Design of Pure Heterodinuclear Lanthanoid Cryptate Complexes

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Submitted date: 30/01/2021 • Posted date: 01/02/2021
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Citation information: Buch, Christian Dirk; Hansen, Steen; Mitcov, Dmitri; Tram, Camilla Mia; Nichol, Gary; Brechin, Euan; et al. (2021): Design of Pure Heterodinuclear Lanthanoid Cryptate Complexes. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.13667729.v1

Heterolanthanide complexes are difficult to synthesize owing to the similar chemistry of the lanthanide ions. Consequently, very few purely heterolanthanide complexes have been synthesized. This is despite the fact that such complexes hold interesting optical and magnetic properties. To fine-tune these properties, it is important that one can choose complexes with any given combination of lanthanides. Herein we report a synthetic procedure which yields pure heterodinuclear lanthanide cryptates LnLn* LX₃ (X = NO₃- or OTf-) based on the cryptand H₃L = N[(CH₂)₂N=CH-R-CH=N-(CH₂)₂]₃N (R = m-C₆H₂OH-2-Me-5). In the synthesis the choice of counter ion and solvent prove crucial in controlling the Ln-Ln* composition. Choosing the optimal solvent and counter ion affords pure heterodinuclear complexes with any given combination of Gd(III)-Lu(III) including Y(III). To demonstrate the versatility of the synthesis all dinuclear combinations of Y(III), Gd(III), Yb(III) and Lu(III) were synthesized resulting in 10 novel complexes of the form LnLn*L(OTf)₃ with LnLn* = YbGd 1, YbY 2, YbLu 3, YbYb 4, LuGd 5, LuY 6, LuLu 7, YGd 8, YY 9 and GdGd 10. Through the use of 1H, 13C NMR and mass spectrometry the heterodinuclear nature of YbGd, YbY, YbLu, LuGd, LuY and YGd was confirmed. Crystal structures of LnLn*L(NO₃)₃ reveal short Ln-Ln distances of ~3.5 Å. Using SQUID magnetometry the exchange coupling between the lanthanide ions was found to be anti-ferromagnetic for GdGd and YbYb while ferromagnetic for YbGd.
Design of Pure Heterodinuclear Lanthanide Cryptate Complexes

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ABSTRACT: Heterolanthanide complexes are difficult to synthesize owing to the similar chemistry of the lanthanide ions. Consequently, very few purely heterolanthanide complexes have been synthesized. This is despite the fact that such complexes hold interesting optical and magnetic properties. To fine-tune these properties, it is important that one can choose complexes with any given combination of lanthanides. Herein we report a synthetic procedure which yields pure heterodinuclear lanthanide cryptates LnLn*+X2 (X = NO3 or OTf) based on the cryptand H2L = N[CH2]N=CH-R-CH=N-[CH2]2N (R = m-C6H4OH-2-Me-5). In the synthesis the choice of counter ion and solvent prove crucial in controlling the Ln-Ln*composition. Choosing the optimal solvent and counter ion affords pure heterodinuclear complexes with any given combination of Gd(III)-Lu(III) including Y(III). To demonstrate the versatility of the synthesis all dinuclear combinations of Y(III), Gd(III), Lu(III), Gd(III) and Lu(III) were synthesized resulting in 10 novel complexes of the form LnLn*+L(OTf)2 with LnLn* = YbGd 1, YbY 2, YbLu 3, YbYb 4, LuGd 5, LuY 6, LuLu 7, YbGd 8, YY 9 and GdGd 10. Through the use of 1H, 13C NMR and mass spectrometry the heterodinuclear nature of YbGd, YbY, YbLu, LuGd, LuY and YbGd was confirmed. Crystal structures of LnLn*+L(NO3)2 reveal short Ln-Ln distances of ~3.5 Å. Using SQUID magnetometry the exchange coupling between the lanthanide ions was found to be anti-ferromagnetic for GdGd and YbYb while ferromagnetic for YbGd.

INTRODUCTION

Lanthanide (Ln) molecular materials have attracted strong interest and have been intensively studied in a wide range of areas such as catalysis,1,5 bioinorganic chemistry,6-7 Magnetic Resonance Imaging,8-10 luminescent materials,11-14 multimodal imaging probes,15-22 Single-Molecule Magnets (SMMs),16-21 and Quantum Information Processing (QIP).22-24 Many of the interesting properties of Ln complexes originate from their special electronic structure, where the 4f subshell is shielded from the environment by the 6s and 5p orbitals.25 For example, this results in a large unquenched orbital-angular momentum which has been essential to build SMMs26-33 with record blocking temperatures,34-35 and leads to sharp absorption and emission bands, due to the lower influence of vibrations on the f-f transitions.

With respect to QIP, Ln complexes form a very exciting but rather unexplored class of molecular materials.27,42-45 We have recently demonstrated that Yb(trensal),46 a member of the Ln(trensal) series,47-54 is a very promising candidate for the realisation of a molecule-based electronic quantum-bit (qubit).47,48 Yb(trensal) is one of the few known Ln-based molecular qubits to date. Furthermore, the potential multilevel nature of Ln molecular materials, resulting from the hyperfine interaction of electronic and nuclear angular momenta or from week ligand field splittings of the Stark sublevels in cases where the orbital angular momentum is quenched, can be exploited as an additional resource for the development of quantum logic algorithms.55,59 In recent ground-breaking work, Grover’s quantum algorithm, relevant to identifying an element within an unsorted database, was implemented on the basis of the four nuclear spin wavefunctions of a bis(phthalocyanine) Tb(III) molecular magnet.60 Nuclear spins were also proposed as physical supports for the implementation of qubits,28,60 since the contraction of nuclear wave functions shields them from the environment, minimizing decoherence effects. This results in nuclear spins having much longer coherence times than their electronic counterparts. However, this isolation also leads to long manipulation times,61 which can be circumvented via the use of molecular systems in which hyperfine interactions are significant, resulting in faster manipulation time-scales.62 We very recently demonstrated that Yb(trensal)46 is a prototypical coupled electronic qubit–nuclear qudit63 (where a qudit is a quantum system comprising more than two levels). The nuclear qudit of the 173Yb isotope nucleus (nuclear spin I = 5/2) displayed coherence times of the order of 10 - 107 microseconds, similar to the best performing, state-of-the-art, nuclear-spin-based qudits.64 Most importantly, the electronuclear multilevel structure of the qudit allowed intrinsic implementation of quantum error corrections concerning encoding of both amplitude and phase shift error corrections.65 QIP algorithms can be performed as a sequence of single qubit rotations and gate operations performed on two entangled qubits. Thus, nuclear spins hosted in molecular magnetic materials are excellent candidates for the implementation of single qubit gates. However, their lack of interaction with the environment creates difficulties for the realization of coupled qubit gates. Hyperfine interactions mix the nuclear and electronic angular momentum wave-functions. Thus, construction of nuclear spin quantum gates appears feasible by simultaneously exploiting the long range coupling of electronic spins via magnetic exchange interactions and the hyperfine interaction-induced mixing of the electronic and nuclear angular momenta, at the single-ion level.65 In order to be individually addressable, the two angular momenta located on the two lanthanide centres composing the quantum gate
have to be different. Thus, the need for the controlled synthesis of pure heterometallic complexes arises.

Synthesis of heterometallic Ln complexes is difficult since the 4f elements all have very similar chemistries. This is further compounded by the bonding interaction with ligands being largely ionic in character, resulting in many synthetic protocols producing impurities from homonuclear complexes (i.e. scrambling). Thus, examples of pure heterometallic Ln complexes remain rare. These are almost solely limited to phthalocyanine and DOTA complexes. An elegant strategy relying on size selection of dissymmetric ligands has been employed to synthesise heteronuclear Ln complexes without scrambling. However, this is only efficient when the included Ln(III) ions are of very different size, greatly limiting the choice of possible combinations.

We present herein a synthetic strategy for the realization of pure heterodinuclear Ln complexes of composition not limited by size selectivity. Thus, for the second half of the lanthanide series (from Gd to Lu, and including Y), our synthetic strategy results in heteronuclear complexes of arbitrary composition. To illustrate this point, we present the synthesis and characterization of heterodinuclear complexes $\text{LnLn}^*$ containing two large Ln centers (Y, Gd), two small Ln centers (Yb, Lu) and one small (Yb or Lu) and one large (Y or Gd) center, corresponding to the following 10 complexes: $\text{YbGd 1}$, $\text{YbY 2}$, $\text{YbLu 3}$, $\text{YbYb 4}$, $\text{LuGd 5}$, $\text{LuY 6}$, $\text{LuLu 7}$, $\text{YGd 8}$, $\text{YY 9}$ and $\text{GdGd 10}$. We also demonstrate the solid-state and solution-state stability of 1-10, and present the static magnetic properties of the paramagnetic members of the family, namely, 1, 2, 3, 4, 5, 8 and 10.

