14	8.42	8.38	8.31	7.68	7.74	7.34

RESULTS AND DISCUSSION

Synthesis and Characterization of 1-8. Complexes 1-8 were prepared through a one-pot synthesis. First, the ligand H₂L (Figure 1) was synthesized in situ through a Schiff base reaction of tren with 3 equiv of DFMP in boiling acetonitrile. Then, $Ln(OTf)_3 \cdot xH_2O$ and base were added, affording the complex as a yellow microcrystalline precipitate. Powder X-ray diffraction (PXRD) measurements showed that all of the complexes are isostructural and that the bulk of the isolated crystalline material is composed by a single crystal phase (Figure S24) which corresponds to that determined by singlecrystal diffraction (vide infra). IR spectra of the complexes confirm that both imine and aldehyde groups are present with bands found at 1624-1625 and 1668-1669 cm⁻¹ (Figures S14-S21), respectively. MALDI-MS data recorded in the positive ion mode show [LnLH]⁺ and [LnLNa]⁺ signals, confirming that the complexes are formed (Figures S5-S12).

We performed the synthesis of **1–8** in acetonitrile, yielding complexes with the ligand H_3L . A similar reaction performed in previous studies in methanol, instead of acetonitrile, resulted in the formation of the acetal derivative H_3L^1 (Figure 1).^{72,73}

The *in situ* generated ligand H₃L contains three aldehyde groups. These could, in principle, react with tren to form the ligand $H_{3}L^{2}$ (Figure 1) and subsequently with Ln(III) to form the mononuclear complexes LnL². In an earlier attempt to synthesize a Zn(II) complex with H₃L only the cryptate complex $[Zn_2L^2]^+$ was isolated, suggesting that H_3L is prone to form the ligand H₃L^{2,74} However, we have not seen any evidence of impurities from cryptate complexes, such as LnL², in the isolated compounds. This was verified by PXRD, which only shows patterns corresponding to the simulated diffractograms. Additionally, the purity of the synthesized complexes can be further verified by IR and NMR. Since the IR spectra of 1-8 are close to identical (Figures S14-S21), only one LnL complex was selected for comparison between the IR spectrum of single crystals and that of a bulk polycrystalline sample. Comparing the IR spectrum of a microcrystalline powder of 7 to that of crushed single crystals of 7, one can see that the IR spectrum of the microcrystalline powder is in full agreement with the IR spectrum of the crushed single crystals of 7 (Figure S23). Furthermore, the NMR spectra of 8 (Figures S3 and S4) show only peaks attributable to 8.

The synthesis of 1-8 is very sensitive to the size of the lanthanide ions. 2-8 are all prepared similarly, while 1 (complex of the larger Gd(III) ion) could only be isolated when the concentration of the complex was 10 times greater than that for the other lanthanides. This concentration dependence might be due to the larger size of the earlier lanthanide ions, resulting in coordination of the solvent. For instance, a very poor crystal structure of the Pr(III) complex revealed that the lanthanide ion, in addition to the ligand, was coordinated by two water molecules. Complexes of the larger lanthanides (such as La(III) and Sm(III)) can be isolated by following the same procedure as for Gd(III). However, the PXRD of these complexes reveals that they are not isostructural with 1-8 and elemental analyses suggest that they contain water in their structure, presumably coordinated to the lanthanide, as for the Pr(III) analogue. Details about the synthesis and properties of the La(III)- to Eu(III)-containing complexes will be presented in future work.

Crystal Structures of 2–8. Crystals of **2–8** suitable for single-crystal X-ray diffraction were obtained directly from the reaction mixture by adjusting the addition of base (for details



Figure 2. (a) Unit cell of 7 viewed along the crystallographic *c* axis. (b) Molecular structure of 7 viewed from the side. Color code: Yb, green; N, blue; O, red; C, gray. Hydrogens have been omitted for clarity, and thermal ellipsoids have been set to 50% probability.



Figure 3. (a) Crystal structure of 9 viewed from the side. (b) Crystal structure of 9 viewed along the pseudo- C_3 axis. Color code: Yb, green; O, red; N, blue; C, gray. Thermal ellipsoids are at 50% probability, and hydrogens have been omitted for clarity.



Figure 4. Temperature dependence of the χT product of 1-7, including Curie constants (C_{Ln}) and best-fit curves, as described in the main text.

see the Supporting Information, page S28). Details of the crystal structures of 2-8 are given in Tables S1-S4 in the Supporting Information.

