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Article

Luminescent Dinuclear Lanthanide Complexes of 5-Me-HXTA

Louise S. Natrajan,[†] Phillipa L. Timmins,[‡] Matthew Lunn,[§] and Sarah L. Heath*,[†]

Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, U.K., Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K., and Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, U.K.

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The synthesis and characterization of a series of anionic homobimetallic lanthanide complexes of the septadentate chelate 5-Me-HXTA (*N*,*N*-(2 hydroxy-5-methyl-1,3-xylylene)bis(*N*-(carboxymethyl)glycine) is described (Ln = Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb). Single X-ray crystallography confirms that the complexes exist as discrete dimeric pairs in the solid state. Proton NMR, diffusion-ordered spectroscopy, and luminescence solution studies suggest that the binuclear stoichiometry is retained in aqueous solution over a range of analytically useful concentrations. The phenolic chromophores effectively sensitize the visible and near-infrared lanthanide-centered emission in the terbium, neodymium, and ytterbium derivatives, giving rise to particularly long-lived green and near-infrared emission. The terbium complex displays a high quantum yield of around 50% in aqueous solution with a low detection limit of 1×10^{-12} M, rendering this compound a potential candidate for time-resolved applications.

1. Introduction

The synthesis of lanthanide chelates that are able to act as luminescent labels for biomedical applications or as dopants in electroluminescent devices has attracted a huge amount of interest in recent years.[1,2] The physical attributes of the trivalent f elements such as spectrally discrete emission bands, a large Stokes' shift, and long-lived luminescence (ranging from millisecond to nanosecond order) lend themselves particularly well to analytical time-resolved bioassay, imaging, and sensor applications where time-gating techniques can be applied to eliminate competitive autofluorescent signals (short nanosecond fluorescence) from surrounding biological molecules.[3] Current interest has further developed in the photophysical properties of lanthanide complexes that are emissive in the near-infrared region (NIR),[4] principally $Yb^{3+}$and Nd^{3+},[5−7] where biological tissue is relatively transparent. The employment of longer wavelength light additionally offers a greater tissue penetration and optical sensitivity and further circumvents the problem of coincidental excitation of biological media. However, since effective relaxation of the Laporte selection rule is

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* To whom correspondence should be addressed. E-mail: sarah.l.heath@man.ac.uk. Fax: 0161 25 4598. Tel: 0161 275 4696.

[†] University of Manchester.

[‡] University of York, Heslington.

[§] University of Sheffield.

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generally disfavored,[8] lanthanide ions are commonly indirectly excited by an aromatic chromophore or "antenna" possessing a reasonably large molar absorption cross section. Lanthanide ions that emit in the visible region, particularly Eu^{3+} and Tb^{3+}, possess a large energy gap between the emissive donor and acceptor levels and are routinely sensitized by UV-absorbing chromophores containing high-energy triplet excited states.[9,10] In contrast, NIR-emitting lanthanides have a comparatively small energy gap between these two states, which markedly extends the available absorption envelope into the visible region and consequent range of sensitizing chromophores that can be employed.[11] Furthermore, for ytterbium(III) complexes, the mechanism of sensitized emission has been shown to vary depending on the nature of the aromatic unit; either the ligand triplet or a ligand-to-metal charge-transfer (LMCT) state is capable of mediating the energy transfer process.[12]

Since vibronic overlap of O−H, N−H, and, to a lesser extent C−H oscillators, with the lanthanide emitting states detrimentally quenches the metal-based emission,[9] successful probes have profited from encapsulation of the cations within a ligand framework possessing a high denticity. Such a ligand design serves to limit the approach of closely diffusing solvent molecules and concurrently augments the quantum yield of luminescence. Of the suitable ligands employed, acyclic and macrocyclic poly(amino)carboxylates, cryptands, and podands have been extensively studied, principally due to the high kinetic and thermodynamic stability of their corresponding lanthanide chelates.[13] However, equivalent complexes of choromophore-bearing acyclic alternatives are often less stable, owing to, in part, an increased susceptibility to hydrolysis in aqueous solution.[14] In this regard, the majority of highly emissive complexes are monomeric in nature.[15] Recently, there has been a growing interest in the design and synthesis of binuclear complexes and other higher nuclearity arrays for the development of new photonic devices[16] and dual luminescent probes.[17] However, with a few notable exceptions,[18,19] the majority of bimetallic complexes prepared to date have been kinetically assembled helicates or macrocyclic compounds where the two metal centers are well separated.[20]