**RESULTS AND DISCUSSION**

**Synthetic strategy.** We initiated a research program to construct pure heterodinuclear Ln complexes the composition of which is not limited by size considerations, meaning that we should also be able to synthesize pure heterodinuclear complexes containing Ln centers of similar size. Given the relevance of Yb(trensal) to QIP, we decided to use the Ln(trensal) motif as the elementary platform upon which our new heterodinuclear complexes would be constructed.

As can be seen from Scheme 1, the heptacoordinated Ln ion in Ln(trensal) occupies all the available coordination positions within the complex. There are therefore no uncoordinated functional sites left to be used as expansion points of the structural motif to accommodate coordination of a second Ln center. Thus, use of a ligand bearing additional chemical functions is necessary. In the first instance we used tris(2-aminoethyl)amine (tren) and 2,6-diformyl-p-cresol (dfmp), a functionalized derivative of salicyaldehyde. Use of dfmp allows for the synthesis of complexes of type LnL$^1$ (Scheme 1) that can be regarded as functionalized derivatives of
Ln(trensal). Subsequently, the template effect of the Ln center in LnL1 was exploited for the condensation of a second tren to create the cryptate complexes LnL, which possess a preformed vacant coordination site that ultimately acts as host for the second Ln center. In the final step, the second Ln* centre is inserted in the cryptate resulting in the targeted heterodinuclear complexes [LnLn*[L][X], with X a monoanion. Cryptand complexes are known to be thermodynamically and kinetically stable,77 with Ln(III) cryptates being considered suitable candidates for MRI contrast agents.78 Such stability is a prerequisite for surface deposition protocols and, ultimately, inclusion in spintronic devices. To the best of our knowledge only homodinuclear Ln(III) cryptates exist.79,82

We have previously presented the synthesis, magnetic and spectroscopic properties of LnL1 and LnL.83,84 Both these families of complexes have merits on their own and should not simply be regarded as mere intermediate compounds in the synthesis of our targeted heterodinuclear complexes. LnL1 contains pendant, reactive amine functions that can be used as anchoring points for surface deposition protocols. These same functionalities can also be exploited in post-synthetic reaction schemes making them truly versatile modules for deposition on various surfaces.84 LnL have previously been considered as targets for the development of novel MRI contrast agents.83

Synthesis and Characterisation. Complexes 1-10 were synthesized in a step-wise procedure. First the cryptate LnL was synthesized according to the procedure we have very recently published.83 To this was then added 3 to 5 equivalents of Ln*(OTf)2·xH2O, depending on the size of the Ln*(III) ion. The resulting yellow pyridine solution was refluxed. Following a workup procedure detailed in the experimental section, the complexes were isolated as pale yellow powders. Interestingly, 3, 4 and 7 involving insertion of the smallest Ln(III) ions require the longest refluxing times and the largest surplus of Ln*(OTf)2·xH2O. This indicates that the size of the Ln ion is important for insertion into LnL and that the smallest Ln(III) ions are the most difficult to insert. It should be noted that 10 was synthesized in a slightly different manner to 1-9, since GdL-4H2O could not be isolated.83 Thus for the synthesis of 10, in situ formation of GdL was followed by addition of Ln*, as described in detail in the experimental section. The presence of the desired heterodinuclear complexes was confirmed by mass spectrometry (Figures 1 and S1-S10). The MALDI mass spectra of 1-10, reveal no signals stemming from the homodinuclear complexes. Furthermore, the experimental and calculated distribution patterns of the MALDI spectra are in excellent agreement, further confirming the presence of the desired heterodinuclear complexes.1H and 13C NMR studies of the diamagnetic complexes (6), (7) and (9)) also reveal that only the desired heterodinuclear complexes are formed (Figure 2 and S50-S54). For (6), the 1H and 13C NMR spectra display signals originating from protons and carbons lying in either the Lu(III) or Y(III) part of the complex with different chemical shifts (Figures 2 and S50), but which integrate to the same value. Additionally, IR spectroscopy confirms that both cooridination sites in (1-(10) are fully occupied as there is a single imine stretch (Figures S28 – S37).

X-ray crystallography. The precipitates obtained for 1-10 are amorphous. In order to ensure phase purity of the synthesized heterodinuclear complexes, samples were recrystallized from ethanol in the presence of a surplus of Bu4NNO3 affording the nitrate analogues LnLn*[L(NO3)2] (1x-10x) as microcrystalline precipitates. Single crystals of 1x-10x were obtained through slow diffusion of 1-10 with 5 equivalents of Bu4NNO3 in ethanol. The complexes (Figure 3) all crystallise in the tetragonal crystal system, in one of the two enantiomorphic space groups P4_2_2 or P4_2_2. This is because the helicity of the cryptand ligand around the Ln ions leads to chirality, defining a right (A) or left (A) helix at each Ln centre, resulting in ΔA or ΔA chiral complexes (Figure 4) crystallising in homochiral single crystals. Thus, upon crystallisation the chiral complexes resolve, with the complexes containing the ΔA conformation crystallizing in the space group P4_2_2 while the AA conformation is present crystallised in the space group P4_2_2 (Figure 4). These two space groups are part of the 65 Schoncke space groups that contain only symmetry operations of the first kind (rotations and translations) and can accommodate chiral molecules.85 For both space groups the whole complex is contained in the asymmetric unit with eight complexes being in the unit cell. All complexes have similar structures with the two Ln ions being placed inside the cryptand ligand, disordered 50:50 over the two metal sites (Figure 3). The Ln ions are hepta-coordinated (LnN2O) by the cryptand ligand, being bonded to three phenoxides, three imines and one tertiary amine. The three phenoxide O-atom bridge between the two Ln ions. This results in short Ln-Ln distances, measuring between 3.4395(3)-3.5035(4) Å, with 7x and 10x having the shortest and longest distance (Table S6), respectively. Going from 10x through 8x and 10x to 8x the Ln-Ln distance decreases according to the Ln* in the GdLn* combination being smaller (Table S6). The Ln ions are also coordinated by one nitrate ion.
each. For complexes $3_N$, $4_N$ and $7_N$ containing the smallest Ln ions the nitrate ions are non-coordinated and each Ln is octacoordinated. In $8_N$, $10_N$ containing the larger Ln ions, each nitrate is bidentate to the Ln ion, and each Ln ion is non-coordinated. For $1_N$, $2_N$, $5_N$ and $6_N$ containing lanthanides of mixed size, one Ln has a bidentate nitrate while the other one has a monodentate nitrate ion. The coordination of the nitrate ion distorts the cryptand ligand such that no threefold symmetry is found around the Ln ion.

PXRD measurements confirm that the isolated powders are isostructural, and have the same structure as the single crystal X-ray structure (Figures S63-S64). PXRD also confirms that the complexes are obtained phase pure. Mass spectrometry reveals $1_N$-$10_N$ remain pure heterodinuclear complexes and that no exchange of Ln ions occurs (Figures S11-S20). This is also confirmed by NMR spectroscopy where $6_N$ shows the same splitting in the $^1$H NMR as $6$ (Figure S60). Additionally, the NMR spectra of $6_N$, $7_N$ and $9_N$ confirm that the complexes remain dinuclear after the recrystallization (Figures S60-S62).

**Stability.** Based on the discussion of the synthetic protocol, the question as to why $1_N$-$10_N$ were not synthesized directly from LnL and Ln*(NO$_3$)$_3$·xH$_2$O, arises. While $1_N$-$10_N$ can be synthesized following this route, it also leads to scrambling. This is evident by comparing the mass spectra corresponding to the two synthetic strategies (Figures S21 and S22). It is perhaps surprising that such a small change has such a tremendous impact on the control of the LnLn* composition. This indicates that the Lewis basicity of the counterion is crucial. Moreover, we also observed that the choice of solvent has a large impact on LnLn* composition. For example, exchanging pyridine for PrCN (which has a similar boiling point 115 °C vs 118 °C) leads to scrambling even when employing Ln(OTf)$_3$·xH$_2$O (Figures S21 and S23). This suggests that the basicity of pyridine inhibits the scrambling. The role of pyridine as a base was confirmed by the $^1$H NMR spectrum of $9$ before treatment with THF, where signals from pyridinium triflate are visible (Figure S59).

To have a truly versatile heterodinuclear Ln complex, the molecule needs to be as robust as possible. This is especially true if the complex is to be included in spintronic devices where surface deposition techniques require stable components. The cryptate complexes presented herein are all stable in solution for several days. This was confirmed using NMR, where the $^1$H-NMR of $6$ dissolved in CD$_2$CN did not change after seven days (Figures 2 and S55). Similar stability was found when dissolved in CD$_3$OD (Figures S57 and S58). To further test the robustness of the complexes 100 equivalents of a third Ln(III) ion were added to a MeOH solution of the complexes. The complexes retain their original LnLn* composition. This was studied by dissolving $4$ and $10$ in methanol and subjecting them to 100 equivalents of either Lu(OTf)$_3$·xH$_2$O or Y(OTf)$_3$·xH$_2$O, respectively. After one week no signals from new species involving either Lu(III) or Y(III) could be observed by mass spectrometry (Figures S24 and S25), confirming the robustness of these complexes.