All complexes crystallize in the trigonal space group $P\overline{3}$, with two complexes in the unit cell (Figure 2a). The crystallographic C_3 axis passes through the molecular C_3 axis such that one-third of the complex is contained in the asymmetric unit. The Ln(III) ion is heptacoordinated by the ligand, binding to three phenoxide groups, three imines, and one tertiary amine. The three aldehyde groups in each complex point away from the lanthanide ion and do not coordinate to it (Figure 2b). As expected, all bonds involving the lanthanide ion are shortened going from Tb to Lu, with Ln-O, Ln-N_{imine}, and Ln-N_{apical} being 2.208, 2.490, and 2.647 Å for 2 and 2.158, 2.416, and 2.605 Å for 8, respectively. The coordination environment around the lanthanide ion and the crystallographic and molecular C_3 symmetry resemble those of Ln-(trensal)^{53-56,58,61} and the previously studied Ln(trenovan) complexes,⁷⁵ with H_3 trenovan = tris(((3-methoxysalicylidene)amino)ethyl)amine. Among the three derivatives the Ln-N_{imine} and Ln-O bond lengths are almost identical. This is evidenced for the Tm(III) complexes, where 6 has Tm– N_{imine} 2.435 Å and Tm-O 2.171 Å, whereas they are 2.449 and 2.167

Å in Tm(trensal), respectively, and 2.463 and 2.140 Å in Tm(trenovan), respectively.^{59,75} In contrast, the Ln– N_{apical} bond length is much shorter in **6** in comparison to that in Tm(trensal), measuring 2.619 and 2.713 Å, respectively, while it is much longer in comparison to Tm(trenovan), where it is 2.554 Å. We speculate that the difference in Ln– N_{apical} bond length is due to the substituent groups on the phenyl rings and that this might be a way to fine-tune the electronic properties of the trensal family of complexes.

Reactivity. The three aldehyde groups of 1-8 point away from the complex and show no interaction with the lanthanide ion. This indicates that they can be used as anchoring points for the surface deposition of 1-8 or for the further functionalization of 1-8 with groups appropriate for the surface deposition of these complexes. For example, the three pendant aldehyde groups of 1-8 can be involved in Schiff base reactions with primary amines, such as benzylamine (Scheme 1). We have investigated the reactivity of these aldehydes using 7.

7 (like 1-6 and 8) is insoluble in most organic solvents. However, upon addition of a surplus of benzylamine to a boiling methanol/chloroform suspension of 7, the precipitate dissolves and forms a yellow solution. By evaporation of the

Table 2 Free Ion Values for Selected In(III) Ions ^a								
Table 2. Free Ion Values for Selected Ln(III) Ions ^a								
Gd(III) Tb(III) Dy(III) Ho(III) Er(III) Tm(III)	Yb(III)							
<i>S</i> 7/2 3 5/2 2 3/2 1	1/2							
L 0 3 5 6 6 5	3							
term symbol ${}^8S_{7/2}$ 7F_6 ${}^6H_{15/2}$ 5I_8 ${}^4F_{15/2}$ 3H_6	${}^{2}F_{7/2}$							
g 2 3/2 4/3 5/4 6/5 7/6	8/7							
$C_{\rm Ln} ({\rm cm}^3 {\rm K} {\rm mol}^{-1})$ 8.10 11.82 14.17 14.07 11.48 7.15	2.57							

 ^{a}S and L are the spin and orbital angular momentum quantum numbers, respectively, and g is the Landé g value.

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Figure 5. EPR spectra (blue) of (a) 1', (b) 3', (c) 5', and (d) 7', with simulations (red) based on the best-fit parameters as described in the text. For (c) the inset provides an enlargement of the y axis to better show the g_{ll} resonance at 2100 G. The spectra were recorded at 20, 15, 16, and 19 K for 1', 3', 5', and 7', respectively.