In order to synthesize luminescent dinuclear complexes where the two metal centers are held in close proximity to one another and the complexes are hydrolytically stable in aqueous solution, we have investigated the coordination chemistry of 5-Me-HXTA (5-Me-HXTA = *N*,*N*-(2 hydroxy-5-methyl-1,3-xylylene)bis (*N*-(carboxymethyl)glycine)[21] with the lanthanide elements (eq 1). Prior to this work, Latva et al. reported the spectroscopic behavior of Eu(III) complexes with a closely related ligand, 2,6-bis[*N*,*N*-bis(carboxymethy-

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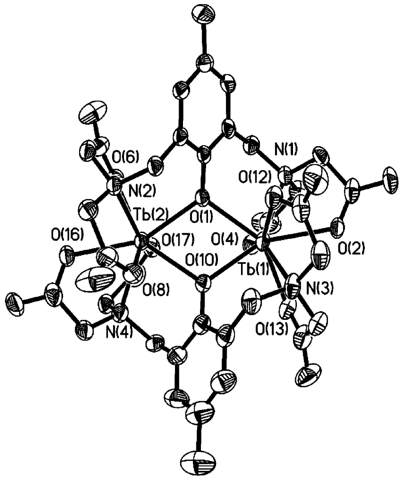
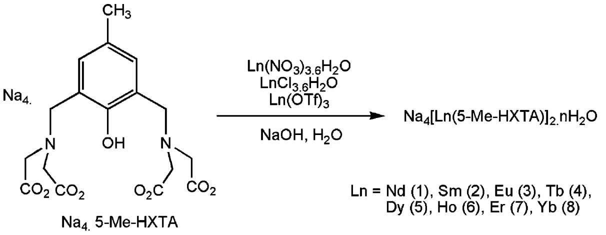


Figure 1. Thermal ellipsoid drawing of **4** $Na_4 \cdot [Tb(5\text{-Me-HXTA})]_2 \cdot 15H_2O$ (50% probability); H atoms, Na counterions, and lattice solvent molecules omitted for clarity.

l)aminomethyl]-4-benzoylphenol;[22] the terbium(III) analogue and related complexes have been employed as novel labeling agents in electrochemically generated time-resolved fluoroimmunoassay.[23] However, while they proposed that the complexes were dinuclear in nature, the complexes were not isolated and no characterization was reported. Here we report the crystal structures and solution behavior of a series M_2L_2 phenoxy-bridged dinuclear lanthanide complexes and the visible and near-infrared luminescent properties of the Tb(III), Nd(III), and Yb(III) complexes in aqueous solution. Dinuclear species such as these, where the metal centers are in such close proximity, are an attractive prospect as they offer the possibility of investigating the effect of the intermetallic separation on the spectroscopic and physical properties of the complex.[24]

2. Results and Discussion

2.1. Synthesis of 5-Me-HXTA Lanthanide Derivatives. Treatment of $Ln(NO_3)_3 \cdot 6H_2O$, $LnCl_3 \cdot 6H_2O$, or $Ln(OTf)_3$ (OTf = trifluoromethanesulfonate) with $Na_3 \cdot$5-Me-HXTA or $Na_4 \cdot$5-Me-HXTA in aqueous solution in a 1:1 ratio yields a series of complexes which, according to combustion analysis, correspond to the formula $Na_4 \cdot [Ln(5\text{-Me-HXTA})]_2 \cdot nH_2O$; Ln = Nd (**1**), Sm (**2**), Eu (**3**), Tb (**4**), Dy (**5**), Ho (**6**), Er (**7**), and Yb (**8**), $n = 10-18$ (eq 1). X-ray quality crystals of all the complexes except **1** were obtained after several weeks from vapor diffusion from H_2O/EtOH or H_2O/MeOH/EtOH/Et_2O (**7** and **8**). A crystallographic investigation of these complexes revealed the structures to be dimeric, in which the two lanthanide ions are bridged by the phenolate head groups of the ligands. Notably, the 2:2 dinuclear complexes are the only isolable products over a large pH range of 4 to 12; no hydrolysis products are identified in the reaction mixtures.