**Magnetic properties.** The static (d.c.) magnetic properties of $1_N$-$5_N$, $8_N$ and $10_N$ were investigated by magnetic susceptibility and variable-temperature-variable-field (VTVB) measurements (Figure 5 and Figures S65-S80). The susceptibility measurements were performed in a magnetic field, $B$, of 1000 Oe in the temperature, $T$, range 2 to 270. VTVB measurements were performed in the temperature range 2 to 10 K in applied magnetic fields up to 5 T.

The d.c. susceptibility data of $1_N$-$5_N$, $8_N$ and $10_N$, are plotted in Figure 5 as $\chi T$ products, where $\chi = M/B$ with $\chi$ the molar magnetic susceptibility and $M$ the magnetization. At 270 K, the $\chi T$ product of all measured complexes approach their Curie constants (10.44, 2.57, 2.57, 5.14, 7.87, 7.87 and 15.74 cm$^3$ K mol$^{-1}$) with values of 9.91, 2.06, 1.99, 4.30, 7.58, 7.89 and 15.74 cm$^3$ K mol$^{-1}$, for $1_N$, $2_N$, $3_N$, $4_N$, $5_N$, $8_N$ and $10_N$, respectively. Upon decreasing the temperature, the $\chi T$ product decreases for $2_N$ - $5_N$, $8_N$ and $10_N$, reaching its lowest value at 2K measuring 1.25, 1.22, 2.39, 7.72, 7.93 and 5.06 cm$^3$ K mol$^{-1}$, respectively. This decrease is due to thermal depopulation of excited $m_f$ states in complexes containing one paramagnetic center ($2_N$, $3_N$, $5_N$ and $8_N$). For $4_N$ and $10_N$ that both contain two paramagnetic centers, the decrease can be attributed to a combination of effects arising from thermal depopulation of excited $m_f$ states and anti-ferromagnetic interactions between the coupled Ln centers. For $4_N$, thermal depopulation of excited $m_f$ states will prevail at higher temperatures, and the weak exchange interactions will occur at lower temperatures. For

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**Figure 3.** Crystal structure of the cation of $1_N$. Color scheme: C, gray; N, blue; O, red; Gd, cyan; Yb, green. Thermal ellipsoids have been omitted for clarity.

**Figure 4.** ΔΔ and ΛΛ enantiomers of the cations of $1_N$ and $6_N$, respectively. The complexes are viewed along the pseudo-trigonal axis.
of the coordination sphere of the Ln ion. For $C_3$ symmetry, as is the case for $2N, 3N, 5N$ and $8N$, twenty seven CF parameters are needed. Determining this number of parameters from the magnetic susceptibility and VTVB measurements alone would result in overparameterization. To remediate this problem, we assume that the local symmetry of the Ln sites is $C_3$, neglecting the effect of the coordinated nitrate anions. By assuming $C_3$ symmetry, the maximum number of CF parameters reduces to nine. However, nine CF parameters is still a large number of parameters to be determined solely from thermodynamic magnetization data. Thus, additional information can be incorporated in the fitting model by exploiting emission and Electron Paramagnetic Resonance (EPR) spectroscopies, as has been previously shown for the Ln(trensal) series.\cite{45-46} Once the CF parameters of Gd(III) and Yb(III) sites determined, quantitative analysis of the magnetic properties of complexes containing two paramagnetic centres was performed by fixing the CF parameters of Gd(III) and/or Yb(III) and fitting only the parameters relevant to the exchange term of Hamiltonian (1).

In the case of complexes containing a paramagnetic Gd(III) ion and a diamagnetic Lu(III) or Y(III) ion ($5N$ and $8N$, respectively), the $4f^0$ electronic configuration of Gd(III) results in an $^5S_{2/2}$ ground term where the orbital angular momentum is quenched. This means that there are no first order contributions to anisotropy and that the associated CF splitting is relatively small with respect to the experimental conditions of magnetization measurements. Hence, very little information on the CF can be extracted solely from magnetization measurements. However, the small CF in Gd(III) means that all transitions within the ground multiplet can be observed using EPR spectroscopy and thus information on the CF parameters can be extracted based on these observations. Using the EPR simulation software Sim,{\textsuperscript{90}} the EPR spectra of $5N$ and $8N$ were simulated using Hamiltonian (1) resulting in the best-fit CF parameters (in Stevens formalism\textsuperscript{90}); $B_{2}^0 = -1.84\times10^{-2}$ cm$^{-1}$, $B_{6}^0 = 1.95\times10^{-4}$ cm$^{-1}$ and $B_{6}^0 = -6.67\times10^{-6}$ cm$^{-1}$ with $g = 2$ (Figures S81-S82). Because of the very broad polycrystalline powder EPR spectra no off-diagonal CF parameters could be determined. The obtained CF parameters were then used to simulate the $\chi_T$ product and the VTVB data (Figures 5, S78-S79). The associated eigen spectrum is shown in Figure S88 where it can be seen that the total CF splitting of $5N$ and $8N$ is of the order of 1 cm$^{-1}$. We note that both complexes display very similar EPR spectra, albeit very broad, (Figures S81-S82), suggesting that the CF of Gd(III) is not dramatically influenced by the size of the second Ln ion.

For the complexes containing a paramagnetic Yb(III) ion and a diamagnetic Y(III) or Lu(III) ion ($2N$ and $3N$, respectively), the $4f^{13}$ electronic configuration of Yb(III) results in an $^2I_{15/2}$ ground term where the orbital angular momentum of Yb(III) is unquenched. Thus, anisotropy to first order is expected for the CF splitting pattern of Yb(III). This means that in the case of Yb(III), emission spectroscopy can be exploited, in addition to EPR, as an additional source of information on the CF. The solid state, room temperature emission spectra of $2N$ and $3N$, diluted at 3% in the diamagnetic host $9N$, reveal that the total CF splitting of the ground term of Yb(III) in these complexes is of the order of 560 cm$^{-1}$ (Figure S85). This is approximately 2/3 of the value observed in the parent Ln(trensal) complex.\textsuperscript{46} However, the polycrystalline powder EPR spectra of these dilute samples of $2N$ and $3N$, are too broad (Figures S83-84) to offer reliable information to be used in the fitting procedure. Furthermore, the $\chi_T$ products and

Figure 5. $\chi_T$ products of $1N, 5N, 8N$ and $10N$ (scatter) with best fits (lines) as described in the text.

$10N$, given the magnetically isotropic nature of Gd(III), this picture is inverted. The $\chi_T$ product of $1N$ also decreases upon lowering the temperature down to 12 K. Below this temperature the $\chi_T$ product of $1N$ rapidly increases, reaching a maximum of 9.44 cm$^{-3}$ K mol$^{-1}$ at 2 K. This behavior indicates ferromagnetic coupling between the Yb(III) and Gd(III) centers.

The quantitative analysis of the static magnetic properties of the studied complexes was performed by simultaneous numerical fitting, by use of the simplex algorithm,\textsuperscript{90} of both the $\chi_T$ and VTVB data to Hamiltonian (1)

$$
\hat{H} = \sum_{i=1,2} \left( \mu_B \vec{B} g_i \vec{J} + \sum_{k=2A,6\; -k\angle g k} B^0_k \mathcal{O}_k \right) + J_{12} \vec{J}_1 \vec{J}_2
$$

(1)

where the first term is the Zeeman interaction, with $\mu_B$ the Bohr magneton, $\vec{B}$ the magnetic field vector, and $g_I$ and $\vec{J}$ the Landé g-factor and total spin-orbit angular momentum operator of multiplet $J$, respectively. The second term expresses the crystal field (CF), with $B^0_k$ the parameter associated to operator $\mathcal{O}_k$, within the Steven’s formalism. The third term accounts for the magnetic exchange between Ln centers, with $J_{12}$ being a general second order exchange tensor that can be decomposed into isotropic, $J_{12}$, antisymmetric, $d_{12}$, and anisotropic, $D_{12}$, contributions.\textsuperscript{85} Not all terms in the general expression of (1) are relevant for the analysis of the magnetic properties of all the studied complexes. The summation over Zeeman and CF terms, as well as the exchange term, are relevant only for complexes containing two paramagnetic centers. For orbitally non-degenerate ions, such as Gd(III), inclusion of only isotropic exchange terms in the Hamiltonian is sufficient. For orbitally degenerate ions, such as Yb(III), anisotropic exchange terms must be considered.\textsuperscript{84} Here, for the sake of simplicity, we consider exchange anisotropy terms only up to second order ($D_{12}$) and neglect antisymmetric interactions.