hot reaction mixture, a yellow microcrystalline precipitate (9) is obtained. In contrast to 7, this precipitate is soluble in many organic solvents such as dichloromethane and pyridine. An IR spectrum (Figure S22) of this precipitate shows no carbonyl stretch at 1668 cm⁻¹, confirming that all of the aldehydes have reacted with benzylamine and have been transformed to imines. MALDI-MS data in positive ion mode show signals corresponding to $[HYbL^*]^+$ (*m*/*z* 1023.38), confirming that 9 has been formed (Figure S13). PXRD of 9 (Figure S25) confirms that the bulk of the material consists of one crystal phase, consistent with the single-crystal structure (vide infra). Crystals of 9 suitable for single-crystal X-ray diffraction were obtained by evaporation of the hot mother liquor. 9 crystallizes in the triclinic space group $P\overline{1}$, with the whole complex contained in the asymmetric unit. As for 7, the Yb(III) center remains heptacoordinated and is bonded to three phenoxide groups, three imines, and one tertiary amine (Figure 3a). The bond lengths between the ligand and Yb(III) are very similar to those found in 7. The Yb– N_{apical} and Yb– N_{imine} bonds are slightly elongated in 9, measuring 2.616 and 2.422-2.426 Å, in comparison to 2.610 and 2.421 Å in 7, respectively. The bonds to the phenoxide groups are both shortened and elongated, measuring 2.143, 2.159, and 2.166 Å, in comparison to 2.160 Å

in 7. The larger spread in bond lengths for Yb-O in comparison to Yb-N_{imine} may be due to the benzyl groups creating some disorder in the bottom part of the structure. Although there is no crystallographically imposed C_3 symmetry, the complex retains a pseudo-3-fold axis (Figure 3b).

Static Magnetic Properties. The static magnetic properties of 1-7 were investigated by dc magnetic susceptibility measurements and variable-temperature-variable-field (VTVB) measurements. The dc magnetic susceptibility measurements (Figure 4) were performed in a static magnetic field, *B*, of 1000 Oe and in the temperature, *T*, range 2-270 K. VTVB measurements were performed in the temperature range 2-10 K with applied magnetic fields of 500, 5000, 10000, 20000, 30000, 40000, and 50000 Oe (Figures S27 and S34-S39).

The dc susceptibility data are plotted in Figure 4 as χT products, where $\chi = M/B$ with χ being the molar magnetic susceptibility and M the magnetization. At 270 K, the χT products of 1-7 reach their highest values at 8.10, 11.07, 13.38, 12.87, 10.63, 6.07, and 1.84 cm³ K mol⁻¹, respectively. These are smaller than the values expected for the free Ln(III) ions (Curie constants, C_{Ln} , Table 2).

The χT product of 1 is the only one to reach the Curie constant, which is found at around 15 K. This indicates that 1 displays a very small magnetic anisotropy, which is expected for Gd(III), where the spin-orbit coupling is quenched (L = 0). The γT products 2–7 do not reach their Curie constant at 270 K, suggesting a total energetic splitting of their ground multiplets larger than the thermal energy at 270 K. Upon cooling, the χT products of 1–7 decrease, reaching at 2 K their lowest values of 7.63, 1.17, 5.86, 5.67, 4.78, 0.34, and 0.89 cm³ K mol⁻¹, respectively. This decrease in the χT products of 1-7 upon cooling is due to the thermal depopulation of their respective m_1 manifolds. dc magnetic susceptibility measurements were performed on 9 (Figure S40) similarly to 1-7. At 270 K the χT product of 9 is 1.93 cm³ K mol⁻¹ which, as for 7, is lower than the Curie constant of Yb(III) (Table 2), suggesting a total energetic splitting of the ground multiplet larger than the thermal energy at 270 K.

Electron Paramagnetic Resonance (EPR) Spectroscopy. X-band EPR spectroscopy was performed on dilute polycrystalline samples 1'-7' at low temperature (around 20 K), because of severe line broadening in 1-7, caused by fast electronic relaxation, making the resonances undetectable. However, only the complexes containing Kramers ions (1', 3')5', 7') displayed EPR resonances (Figure 5). 3', 5', and 7' contain anisotropic Ln ions, for which the g_{\parallel} and g_{\perp} resonances should be resolved. However, both the resonances corresponding to g_{\parallel} and g_{\perp} were observed only in the case of 5', while for 3' and 7' only the resonance corresponding to g_{\perp} was observed. This is because for a polycrystalline sample the g_{\parallel} transition is much less intense than the g_{\perp} transition, which combined with inhomogeneous broadening makes detection of the g_{\parallel} transition challenging in some cases. Indeed, in the case of 5', the observed g_{\parallel} resonance was very broad and weak. For 3', 5', and 7' containing anisotropic Ln ions, only the ground Kramers doublet is thermally populated at the temperature of measurement (about 20 K). However, more than one line is observed in the experimental EPR spectra of these complexes. This is due to hyperfine interactions between the electronic and nuclear spins of Ln centers in complexes containing isotopes of the Ln center with nuclear spin $I \neq 0$. Dy, Er, and Yb have such isotopes with nuclear spin $I \neq 0$: ¹⁶¹Dy (19%) and ¹⁶³Dy (25%) with I = 5/2; ¹⁶⁷Er (23%) with I = 7/2; ¹⁷¹Yb (14%) and ¹⁷³Yb (16%) with I = 1/2 and I = 5/2, respectively.

Emission Spectroscopy. The experimental determination of the total energetic splitting of the ground term of each of the studied complexes requires the use of emission spectroscopy. This is because, with the exception of 1, all studied complexes contain anisotropic lanthanide ions leading to total ground multiplet splittings much larger than the thermal energy at room temperature, as suggested by the observed χT products of 2–7 that do not reach their respective Curie constants at 270 K. Thus, these total ground multiplet splittings are inaccessible, at least in detail, by use of magnetometry and EPR spectroscopy. The purpose of obtaining the total splitting of the ground multiplet of each studied complex is to combine this information with the analysis of their static magnetic properties and EPR spectra, to obtain a detailed quantitative description of their electronic properties.

In the first instance, luminescence spectra of polycrystalline 8 were recorded at 300 K. An excitation spectrum of 8 (Figure S42), detecting emission at 500 nm, showed the ligand to be excitable over a broad range of wavelengths (275-475 nm). The emission spectrum of 8 (Figures S43 and S44) revealed

that the ligand emits in most of the visible range and in parts of the NIR range, precluding luminescence studies of all Ln ions except for Yb(III). For Yb(III), the zero-phonon line of the emission spectrum of 7' could be identified in the NIR range (Figure 6). An emission spectrum of 8 (Figure S45) showed



Figure 6. Emission spectrum of 7' with excitation at 300 nm, recorded at 300 K. The asterisk indicates the zero-phonon line of 7'.

no emission from the ligand in the NIR range, when the complex was excited at the wavelength of the zero-phonon line (972 nm) of 7'. Thus, on excitation of the zero-phonon line of Yb(III), the emission spectrum of 7' was partially revealed (Figure S46) without any fluorescence from the ligand. From this luminescence spectrum of 7', the total energy splitting of the ${}^{2}F_{7/2}$ ground multiplet of Yb(III) in 7' was found to be 880 cm⁻¹.

Determination of Crystal Field Parameters. Determination of the crystal field (CF) parameters of 1-7 was performed by the quantitative interpretation of the static magnetic properties of 1-7. For 1, 3, and 5, EPR spectroscopy data were simultaneously taken into account in addition to the static magnetization data. In the case of 7, the total ground multiplet splitting was also simultaneously taken into account with the corresponding magnetization and EPR data. dc magnetic susceptibility, VTVB magnetization measurements, and eventually EPR (in the cases of 1, 3, 5, and 7) and emission (in the case of 7) data were simultaneously numerically fitted to Hamiltonian (1), by full-matrix numerical diagonalization of its matrix representation and by use of the Simplex algorithm.⁷⁶ Hamiltonian (1) includes Zeeman and CF terms:

$$\hat{H} = g_{\rm T} \mu_{\rm B} \hat{J} B + \hat{H}_{\rm CF} \tag{1}$$

where $\mu_{\rm B}$ is the Bohr magneton, g_J is the Landé *g* factor, \hat{J} is the total angular momentum operator of the ground multiplet, and *B* is the magnetic field. The CF operator is described using the Stevens formalism:⁷⁷

$$\hat{H}_{\rm CF} = \sum_{k, -k \le q \le k} B_k^q \hat{O}_k^q$$

In the case of 1, the isotropic nature of Gd(III) means that its χT versus *T* product consists essentially of the Curie constant of Gd(III) down to about 15 K. Thus the χT versus *T* curve is of limited significance for the determination of the best-fit CF parameters of 1, since its inclusion in the simultaneous fit of the magnetization and EPR data will only result in an over-