We performed the quantitative analysis of the static magnetic properties in two steps. Initially the CF parameters of Gd(III) or Yb(III) sites in complexes containing only a paramagnetic centre ($2N, 3N, 5N$ and $8N$) were determined. The number of CF parameters required depends on the symmetry...
VTVB measurements of $2_N$ and $3_N$ are very similar (Figures 5, S70 and S72). This suggests that the CF of Yb(III) in these two complexes is very similar, and similar to that observed for Gd(III) in $5_N$ and $8_N$. Therefore, CF parameters were extracted only from measurements on $2_N$. Thus, the CF parameters of $2_N$ were obtained by simultaneously fitting to Hamiltonian (1) its $\gamma T$ product, VTVB data and total multiplet splitting, determined by emission spectroscopy. As initial parameters for modelling, the CF parameters of Yb(III) were used.\textsuperscript{35} Using this model and allowing all nine CF parameters to vary, good agreement between the predicted and measured VTVB and susceptibility curves was obtained (Figures 5 and S70). The nine best-fit CF parameters are given in Tables S1 and S2 in Stevens and Wybourne notations, respectively. The associated eigen spectrum is shown in Figure S88 where it can be seen that the total CF splitting of $2_N$ and $3_N$ is of the order of 560 cm$^{-1}$. This set of parameters also reproduces the susceptibility and VTVB measurements of $3_N$, demonstrating that the CF of Yb(III) in these complexes does not dramatically depend on the size of the second Ln ion (Figures S70-S71).

In the case of $10_N$, the magnetic exchange interaction between the two Gd(III) centers can be treated by including in Hamiltonian (1) only isotropic exchange terms ($J_{\text{Gd-Gd}}$). Thus, by fixing the CF parameters of Gd(III) to the ones determined for $5_N$ and $8_N$, $J_{\text{Gd-Gd}}$ was determined to be -0.137 cm$^{-1}$ (in the -2J convention), by a simultaneous fit of the $\gamma T$ product and the VTVB data to Hamiltonian (1). The model reproduced the measurements well with an anti-ferromagnetic interaction between the two Gd(III) ions (Figures 5 and S80). The associated eigenspectrum of $10_N$ is shown in Figure S88 where it can be seen that the antiferromagnetic interactions in $10_N$ result in a group of sixty four closely packed states, spread over a total range of ~9 cm$^{-1}$. The antiferromagnetic ground state is a singlet separated from the first excited state by just 0.05 cm$^{-1}$. The determined best-fit value is lower than that previously reported ($J_{\text{iso}} = -0.194$) for this complex using a spin-only expression,\textsuperscript{80} where only magnetic susceptibility data (not VTVB data) were analyzed.

For $1_N$ and $4_N$ containing the orbitally degenerate Yb(III) ion, anisotropic exchange, in addition to isotropic exchange, should be included. However, such a model (Table 3) produced the same results as those obtained using only isotropic exchange (Figure 5), only anisotropic exchange, or both anisotropic and isotropic exchange (Figures S65-S67 and S73-S76). This is most likely due to the fact that the polycrystalline powder data used in the modelling are insufficient to probe the orientation sensitivity of the anisotropic exchange terms, as previously discussed.\textsuperscript{85} Small crystal size precludes orientation dependent single crystal magnetization and EPR measurements. Performing the modelling without including exchange terms results in poorer agreement with experiment, clearly demonstrating that magnetic exchange interactions are operating in $1_N$ and $4_N$ (Figures S65 and S69 for $1_N$ and S73 and S77 for $4_N$). This is observed in the temperature dependence of the $\gamma T$ product of $1_N$, which increases upon cooling from 12 to 2 K. Using only an isotropic exchange term in $1_N$ and $4_N$ yielded a ferromagnetic interaction in $1_N$ ($J_{\text{iso}} = 1.78 \times 10^2$ cm$^{-1}$) and an anti-ferromagnetic interaction in $4_N$ ($J_{\text{iso}} = -7.21 \times 10^3$ cm$^{-1}$). The associated eigenspectra of $1_N$ and $4_N$ are shown in Figure S88. In the case of $1_N$ the sixty four levels are grouped into four sets of sixteen, corresponding to the interaction of each of the four Kramers doublets of Yb(III) with the four Kramers doublets of Gd(III), spread over a range of ~700 cm$^{-1}$.

In the case of $4_N$ the sixty four levels are grouped in ten sets spread over a range of ~1100 cm$^{-1}$.

**CONCLUSIONS**

We have developed a synthetic strategy for the synthesis of pure heterodinuclear Ln cryptate complexes, of arbitrary composition. The LnLn*$ distribution obtained through this synthetic protocol is dependent on the counterion used. The presence of nitrate instead of triflate leads to scrambling of the Ln ions. This suggests that the Lewis basicity of the counter ion is crucial. The Brønsted basicity of the solvent also proved crucial in controlling the scrambling ratio, with pyridine offering the best control. Complexes $1_N$-$10_N$ are all obtained in the same crystal phase, with the complexes crystallizing in one of the enantiomorphous space groups $P4_212_1$ or $P4_212_2$. These chiral Ln complexes that display sizeable spin-orbit coupling interactions will be of particular interest for probing electric field effects on their magnetization via magnetoelectric coupling,\textsuperscript{91-94} which is relevant to the development of molecular spintronic devices.

The Ln-Ln distance, bridged by three phenoxide O-atoms, was found to be ~3.5 Å with GdGd having the largest distance at 3.5035(4) Å and LuLu possessing the smallest distance at 3.4395(3) Å. This results in relatively strong magnetic exchange coupling between the metals with respect to QIP protocols. For both $4_N$ and $10_N$ the lanthanide ions are coupled antiferromagnetically. On the contrary, $1_N$ shows ferromagnetic coupling between the two lanthanide ions. In future studies on single crystals, the exchange coupling between the isotropic Gd(III) ion and/or oblate and/or prolate Ln(III) ions will be investigated in detail.

**EXPERIMENTAL SECTION**

**Materials and Methods.** During the syntheses no attempts were made to exclude neither moisture nor oxygen. All solvents were purchased commercially and used as received. Tris(2-aminomethyl)amine (tren) and tetrabutylammonium nitrate were also obtained commercially and used as received. 2,6-diformyl-p-cresol was obtained following a literature procedure.\textsuperscript{95} For its synthesis glacial acetic acid, conc. sulfuric acid, paraformaldehyde, p-cresol and hexamethylene tetramine were obtained commercially and used as received. The Ln(OTf)$_3$:xH$_2$O salts were obtained following a literature procedure\textsuperscript{96} and their water content was checked using an EDTA titration with xylene orange as the indicator.

**Synthesis of 1-3H$_2$O.** To a pyridine (60 ml) solution of Gd(OTf)$_3$:9H$_2$O (500 mg; 0.65 mmol) YbL-4H$_2$O (200 mg; 0.22 mmol) is added. When a clear orange solution has formed, the solution is heated to boiling and refluxed for 3 hours. After being refluxed the solution is cooled to room temperature and then poured into diethyl ether (300 ml) which is vigorously stirred. This produces a fine orange precipitate which is isolated, washed twice with diethyl ether (2 x 100 ml) and then dried. The product is then extracted with dichloromethane (100 ml). The orange dichloromethane solution is filtered and evaporated to dryness. To the orange precipitate THF (25 ml) is added and the mixture is stirred overnight (in some cases all the precipitate dissolves at first, but overnight a pale yellow precipitate forms). The pale yellow is isolated and washed with THF (3 x 15 ml) and diethyl ether (2 x 10 ml). Yield: 217 mg (66 %). Analysis calculated for
Synthesis of $2-9$. The synthesis of 2 - 9 were performed analogously to 1. However, for 3, 4 and 7 five equivalents of Yb(OOTf)$_3$·9H$_2$O, Yb(OOTf)$_3$·9H$_2$O and Lu(OOTf)$_3$·9H$_2$O were used, respectively. In addition, 3 was refluxed for 5 hours while 4 and 7 were refluxed for 24 hours.

Synthesis of 3-2H$_2$O. LuL-4H$_2$O (200 mg; 0.22 mmol), Yb(OOTf)$_3$·9H$_2$O (850; 1.1 mmol), refluxed for 1 day. Yield: 46 mg (14%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$YbLu. Calcd.: C, 33.52; H, 3.28; N, 7.45; S, 6.39. Found: C, 33.44; H, 4.16; N, 7.13; S, 6.58. IR(ν=N): 1637 cm$^{-1}$ (Figure S30). MALDI-MS positive mode: 1320.15 m/z [LuYb(OOTf)$_3$]$^+$ (Figure S3).

Synthesis of Synt 5-3H$_2$O. LuL-4H$_2$O (200 mg; 0.22 mmol), Gd(OOTf)$_3$·9H$_2$O (500mg; 0.66 mmol), refluxed 3 hr. Yield: 179 mg (55%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$LuGd. Calcd.: C, 33.47; H, 3.41; N, 7.43; S, 6.38. Found: C, 33.51; H, 3.24; N, 7.20; S, 6.46. IR(ν=N): 1636 cm$^{-1}$ (Figure S31). MALDI-MS positive mode: 1319.15 m/z [LuYb(OOTf)$_3$]$^+$ (Figure S4).

Synthesis of 5-3H$_2$O. LuL-4H$_2$O (200 mg; 0.22 mmol), Yb(OOTf)$_3$·9H$_2$O (850; 1.1 mmol), refluxed for 1 day. Yield: 177 mg (53%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$Yb. Calcd.: C, 33.16; H, 3.38; N, 7.37; S, 6.32. Found: C, 33.66; H, 3.30; N, 7.25; S, 6.58. IR(ν=N): 1636 cm$^{-1}$ (Figure S31). MALDI-MS positive mode: 1319.15 m/z [LuYb(OOTf)$_3$]$^+$ (Figure S5).

Synthesis of 6-3H$_2$O. LuL-4H$_2$O (200 mg; 0.22 mmol), Yb(OOTf)$_3$·9H$_2$O (457 mg; 0.66 mmol), refluxed 3 hr. Yield: 141mg (45%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$LuY. Calcd.: C, 35.06; H, 3.57; N, 7.79; S, 6.68. Found: C, 35.37; H, 3.82; N, 7.58; S, 6.38. IR(ν=N): 1636 cm$^{-1}$ (Figure S33). MALDI-MS positive mode: 1235.14 m/z [LuYb(L)$_2$(OTf)$_3$]$^+$ (Figure S6). $^1$H NMR (500 MHz, CD$_2$CN) δ/ppm 8.31 (s, 3H), 8.30 (s, 3H), 7.48 (s, 3H), 7.47 (s, 3H), 3.79 (m, 6H), 3.68 (m, 6H), 3.31 (m, 6H), 2.86 (m, 6H), and 2.31 (s, 9H) (Figure 2). $^1$C NMR (125.74 MHz, CD$_2$CN) δ/ppm 172.6, 172.0, 159.5, 144.2, 143.8, 128.5, 124.34, 124.28, 62.0, 61.6, 61.03, 60.95, and 19.5 (Figure S5).

Synthesis of 7-2H$_2$O. LuL-4H$_2$O (200 mg; 0.22 mmol), Lu(OOTf)$_3$·9H$_2$O (852 mg; 1.1 mmol), refluxed for 1 day. Yield: 140 mg (43%). Analysis calculated for C$_{43}$H$_{40}$N$_2$O$_4$S$_2$Lu. Calcd.: C, 33.47; H, 3.28; N, 7.44; S, 6.38. Found: C, 33.42; H, 3.43; N, 7.18; S, 6.57. IR(ν=N): 1637 cm$^{-1}$ (Figure S34). MALDI-MS positive mode: 1321.19 m/z [Lu(L)$_2$(OTf)$_3$]$^+$ (Figure S7). $^1$H NMR (500 MHz, CD$_2$CN) δ/ppm 8.30 (s, 6H), 7.48 (s, 6H), 3.79 (m, 6H), 3.68 (m, 6H), 3.31 (m, 6H), 2.86 (m, 6H), and 2.31 (s, 9H) (Figure S51). $^1$C NMR (125.74 MHz, CD$_2$CN) δ/ppm 172.4, 159.5, 143.8, 128.6, 124.4, 62.0, 60.9, and 19.5 (Figure S52).

Synthesis of 8-3H$_2$O. YL-4H$_2$O (200 mg; 0.24 mmol), Gd(OOTf)$_3$·9H$_2$O (552 mg; 0.72 mmol), refluxed 3 hr. Yield: 192 mg (56%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$GdY. Calcd.: C, 35.49; H, 3.62; N, 7.88; S, 6.77. Found: C, 35.54; H, 3.91; N, 7.68; S, 6.83. IR(ν=N): 1636 cm$^{-1}$ (Figure S35). MALDI-MS positive mode: 1218.11 m/z [Yb(L)$_2$(OTf)$_3$]$^+$ (Figure S8).

Synthesis of 9-3H$_2$O. YL-4H$_2$O (200 mg; 0.24 mmol), Y(OOTf)$_3$·9H$_2$O (552 mg; 0.72 mmol), refluxed 3 hr. Yield: 192 (57%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$Y$_2$. Calcd.: C, 37.29; H, 3.80; N, 8.28; S, 7.11. Found: C, 37.22; H, 4.45; N, 7.98; S, 7.39. IR(ν=N): 1637 cm$^{-1}$ (Figure S36). MALDI-MS positive mode: 1149.10 m/z [Y(L)$_2$(OTf)$_3$]$^+$ (Figure S9). $^1$H NMR (500 MHz, CD$_2$CN) δ/ppm 8.31 (s, 6H), 7.47 (s, 6H), 3.80 (m, 6H), 3.70 (m, 6H), 3.32 (m, 6H), 2.86 (m, 6H), and 2.30 (s, 9H) (Figure S53). $^1$C NMR (125.74 MHz, CD$_2$CN) δ/ppm 172.1, 159.4, 144.3, 128.4, 124.3, 61.7, 61.1, and 19.5 (Figure S54).

Synthesis of 10-3H$_2$O. To a suspension of GdL* (210 mg; 0.28 mmol) in pyridine (60 ml) Gd(OOTf)$_3$·9H$_2$O (654 mg; 0.85 mmol) is added. The solution is heated to boiling and trecn (42 mg; 0.29 mmol) in pyridine (5 ml) is added dropwise. The red solution is then refluxed for 3 hours. After being cooled to room temperature the solution is poured into 300 ml vigorously stirred diethyl ether (300 ml) yielding an orange precipitate. This is isolated and washed twice with diethyl ether (100 ml) and dried. The product is extracted with dichloromethane (100 ml). The orange dichloromethane solution is then filtered and evaporated to dryness. To the orange precipitate is added 25 ml tetrahydrofuran and the suspension is stirred overnight forming a pale yellow precipitate. This is isolated and washed with 3x15 ml tetrahydrofuran and 2x10 ml diethyl ether. Yield: 143 mg (34%). Analysis calculated for C$_{42}$H$_{39}$N$_2$O$_4$S$_2$GdL. Calcd.: C, 33.87; H, 3.45; N, 7.52; S, 6.46. Found: C, 33.73; H, 3.12; N, 7.26; S, 6.60. IR(ν=N): 1632 cm$^{-1}$ (Figure S37). MALDI-MS positive mode: 1287.12 m/z [Gd(L)$_2$(OTf)$_3$]$^+$ (Figure S10).

Synthesis of 1$_x$ - 1$_{10}$. The nitrate analogs of 1 - 10 (1$_x$ - 1$_{10}$) were obtained through a recrystallization of 1 - 10.
Synthesis of 4µ-EtOH·2H2O. Bu4NNO3 (75 mg; 0.25 mmol), 4-3H2O (72 mg; 47 µmol). Yield: 39 mg (64 %). Analysis calculated for C6H16NO2: H 4.30; N 11.96. Found: C; 37.79; H; 4.29; N; 11.67. IR(v=ν(N)); 1636 cm⁻¹ (Figure S41). MALDI-MS positive mode: 1143.21 m/z [Yb4L(3NO3)3]+ (Figure S14).

Synthesis of 5µ-EtOH·3H2O. Bu4NNO3 (94 mg; 309 µmol), 5-3H2O (92 mg; 62 µmol). Yield: 45 mg (57 %). Analysis calculated for C6H16NO2: H 4.45; N 11.92. Found: C; 37.83; H; 4.13; N; 11.47. IR(v=ν(N)); 1637 cm⁻¹ (Figure S42). MALDI-MS positive mode: 1130.21 m/z [Lu4Gd(3NO3)3]+ (Figure S15).

Synthesis of 6µ-EtOH·3H2O. Bu4NNO3 (65 mg; 0.21 mmol) and 6-3H2O (60 mg; 42 µmol). Yield: 28 mg (54 %). Analysis calculated for C6H16NO2: H 4.74; N; 12.50. Found: C; 39.42; H; 4.49; N; 12.15. IR(v=ν(N)); 1635 cm⁻¹ (Figure S43). MALDI-MS positive mode: 1162.26 m/z [Lu4YL(3NO3)3]+ (Figure S16). 1H NMR (500 MHz, D2O) δ/ppm 8.39 (s, 6H), 7.56 (s, 3H), 7.54 (s, 3H), 3.38 (m, 6H), 3.36 (m, 6H), 3.34 (m, 6H, 2.93 (m, 6H), 2.32 (s, 9H) (Figure S60).

Synthesis of 7µ-EtOH·3H2O·2H2O. Bu4NNO3 (100 mg; 382 µmol) and 8-3H2O (100 mg; 66 µmol). Yield: 59 mg (67 %). Analysis calculated for C6H16NO2: H 4.88; N; 11.80. Found: C; 39.63; H; 4.09; N; 11.33. IR(v=ν(N)); 1637 cm⁻¹ (Figure S44). MALDI-MS positive mode: 1147.22 m/z [Lu4Gd(3NO3)3]+ (Figure S17). 1H NMR (500 MHz, D2O) δ/ppm 8.39 (s, 6H), 7.55 (s, 6H), 3.87 (m, 6H), 3.76 (m, 6H), 3.35 (m, 6H), 2.91 (m, 6H), and 2.32 (s, 9H) (Figure S61).