representation of the contribution of the Curie constant of Gd(III) in the χ^2 statistic of the fit. Thus, only the VTVB data of 1 and the EPR data of 1' were simultaneously numerically fitted to Hamiltonian (1). This resulted in the best fit parameters: $g_z = 2.00$, $g_x = g_y = 1.97$, $D = 3B_4^0 = -1.747 \times 10^{-3}$ cm⁻¹, and $B_4^0 = -1.099 \times 10^{-4}$ cm⁻¹. The best-fit VTVB curves of 1 and the corresponding simulated polycrystalline powder EPR X-band spectrum of 1' are shown in Figure S27 and Figure 5a, respectively, where for the simulation of the X-band EPR spectrum⁷⁸ a line width of 40 G and standard deviations of 3×10^{-4} and 1.2×10^{-5} cm⁻¹ for D and B_{4}^{0} , respectively, were used, assuming these parameters to obey a Gaussian distribution. In addition, the obtained best-fit parameters resulted in a good agreement between the experimental and calculated temperature dependence of the χT product of 1 (Figure 4). Employing extended models including additional CF parameters allowed in trigonal symmetry did not result in better fits. The temperature dependence of the EPR spectrum of 1' was measured between 100 and 20 K (Figure S47). When the temperature of the measurement can be varied from being of the same order of magnitude as the probed energy splittings to being lower than these, Boltzmann depopulation effects of the probed eigenvectors allow in general for the determination of the sign of anisotropy parameters entering the Hamiltonian of the system. However, in the specific case of 1, two competing anisotropy parameters with the same sign are included in the Hamiltonian ($D = 3B_2^0 = -1.747 \times 10^{-3} \text{ cm}^{-1}$ and $B_4^0 = -1.099 \times 10^{-4} \text{ cm}^{-1}$), making deconvolution of their effects difficult. Furthermore, the small magnitude of these parameters results in a total splitting of the ⁸S_{7/2} multiplet of Gd(III) in 1 of 0.14 cm⁻¹, corresponding to about 0.2 K. Under these conditions, even measurements at 4.2 K would not be able to modify the Boltzman population of each of the m_{I} (or m_{S}) sublevels from the value of 1/8, at zero applied magnetic field. Application of a magnetic field on the order of 3500 G only perturbs this picture to a minor extent. Thus, given the attainable experimental conditions, the sign of the anisotropy parameters of 1 entering Hamiltonian (1) cannot be determined and these should be quoted as $D = 3B_2^0 = \pm$ $1.747 \times 10^{-3} \text{ cm}^{-1}$ and $B_4^0 = \pm 1.099 \times 10^{-4} \text{ cm}^{-1}$.

In a recent study, the static magnetic properties of Ln(trenovan) complexes were modeled using the CF parameters of the structurally and chemically related Ln-(trensal) complexes (Tables S5 and S6 for the CF parameters in the Stevens and Wybourne formalisms, respectively), as starting parameters.⁷⁵ Crystal structures of 2–7 show a great resemblance to those of the corresponding Ln(trensal) complexes. Hence, the CF parameters determined for the Ln(trensal) complexes were used as starting parameters in the fits of the experimental data for 2–7 to Hamiltonian (1).

For the modeling of the magnetic properties of **2**, **4**, and **6**, and to avoid overparameterization, only diagonal parameters $(B_2^0, B_4^0, \text{ and } B_6^0)$, in the first place, were included in the model. This resulted in the best-fit parameters given in Table S7. However, this model was too simple, as it failed to reproduce the χT products and VTVB measurements especially for **6** (Figures S28–S33). To improve the model, we subsequently used all eight parameters that are nonzero in C_3 symmetry to describe the CF. Thus, the off-diagonal CF parameters $(B_4^{+3}, B_6^{\pm 3}, \text{ and } B_6^{\pm 6})$ were included in the model, while B_4^{-3} vanishes for an appropriate choice of coordinate frame.⁵⁷ Again, to avoid overparametrization, only the diagonal CF parameters were fitted, fixing the off-diagonal parameters to the values of the Ln(trensal) complexes. This model produced good fits of the χT products (Figure 4) and VTVB measurements (Figures S34, S36, and S38) with parameters that can be found in Tables S9 (Stevens formalism) and S10 (Wybourne formalism). Obtaining good fits with fixed values of the off-diagonal parameters indicates that the CF parameters of 2, 4, and 6 are very similar to those found in the corresponding Ln(trensal) complexes, at least in what concerns the states that are thermally accessible at room temperature.

For the Kramers-ion-containing complexes (3, 5 and 7) modeling was initially done by simultaneously fitting the dc magnetic susceptibility and the VTVB measurements to a model containing all eight parameters $(B_2^0, B_4^0, B_6^0, B_4^{+3}, B_6^{\pm 3}, and$ $B_6^{\pm 3}$) which are nonzero in C_3 symmetry. In a first approximation only the diagonal parameters were fitted, while the off-diagonal parameters were fixed to the corresponding Ln(trensal) values. This produced the parameters presented in Table S8. These parameters were then used as starting point parameters for the simultaneous fits of the detected EPR resonances, of the dc magnetic susceptibilities, and of the VTVB measurements, as well as the total multiplet splitting determined by luminescence measurements in the case of 7. In this new model both diagonal and off-diagonal parameters were fitted, yielding the parameters found in Tables S9 (Stevens formalism) and S10 (Wybourne formalism). These deduced best-fit parameters reproduced well the χT product (Figure 4), VTVB (Figures S35, S37, and S39), and EPR measurements (Figure 5).