Synthesis of 8µ-EtOH·3H2O·2H2O. Bu4NNO3 (88 mg; 0.29 mmol) and 8-3H2O (81 mg; 57 µmol). Yield: 47 mg (68 %). Analysis calculated for C6H16NO2: H 4.88; N; 12.77. Found: C; 40.66; H; 4.41; N; 12.41. IR(v=ν(N)); 1636 cm⁻¹ (Figure S45). MALDI-MS positive mode: 1044.17 m/z [Yb4Gd(3NO3)3]+ (Figure S18).

Synthesis of 9µ-EtOH·3H2O·4H2O. Bu4NNO3 (114 mg; 374 µmol) and 10-3H2O (150 mg; 74 µmol). Yield: 55.4 mg (66 %). Analysis calculated for C6H16NO2: H 5.05; N; 13.54. Found: C; 43.79; H; 4.84; N; 12.87. IR(v=ν(N)); 1636 cm⁻¹ (Figure S46). MALDI-MS positive mode: 975.15 m/z [Yb3(L(3NO3)2)]+ (Figure S19). 1H NMR (500 MHz, D2O) δ/ppm 8.40 (s, 6H), 7.55 (s, 6H), 3.89 (m, 6H), 3.78 (m, 6H), 3.35 (m, 6H), 2.94 (m, 6H), and 2.32 (s, 9H) (Figure S62).

Synthesis of 10µ-EtOH·3H2O·4H2O. Bu4NNO3 (81 mg; 0.27 mmol) and 10-3H2O (80 mg; 54 µmol). Yield: 33 mg (48 %). Analysis calculated for C6H16NO2: H 4.51; N; 12.09. Found: C; 38.86; H; 3.94; N; 11.91. IR(v=ν(N)); 1634 cm⁻¹ (Figure S47). MALDI-MS positive mode: 1113.21 m/z [Gd4(3NO3)3]+ (Figure S20).

Synthesis of YL·4H2O and LuL·4H2O. The complexes YL·4H2O and LuL·4H2O were synthesised using a similar procedure to one employed for YbL·4H2O.

Synthesis of YL·4H2O. DFMP (2.5 g; 15 mmol) and Y(OTf)3·9H2O (3.55 g; 5 mmol) are dissolved in hot acetonitrile (300 ml). To this a solution of tris(2-aminoethyl)amine (tren, 1.50 g; 10 mmol) in methanol (25 ml) is added dropwise during 30 min. The resulting orange solution is boiled for 10 min and then triethylamine (2.5 ml; 18 mmol) is added to the boiling solution, which is quickly removed from the heat. During a few hours a yellow precipitate forms, which is isolated and washed with ether and diethyl ether. Yield: 2.79 g (66 %). Anal. Calcd for C6H16NO2: Y; 56.11; H; 6.40; N; 13.42. Found: C; 55.81; H; 5.89; N; 13.59. IR(v=ν(N)); 1619 and 1599 cm⁻¹ (Figure S48). MALDI-MS positive mode 763.28 m/z [YL]+ (Figure S26).

Synthesis of GdL·4H2O. The synthesis of LuL·4H2O was performed analogously to YL·4H2O. DFMP (1.88 g; 11 mmol), Lu(OTf)3·9H2O (3.00 g; 3.8 mmol), tren (1.13 g; 7.7 mmol) and triethylamine (1.6 ml; 12 mmol). Yield: 2.59 (73 %). Anal. Calcd for C6H16NO2: Lu; C; 50.87; H; 5.80; N; 12.17. Found: C; 50.87; H; 5.36; N; 11.87. IR(v=ν(N)); 1618 and 1600 cm⁻¹ (Figure S49). MALDI-MS positive mode 849.31 m/z (Figure S27).

Synthesis of GdL·4H2O. GdL was synthesized according to literature.83 YbL·4H2O was synthesised according to a literature procedure.83 2ν and 3ν are dilute samples of 2ν and 3ν in a host of 9ν. The powders were prepared similarly to the synthesis of 9ν, by employing a 3.97 molar ratio of (2ν, 3ν) and 9ν.

Mass Spectrometry. MALDI mass spectrometry was performed on a Bruker Solarix XR 7T ESI/MALDI FT-ICR MS at The Department of Chemistry University of Copenhagen.

NMR Spectroscopy. 1H and 13C NMR spectra were recorded on a Bruker 500 MHz instrument with a cryoprobe. Calibration of the 1H and 13C NMR was done against the deuterated solvent signal.

Infrared Spectroscopy. IR spectra were recorded on an Agilent Technologies Cary 630 FTIR.

Elemental Analyses. CHNS elemental analyses were obtained using a FLASHEA 1112 instrument at The Microanalytical Laboratory at The Department of Chemistry University of Copenhagen.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) data were obtained using a BRUKER D8 ADVANCE powder diffractometer equipped with a Mo Kα high-brilliance X’Pert S3 radiation source (λ = 0.71073 Å), a PHOTON 100 CMOS detector and an Oxford Cryosystems cooling system. The APEX2 software package was used to control the setup. The applications SAINT85 and SADABS86 were used for the data reduction and absorption corrections of the data, respectively. Structures were solved using SHELXT87 intrinsic phasing and refined using SHELXL88,89 with least-squares. To visualize the data during data refinement the OLEX2 program package was used.100,101 All atoms except hydrogen were refined anisotropically. Hydrogen atoms were also placed at calculated positions, due to their natural low electron count. For the heterodinuclear complexes the two Ln ions are disordered over two positions. To account for this the SHELX compatible constraints EADP and EXYZ were used on the Ln ions, and the occupancy of each Ln ion was set to 0.5 in each coordination site. The non-coordinating nitrate counter ion is displaced over two positions. To account for this the “Split SAME” command was used in OLEX2 and each fragment was given an occupancy of 0.5. Additionally, the SHELX compatible constraint EADP was used on the atoms in each nitrate fragment.

Magnetochemistry. Direct current magnetic susceptibility measurements were performed on polycrystalline samples of
1,5,8,9, and 10, fixed in n-hexadecane using a Quantum-Design MPMS-XL SQUID magnetometer. \(\gamma T\) data were corrected for diamagnetism of the sample and n-hexadecane following Pascal’s constants.

**Electron paramagnetic resonance.** The spectra were recorded on a Bruker Elexysy E500 instrument.

**Luminescence spectroscopy.** The spectra were recorded on a Horiba-Jobin Yvon Fluorolog fluorimeter equipped with an InGaAs nearinfrared detector.

**ASSOCIATED CONTENT**

Supporting Information contains experimental details and characterisation and magnetisation data. CCDC 2059654 (10), 2059655 (5\(\alpha\)), 2059656 (7\(\alpha\), 2059657 (3\(\beta\)), 2059658 (6\(\alpha\)), 2059659 (1\(\beta\)), 2059660 (4\(\beta\)), 2059661 (2\(\alpha\)), 2059662 (8\(\alpha\), 2059663 (9\(\alpha\), 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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**Author Contributions**
The manuscript was written through contributions of all authors.

**Funding Sources**
VILLUM FONDEN.

**ACKNOWLEDGMENT**
S.P. thanks the VILLUM FONDEN for research grant 13376.

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Supporting information
for
Design of Pure Heterodinuclear Lanthanoid Cryptate Complexes

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**Figure S25.** MALDI positive mode mass spectrum of a solution of 4 and 100 eq. of Y(OTf)$_3$·9H$_2$O stirred for one week in MeOH. Color code: Signal (black), predicted isotope pattern for [Yb$_2$L(OTf)$_2$]$^+$ (green), predicted isotope pattern for [Y$_2$L(OTf)$_2$]$^+$ (red) and predicted isotope pattern for [YbYL(OTf)$_2$]$^+$ (orange).
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Magnetic properties and modelling of $1_{N}$-$5_{N}$, $8_{N}$ and $10_{N}$

**Figure S65.** The temperature dependence of the $\chi T$ product of $1_{N}$ (scatter) with the best fit obtained with a model including isotropic exchange and anisotropic exchange (orange), only isotropic exchange (red), only anisotropic exchange (green) and no exchange (black). The fits are based on the CF parameters in Table S1 and exchange couplings in Table S3.

**Figure S66.** VTVB measurements of $1_{N}$ (scatter) including the best fit (lines) obtained with a model including isotropic exchange and anisotropic exchange. The fit is based on the CF parameters in Table S1 and exchange couplings in Table S3.
Figure S67. VTVB measurements of $1_N$ (scatter) including the best fit (lines) obtained with a model including isotropic exchange. The fit is based on the CF parameters in Table S1 and exchange couplings in Table S3.

Figure S68. VTVB measurements of $1_N$ (scatter) including the best fit (lines) obtained with a model including anisotropic exchange. The fit is based on the CF parameters in Table S1 and exchange couplings in Table S3.
Figure S69. VTVB measurements of $\text{1}_N$ (scatter) including the best fit (lines) obtained with a model with no exchange. The fit is based on the CF parameters in Table S1.

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Figure S72. VTVB measurements of $3_N$ (scatter) including the best fit (lines) obtained with the model described in the main text. The CF parameters can be found in Table S1.
Figure S73. Temperature dependence of the $\chi T$ product of 4$_N$ (scatter) with the best fit obtained with a model including isotropic exchange and anisotropic exchange (orange), only isotropic exchange (red), only anisotropic exchange (green) and no exchange (black). The fits are based on the CF parameters in Table S1 and exchange couplings in Table S3.

Figure S74. VT VB measurements of 4$_N$ (scatter) including the best fit (lines) obtained with a model including isotropic exchange and anisotropic exhcange. The fit is based on the CF parameters in Table S1 and exchange couplings in Table S3.
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**Figure S76.** VTVB measurements of $4_N$ (scatter) including the best fit (lines) obtained with a model including anisotropic exchange. The fit is based on the CF parameters in Table S1 and exchange couplings in Table S3.
Figure S77. VTVB measurements of $4_N$ (scatter) including the best fit (lines) obtained with a model including no exchange. The fit is based on the CF parameters in Table S1.

Figure S78. VTVB measurements of $5_N$ (scatter) including the best fit (lines) obtained with the model described in the main text. The CF parameters can be found in Table S1.
Figure S79. VTVB measurements of $8_N$ (scatter) including the best fit (lines) obtained with the model described in the main text. The CF parameters can be found in Table S1.

Figure S80. VTVB measurements of $10_N$ (scatter) including the best fit (lines) obtained with the model described in the main text.
Electron paramagnetic resonance

Figure S81. X-band cw EPR spectrum of $\text{5}_N$ (black) including a simulation (red) based on the parameters in Table S1. The spectrum was recorded at 300 K. In the simulation linewidth broadening (40 G) and $D$ strain were used.

Figure S82. X-band cw EPR spectrum of $\text{8}_N$ (black) including a simulation (red) based on the parameters in Table S1. The spectrum was recorded at 300 K. In the simulation linewidth broadening (40 G) and $D$ strain were used.
Figure S83. X-band cw EPR spectrum of $3_N$ recorded at 19 K.

Figure S84. X-band cw EPR spectrum of $4_N$ recorded at 18 K.
Luminescence

**Figure S85.** Emission spectra at 300 K of $9_N$ (black), $2_N'$ (red) and $3_N'$ (blue). For the spectra an excitation wavelength of 380 nm was used, this was based on the excitation spectrum of $9_N$, Figure S86.

**Figure S86.** Excitation spectrum of $9_N$ measured at 300 K with emission detected at 500 nm. The detection of the emission was chosen to where the ligand emits the most, Figure S87.
Figure S87. Emission spectrum of $9_N$ measured at 300 K with excitation at 290 nm.
**Energy level splitting**

![Energy level splitting diagram](image)

**Figure S88.** Energy level splitting in a) $5_N$ and $8_N$, b) $2_N$ and $3_N$, c) $10_N$, d) $1_N$ and e) $4_N$. 
Modelling parameters

**Table S1.** Best fit CF parameters (cm\(^{-1}\)) in Stevens formalism

| Parameters | \(2_N\)  | \(3_N\)  | \(5_N\)  | \(8_N\)  |
|------------|----------|----------|----------|----------|
| \(B_2^0\) | -7.10    | -7.10    | -1.84 \(\cdot 10^{-2}\) | -1.84 \(\cdot 10^{-2}\) |
| \(B_4^0\) | 4.78 \(\cdot 10^{-2}\) | 4.78 \(\cdot 10^{-2}\) | 1.95 \(\cdot 10^{-4}\) | 1.95 \(\cdot 10^{-4}\) |
| \(B_4^{+3}\) | 1.206    | 1.206    |          |          |
| \(B_4^{-3}\) | 1.49 \(\cdot 10^{-5}\) | 1.49 \(\cdot 10^{-5}\) |          |          |
| \(B_6^{-6}\) | 0.101    | 0.101    |          |          |
| \(B_6^{-3}\) | 0.699    | 0.699    |          |          |
| \(B_6^0\) | -1.22 \(\cdot 10^{-2}\) | -1.22 \(\cdot 10^{-2}\) | -6.67 \(\cdot 10^{-6}\) | -6.67 \(\cdot 10^{-6}\) |
| \(B_6^{+3}\) | 0.239    | 0.239    |          |          |
| \(B_6^{+6}\) | 3.12 \(\cdot 10^{-2}\) | 3.12 \(\cdot 10^{-2}\) |          |          |

**Table S2.** Best fit CF parameters (cm\(^{-1}\)) in Wybourne formalism

| Parameters | \(2_N\)          | \(3_N\) |
|------------|------------------|---------|
| \(B_{20}\) | -4.47 \(\cdot 10^{2}\) | -4.47 \(\cdot 10^{2}\) |
| \(B_{40}\) | -2.21 \(\cdot 10^{2}\) | -2.21 \(\cdot 10^{2}\) |
| \(B_{43}\) | 2.35 \(\cdot 10^{2}\) + i2.91 \(\cdot 10^{3}\) | 2.35 \(\cdot 10^{2}\) + i2.91 \(\cdot 10^{3}\) |
| \(B_{60}\) | -1.32 \(\cdot 10^{3}\) | -1.32 \(\cdot 10^{3}\) |
| \(B_{63}\) | -1.26 \(\cdot 10^{3}\) – i3.69 \(\cdot 10^{3}\) | -1.26 \(\cdot 10^{3}\) – i3.69 \(\cdot 10^{3}\) |
| \(B_{66}\) | 2.22 \(\cdot 10^{2}\) + i7.18 \(\cdot 10^{2}\) | 2.22 \(\cdot 10^{2}\) + i7.18 \(\cdot 10^{2}\) |
**Table S3.** Exchange coupling parameters (cm\(^{-1}\)) in \(1_N, 4_N\) and \(10_N\) modelled with isotropic (\(J_{iso}\)) and anisotropic (\(D_{ex}\)) exchange, only isotropic exchange (\(J_{iso}\)) or only anisotropic exchange (\(D_{ex}\)).