For the simulation of the EPR spectra of 3', 5', and 7'(Figure 5) we used Weihe's Sim EPR simulation software.⁷⁸ For this purpose, we used the vector space spanned by the full | J, m_1 eigenbasis of the ground multiplet of each complex, necessary for the simultaneous fitting of susceptibility, VTVB, and EPR data. Hyperfine interactions in 3', 5', and 7' were accounted for by isotropic hyperfine coupling constants (A), given that the full ground multiplet basis was used. As already mentioned, Dy has two isotopes with nuclear spin I = 5/2. However, the difference in the hyperfine couplings of the two isotopes could not be determined from the EPR spectrum of 3'. Hence, a common hyperfine coupling constant has been determined for both isotopes. The determined hyperfine coupling constants according to this methodology were as follows: $A_{\text{Dy}} = 0.0054 \text{ cm}^{-1}$ for ¹⁶¹Dy and ¹⁶³Dy; $A_{\text{Er}} = 0.0043 \text{ cm}^{-1}$ for ¹⁶⁷Er; $A_{171\text{Yb}} = 0.030 \text{ cm}^{-1}$ for ¹⁷¹Yb; $A_{173\text{Yb}} = -0.0083 \text{ cm}^{-1}$ for ¹⁷³Yb. The simulation of 7' does not account for all observed resonances, the unaccounted resonances originating from intermolecular interactions between sites of neighboring paramagnetic molecules in the diamagnetic host lattice, as has previously been observed for Yb(trensal).³⁰

Finally, modeling of the magnetic susceptibility and VTVB data of **9** was performed in a way analogous to what was described above, assuming trigonal symmetry and using as starting point parameters the best-fit parameters of 7, to fit the experimental data of **9** to Hamiltonian (1). The determined best-fit parameters are given in Tables S9 and S10 (Stevens and Wybourne formalisms, respectively) and the best-fit χT product versus *T* and VTVB magnetization curves are given in Figure S40 and S41, respectively, where good agreement between experimental and calculated data is observed.

The eigenvalues and eigenvector composition determined for 1-7 and 9 by the above quantitative analysis are given in Figure S49 and Table S11 (eigenvalues) and in Tables S12– S19 (eigenvector composition). The obtained total ground multiplet splittings for 2-7 are of the same order of magnitude as those of the corresponding Ln(trensal) complexes, with the exception of 2, for which the total splitting of the ground multiplet is about 3 times larger than that of the corresponding Tb(trensal) complex. This is likely due to the temperature dependence of the γT product and VTVB measurements of 2 not providing enough information for a good description of the CF splitting solely based on fits to these. Furthermore, since 1-7 display trigonal symmetry, their eigenvectors (Tables S12-S18) are not pure m_1 states but linear combinations of these, containing components differing by $\Delta m_1 = \pm 3$, as dictated by the trigonal symmetry. The same is true for the corresponding Ln(trensal) complexes. Thus, modification of the trensal ligand to obtain the functionalized derivative H₃L and the associated complexes LnL does not lead to a radical modification of the ligand field experienced by the Ln center. Thus, the static magnetic properties of the two series of complexes should be similar, in agreement with what our experimental results demonstrate. Furthermore, the total multiplet splitting of 9 is about 20% smaller than that of 7 (Figure S49 and Table S11) but the splitting patterns of the three first Kramers doublets spanning an energy interval of about 450 cm⁻¹ are quite similar. This fact, combined with very similar eigenvector compositions of 7 and 9 (Tables S18 and \$19, respectively) suggests the occurrence of very similar, at least static, magnetic properties for the two complexes, in temperature regimes up to room temperature.

In order to estimate the total multiplet splitting of a given Ln center, the ligand field (LF) strength of the ligand H₃L exerted on each Ln ion can be quantified by the parameter $N_v/(4\pi)^{1/2}$:⁵⁹

$$N_{\rm v}/(4\pi)^{1/2} = \left(\sum_{k=2,4,6} \frac{1}{2k+1} \left(B_{k0}^2 + 2\sum_{q=1}^k |B_{kq}|^2\right)\right)^{1/2}$$
(2)

where B_{kq} are the corresponding Wybourne parameters. On comparison of the LF strengths of 2–7 with those of the corresponding Ln(trensal) complexes (Table S20), $N_v/(4\pi)^{1/2}$ is found to be generally larger for complexes 2–7. However, the total multiplet splittings of 4–7 are actually a bit lower than those of the corresponding Ln(trensal) complexes. This shows that one has to be cautious when correlating the total multiplet splitting with the LF strength parameter, as has been previously noted,⁷⁹ since $N_v/(4\pi)^{1/2}$ is defined for the full electronic configuration of the Ln ion and not for a specific multiplet. Thus, parameters corresponding to different tensor ranks of LF operators are weighted differently in $N_v/(4\pi)^{1/2}$, for different multiplets.

Finally, the influence of the contraction of the $Ln-N_{apical}$ distance in 2–7 with respect to the corresponding Ln(trensal) complexes (Table S20) should lead to an increase in the LF for the former series since the σ -donating effect of a ligand is related inversely proportional to the fifth power of the metal to ligand distance.⁸⁰ However, this effect of the apical nitrogen ligand and that both σ - and π -donating effects of all seven ligating atoms have to be taken into account for the calculation of the LF potential, thus making the effect of the aforementioned apical distance contraction not directly proportional to the total LF potential. Ln(trenovan) is another member of the Ln(trensal) family. As for 1–8, Ln(trenovan)

also experiences a much shorter Ln-N_{apical} distance in comparison to the corresponding Ln(trensal). As mentioned above (see the crystallography section) $Ln-N_{apical}$ is shorter in Ln(trenovan) than in 1-8. In a study of the electronic structure of these complexes,75 the LF strength of the H₃trenovan ligand was found to be larger than that of the corresponding H₃trensal ligand (Table S20), which was ascribed to the much shorter $Ln-N_{apical}$ distance, as in 1-8. On comparison of the LF strength of Ln(trenovan) with those of 2-6 (no LF strength has been determined for Yb-(trenovan)), the ligand in 2-6 is generally found to exert a larger LF potential in comparison to that in Ln(trenovan), although Ln-N_{apical} is shorter in Ln(trenovan). This counterintuitive result is likely due to the effect of the six other ligating atoms (three imines and three phenoxides), as mentioned above.

Dynamic Magnetic Properties. ac susceptibility measurements were performed on 1-7 and 9 with an oscillating field of 3.5 Oe at frequencies in the range 0.1-1500 Hz and with applied static magnetic fields ranging from 0 up to 10000 Oe (Figures S50-S69 and S71-S74). When no static magnetic field was applied, none of the samples displayed slow magnetic relaxation with respect to the available frequency range. This is probably due to a large amount of quantum tunneling of the magnetization (QTM), as has been previously found in similar compounds.⁶⁰ Application of a static magnetic field to quench the QTM resulted in the observation of out-of-phase ac magnetic susceptibility only for the Kramers-ion-containing complexes: namely, 1, 3, 5, 7, and 9. To investigate the dynamic magnetic properties of these further, the ac susceptibility of the complexes was studied at varying temperatures. For 1, 3, and 5 two different relaxation processes were found. When a small static magnetic field of 1000 Oe was applied, an out-of-phase signal was observed in the highfrequency range (Figures S50, S51, S56, S57, S60, and S61). This relaxation process is faster than our instrument's time scale, which prevented us from studying it in detail. Applying a static field of 5000, 2500, and 5000 Oe for 1, 3, and 5, respectively, results in the emergence of a relaxation process at low frequencies. For 1 and 5 the temperature dependence of this process was studied (Figures S52, S53, S62, and S63). For both complexes the relaxation rate of this process shows little temperature dependence and its intensity decreases rapidly with temperature. 7 displays only one out-of-phase signal at 1.8 K at about 500 Hz (Figure S67) when a magnetic field is applied (Figures S66 and S67). The optimal conditions, with respect to the amplitude of the out-of-phase response, were obtained with an applied field of 2000 Oe. The temperature dependence of this process was fitted to the generalized Debye model using CC-FIT2⁸¹ (parameters can be found in Table S21). However, the characteristic relaxation time of this process quickly moves outside the window of available frequencies on our instrument (Figure S69), preventing a detailed analysis of the associated relaxation mechanisms (see Figure S70 for a plot of the relaxation time (τ) vs *T*).