| Parameters \(J_{iso}, D_{ex}\) | \(1_N\)          | \(4_N\)          | \(10_N\)         |
|---------------------------------|-------------------|-------------------|-------------------|
| \(J_{iso}\)                    | 1.78 \(\cdot\) 10\(^{-2}\) | -7.21 \(\cdot\) 10\(^{-3}\) | -0.137            |
| \(D_{ex}\)                     | -2.20 \(\cdot\) 10\(^{-2}\) | 7.38 \(\cdot\) 10\(^{-3}\) | -                 |
|                  | 1<sub>N</sub> | 2<sub>N</sub> | 3<sub>N</sub> | 4<sub>N</sub> | 5<sub>N</sub> |
|------------------|--------------|--------------|--------------|--------------|--------------|
| **Formula**      | C<sub>39</sub>H<sub>48</sub>GdN<sub>11</sub>O<sub>13.5</sub>Yb | C<sub>39</sub>H<sub>48</sub>N<sub>11</sub>O<sub>13.5</sub>Yb | C<sub>39</sub>H<sub>48</sub>LuN<sub>11</sub>O<sub>13.5</sub>Yb | C<sub>39</sub>H<sub>48</sub>N<sub>11</sub>O<sub>13.5</sub>Yb<sub>2</sub> | C<sub>39</sub>H<sub>48</sub>GdLuN<sub>11</sub>O<sub>13.5</sub>Yb |
| **Formula weight g/mol** | 1217.17 | 1148.83 | 1234.89 | 1232.96 | 1219.10 |
| **Temperature/K** | 100 | 100 | 100 | 100 | 100 |
| **Crystal system** | tetragonal | tetragonal | tetragonal | tetragonal | tetragonal |
| **Space group** | P<sub>4</sub>2<sub>1</sub> | P<sub>4</sub>2<sub>1</sub> | P<sub>4</sub>2<sub>1</sub> | P<sub>4</sub>2<sub>1</sub> | P<sub>4</sub>2<sub>1</sub> |
| **a/Å** | 17.6212(3) | 17.5997(5) | 17.5896(7) | 17.5867(5) | 17.6236(4) |
| **b/Å** | 17.6212(3) | 17.5997(5) | 17.5896(7) | 17.5867(5) | 17.6236(4) |
| **c/Å** | 29.1165(10) | 28.9790(12) | 28.9543(19) | 28.9660(13) | 29.0620(11) |
| **α/°** | 90 | 90 | 90 | 90 | 90 |
| **β/°** | 90 | 90 | 90 | 90 | 90 |
| **γ/°** | 90 | 90 | 90 | 90 | 90 |
| **V/Å<sup>3</sup>** | 9040.9(4) | 8976.2(6) | 8958.3(9) | 8959.0(6) | 9026.4(5) |
| **Z** | 8 | 8 | 8 | 8 | 8 |
| **ρ<sub>calc</sub> g/cm<sup>3</sup>** | 1.788 | 1.700 | 1.831 | 1.828 | 1.794 |
| **μ/mm<sup>-1</sup>** | 3.587 | 3.434 | 4.343 | 4.227 | 3.708 |
| **F(000)** | 4808.0 | 4608.0 | 4864.0 | 4856.0 | 4816.0 |
| **Crystal size/mm<sup>3</sup>** | 0.414 × 0.067 × 0.062 | 0.282 × 0.141 × 0.062 | 0.478 × 0.08 × 0.068 | 0.288 × 0.075 × 0.065 | 0.284 × 0.14 × 0.086 |
| **λ (MoKα)** | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **2Θ range for data collection/°** | 3.628 to 50.698 | 3.64 to 50.05 | 3.64 to 54.96 | 3.64 to 55.754 | 3.556 to 55.748 |
| **Reflections collected** | 70736 | 69411 | 115698 | 155594 | 126527 |
| **Independent reflections** | 8260 [R<sub>int</sub> = 0.0469, R<sub>sigma</sub> = 0.0248] | 7921 [R<sub>int</sub> = 0.0503, R<sub>sigma</sub> = 0.0277] | 10263 [R<sub>int</sub> = 0.0507, R<sub>sigma</sub> = 0.0256] | 10689 [R<sub>int</sub> = 0.0642, R<sub>sigma</sub> = 0.0273] | 10768 [R<sub>int</sub> = 0.0538, R<sub>sigma</sub> = 0.0252] |
| **Data/restraints/parameters** | 8260/24/601 | 7921/6/604 | 10263/6/613 | 10689/6/613 | 10768/6/604 |
| **Goodness-of-fit on F<sup>2</sup>** | 1.079 | 1.099 | 1.136 | 1.135 | 1.091 |
| **R<sub>1</sub>, wR<sub>2</sub> [I>2σ (I)]** | 0.0332, 0.0893 | 0.0325, 0.0922 | 0.0313, 0.0772 | 0.0313, 0.0799 | 0.0300, 0.0836 |
| **R<sub>1</sub>, wR<sub>2</sub> (all data)** | 0.0365, 0.0927 | 0.0363, 0.0961 | 0.0368, 0.0814 | 0.0394, 0.0849 | 0.0358, 0.0909 |
| **Residual electron density / e Å<sup>-3</sup>** | 3.33/-1.23 | 2.13/-0.93 | 2.38/-1.23 | 2.13/-1.10 | 2.67/-1.00 |
| **Flack parameter** | -0.009(4) | -0.013(3) | -0.014(3) | -0.023(4) | -0.012(4) |
|                      | 6<sub>N</sub> | 7<sub>N</sub> | 8<sub>N</sub> | 9<sub>N</sub> | 10<sub>N</sub> |
|----------------------|--------------|--------------|--------------|--------------|--------------|
| **Formula**          | C<sub>39</sub>H<sub>48</sub>Lu<sub>2</sub>N<sub>11</sub>O<sub>13.5</sub> | C<sub>39</sub>H<sub>48</sub>Lu<sub>2</sub>N<sub>11</sub>O<sub>13.5</sub> | C<sub>39</sub>H<sub>48</sub>Gd<sub>2</sub>N<sub>11</sub>O<sub>13.5</sub> | C<sub>39</sub>H<sub>48</sub>N<sub>11</sub>O<sub>13.5</sub> | C<sub>39</sub>H<sub>48</sub>Gd<sub>2</sub>N<sub>11</sub>O<sub>13.5</sub> |
| **Formula weight g/mol** | 1150.76     | 1236.82     | 1133.04     | 1064.70     | 1201.38     |
| **Temperature/K**    | 100         | 100         | 100         | 100         | 100         |
| **Crystal system**    | tetragonal  | tetragonal  | tetragonal  | tetragonal  | tetragonal  |
| **Space group**       | P4<sub>3</sub>2<sub>1</sub>2<sub>1</sub> | P4<sub>3</sub>2<sub>1</sub>2<sub>1</sub> | P4<sub>3</sub>2<sub>1</sub>2<sub>1</sub> | P4<sub>3</sub>2<sub>1</sub>2<sub>1</sub> | P4<sub>3</sub>2<sub>1</sub>2<sub>1</sub> |
| **a/Å**               | 17.5884(5)  | 17.5856(5)  | 17.6312(4)  | 17.6029(6)  | 17.6388(4)  |
| **b/Å**               | 17.5884(5)  | 17.5856(5)  | 17.6312(4)  | 17.6029(6)  | 17.6388(4)  |
| **c/Å**               | 28.9743(13) | 28.9382(12) | 29.2044(12) | 29.0488(15) | 29.2421(10) |
| **α/°**               | 90          | 90          | 90          | 90          | 90          |
| **β/°**               | 90          | 90          | 90          | 90          | 90          |
| **γ/°**               | 90          | 90          | 90          | 90          | 90          |
| **V/Å<sup>3</sup>**   | 8963.3(6)   | 8949.2(6)   | 9078.5(6)   | 9001.1(8)   | 9098.0(5)   |
| **Z**                 | 8           | 8           | 8           | 8           | 8           |
| **ρ_<sub>calc</sub> g/cm<sup>3</sup>** | 1.706       | 1.836       | 1.658       | 1.571       | 1.754       |
| **μ/mm<sup>-1</sup>** | 3.555       | 4.464       | 2.796       | 2.643       | 2.966       |
| **F(000)**            | 4616.0      | 4872.0      | 4560.0      | 4360.0      | 4760.0      |
| **Crystal size/mm<sup>3</sup>** | 0.264 × 0.09 × 0.06 | 0.302 × 0.119 × 0.113 | 0.9 × 0.12 × 0.104 | 0.36 × 0.124 × 0.114 | 0.262 × 0.102 × 0.06 |
| **λ (MoKα)**          | 0.71073 Å   | 0.71073 Å   | 0.71073 Å   | 0.71073 Å   | 0.71073 Å   |
| **2θ range for data collection/°** | 3.274 to 54.96 | 3.646 to 52.742 | 3.266 to 54.968 | 3.636 to 50.054 | 3.618 to 55.746 |
| **Reflections collected** | 118535     | 106057     | 118547     | 126951     | 153214     |
| **Independent reflections** | 10271 [R<sub>int</sub> = 0.0595, R<sub>sigma</sub> = 0.0280] | 9133 [R<sub>int</sub> = 0.0367, R<sub>sigma</sub> = 0.0195] | 10417 [R<sub>int</sub> = 0.0524, R<sub>sigma</sub> = 0.0287] | 7957 [R<sub>int</sub> = 0.0932, R<sub>sigma</sub> = 0.0419] | 10851 [R<sub>int</sub> = 0.0568, R<sub>sigma</sub> = 0.0249] |
| **Data/restraints/parameters** | 10271/0/601 | 9133/6/613 | 10417/6/604 | 7957/6/613 | 10851/6/608 |
| **Goodness-of-fit on F<sup>2</sup>** | 1.133       | 1.076       | 1.108       | 1.058       | 1.073       |
| **R<sub>1</sub>, wR<sub>2</sub> [I>2σ (I)]** | 0.0353, 0.1047 | 0.0246, 0.0670 | 0.0410, 0.1221 | 0.0487, 0.1325 | 0.0316, 0.0858 |
| **R<sub>1</sub>, wR<sub>2</sub> (all data)** | 0.0414, 0.1135 | 0.0268, 0.0688 | 0.0506, 0.1349 | 0.0621, 0.1428 | 0.0369, 0.0895 |
| **Residual electron density / e Å<sup>-3</sup>** | 3.13/-1.11 | 2.04/-1.06 | 2.40/-1.39 | 2.05/-0.84 | 2.05/-0.99 |
| **Flack parameter**   | -0.017(3)   | -0.013(3)   | -0.016(3)   | -0.033(3)   | -0.018(4)   |
Table S6. Ln-Ln distance (esd) in \(1_N \text{ - } 10_N\)

| Compound | Ln-Ln distance / Å |
|----------|-------------------|
| \(1_N\)  | 3.4782(4)         |
| \(2_N\)  | 3.4567(4)         |
| \(3_N\)  | 3.4424(4)         |
| \(4_N\)  | 3.4438(4)         |
| \(5_N\)  | 3.4752(3)         |
| \(6_N\)  | 3.4564(4)         |
| \(7_N\)  | 3.4395(3)         |
| \(8_N\)  | 3.4912(4)         |
| \(9_N\)  | 3.4669(7)         |
| \(10_N\) | 3.5035(4)         |