9 only displays slow magnetic relaxation in an applied magnetic field, indicating a large amount of QTM. Similar to the case for 7, only one maximum (at about 50 Hz) in the out-of-phase part of the ac susceptibility is found on varying the frequency at 1.8 K, with the optimal field being 2000 Oe (Figures S71 and S72). The out-of-phase maximum shows a pronounced temperature dependence. The characteristic relaxation time of this process was fitted to the generalized

Debye model (Figures S73 and S74), using CC-FIT2.⁸¹ An Arrhenius plot of the extracted relaxation times versus temperature (Figure S75) shows a curvature which indicates that direct and Raman processes are involved in the relaxation rather than an Orbach process,⁸² as was demonstrated for the closely related Yb(trensal).⁶¹ We fitted the extracted relaxation



Figure 7. Relaxation times extracted for 9 together with the best fit obtained using eq 3.

times to a Raman and direct relaxation processes (Figure 7), according to eq 3

$$\tau^{-1} = CT^n + DT \tag{3}$$

which resulted in the best fit parameters $C = 41(4) \text{ s}^{-1} \text{ K}^{-3}, ^{37} n$ = 3.37(6), and $D = 134(10) \text{ s}^{-1} \text{ K}^{-1}$. The Raman exponent n =3.37 is much lower than n = 9, which is expected for a twophonon Raman process in Kramers ions.⁸³ However, depending on the CF, the Raman exponent may be much smaller than 9.⁸⁴ For instance, for a previously investigated Yb(III) complex the Raman exponent was found to be n = 2.37.⁸⁵

Comparing the dynamic magnetic properties of 7 and 9, one can conclude that the lowering of symmetry associated with the postfunctionalization of the ligand is not radically detrimental to the dynamic magnetic properties of 7, since slower magnetic relaxation of about 1 order of magnitude at 1.8 K is observed for 9 with respect to 7. In addition to symmetry considerations, other factors such as the magnetoelastic coupling constant and the density of phonons within the studied materials are important for the observed spin dynamics. These results are important for the perspective of depositing such Ln-based molecular materials on surfaces, since the lowering of symmetry that would normally be associated with the surface deposition process can by itself be considered a priori as radically detrimental to the dynamic magnetic properties of the surface-deposited species. Thus, detailed studies of specific surface deposited systems are required to gain insight into this respect.

CONCLUSION

The reaction of the *in situ* generated ligand H_3L and $Ln(OTf)_3 \cdot xH_2O$ in the presence of base afforded the isolation of eight novel complexes LnL, with Ln = Gd-Lu. All

complexes are isostructural and crystallize in the trigonal space group $P\overline{3}$, with the crystallographic C_3 axis coinciding with that of the complex. These complexes display the same symmetries and coordination spheres as the previously studied Ln(trensal) series. This similarity allowed use of the CF parameters of Ln(trensal) as initial values for modeling of the static magnetic properties of LnL. Overall the CF parameters were found to be very similar between Ln(trensal) and LnL. Only the complexes containing Kramers ions (Gd(III), Dy(III), Er(III), and Yb(III)) display slow magnetic relaxation on the investigated time scales, and only in an applied magnetic field. In addition, EPR spectra were observed only for these species.

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1-8 contain three aldehyde groups which are noncoordinating and can thus be used for the direct deposition of these complexes on surfaces functionalized with, for example, amino groups. Furthermore, these carbonyl functions react readily with primary amines. Reacting 7 with an excess of benzylamine in a chloroform/methanol mixture afforded the isolation of the benzylamine-functionalized complex 9. This complex has a coordination environment similar to that of the LnL complexes. 9 also displays slow magnetic relaxation in an applied magnetic field on the investigated time scales, with the magnetic relaxation being governed by direct and Raman processes. The lowering of symmetry to which 9 is subjected as a consequence of the postfunctionalization of 7 does not lead to a drastic deterioration of its dynamic magnetic properties. These results are relevant from the perspective of deposition of such Ln-based molecular materials on surfaces, since the surface deposition process is most likely accompanied by a lowering of symmetry of the deposited species.

Surface deposition of SIMs for integration in QIP devices requires specific surface deposition protocols to be developed. We demonstrate herein that our previously studied Yb(trensal) molecular qubit, and by extension all the members of the Ln(trensal) series, can be derivatized with carbonyl functions that serve as anchoring points to surfaces functionalized by amino groups. Furthermore, postfunctionalization of LnL results in pendant anchoring groups that would make possible the surface deposition of LnL on surfaces that initially were not compatible with LnL. Thus, our study establishes LnL as a truly versatile module for the surface deposition of Ln-based SIMs with relevance to QIP.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02121.

Experimental details and characterization and magnetization data (PDF)

Accession Codes

CCDC 2016912–2016919 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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