(1)

In the terbium complex **4** (Figure 1), each terbium ion displays a distorted-square antiprismatic coordination geometry with the eight coordination sites comprised of two carboxylate oxygens from each of the ligands (Tb(1) = O(2), O(4), O(12), and O(13) and Tb(2) = O(6), O(8), O(16), and O(17)), one nitrogen from each ligand (Tb(1) = N(1) and N(3) and Tb(2) = N(2) and N(4)), and the phenolate oxygens of each ligand (O(1) and O(10)), which bridge the two metals at an angle of approximately 109°; Tb(1)−O(1)−Tb(2) = 109.7° and Tb(1)−O(10)−Tb(2) = 109.1°. One square of the antiprism around Tb(1) is described by the two phenolic oxygen atoms, a carboxylate oxygen atom (O(2)), and one iminodiacetate nitrogen atom (N(2)); the remaining donor atoms form the orthogonal square plane. The $Tb-O_{phenolate}$, $Tb-O_{carboxylate}$, and Tb−N interatomic distances fall within a narrow range (2.335−2.336, 2.328−2.385, and 2.539−2.567 Å, respectively), are consistent with similar lanthanide carboxylate- and lanthanide phenolate-containing compounds,[25,18] and provide an indication that, at least in the solid state, both lanthanide cations lie in equivalent coordination environments.[26] To achieve overall charge neutrality, four sodium counterions are included in the asymmetric formula unit, and in the extended structure, these assemble into a one-dimensional (1D) polymeric chain via ligation from carboxylate oxygens of adjacent dimeric units.

In all the structures, the chelating iminodiacetic acid arms effectively wrap around the metal centers so that 5-Me-HXTA completely satisfies the coordination requirements of the lanthanide cations. Unusually, for eight-coordinate Ln-

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for **2**−**8**

	2	**3**	**4**	**5**	**6**	**7**	**8**
Ln(1)−O(1)	2.345(4)	2.366(5)	2.335(5)	2.301(5)	2.331(8)	2.281(2)	2.269(9)
Ln(1)−O(10)	2.394(4)	2.332(5)	2.303(5)	2.343(5)	2.296(8)	2.323(2)	2.306(9)
Ln(1)−O(12)	2.410(5)	2.405(5)	2.352(5)	2.349(5)	2.350(8)	2.342(2)	2.340(9)
Ln(1)−O(13)	2.394(4)	2.404(6)	2.341(6)	2.379(5)	2.380(8)	2.317(2)	2.336(9)
Ln(1)−N(1)	2.620(5)	2.619(6)	2.548(7)	2.560(7)	2.614(9)	2.540(3)	2.531(12)
Ln(1)−N(3)	2.623(5)	2.593(6)	2.572(7)	2.520(6)	2.601(10)	2.549(3)	2.507(10)
Ln(2)−O(1)	2.390(4)	2.306(5)	2.335(5)	2.330(5)	2.300(9)	2.324(2)	2.307(10)
Ln(2)−O(10)	2.320(4)	2.360(5)	2.352(5)	2.284(5)	2.312(7)	2.292(2)	2.266(8)
Ln(2)−O(6)	2.401(5)	2.355(5)	2.343(6)	2.357(6)	2.306(7)	2.338(2)	2.356(9)
Ln(2)−O(8)	2.401(5)	2.379(5)	2.338(6)	2.330(6)	2.298(7)	2.330(2)	2.330(9)
Ln(2)−N(2)	2.591(5)	2.612(7)	2.556(6)	2.608(7)	2.543(10)	2.551(3)	2.550(11)
Ln(2)−N(4)	2.617(5)	2.570(6)	2.565(6)	2.568(7)	2.534(10)	2.540(3)	2.554(11)
Ln(1)−Ln(2)	3.8546(6)	3.8236(5)	3.8040(5)	3.7819(5)	3.7706(10)	3.7690(2)	3.7341(8)
O(10)−Ln(1)−O(1)	69.68(15)	69.29(17)	70.14(17)	69.26(18)	69.5(3)	70.10(7)	69.4(3)
O(1)−Ln(1)−O(13)	91.92(16)	72.11(18)	145.38(18)	152.84(18)	148.0(3)	90.92(8)	88.8(3)
O(1)−Ln(1)−O(2)	103.89(16)	130.06(18)	134.18(18)	109.4(2)	93.5(3)	78.04(8)	106.7(3)
O(2)−Ln(1)−O(4)	129.86(16)	97.1(2)	97.93(19)	132.0(2)	156.4(3)	133.07(8)	134.0(3)
O(12)−Ln(1)−N(1)	79.19(16)	122.9(2)	84.3(2)	145.6(2)	83.4(3)	76.70(9)	153.1(3)
O(10)−Ln(2)−O(17)	79.86(15)	88.7(2)	89.07(18)	80.8(2)	84.1(3)	77.62(8)	106.1(3)
O(8)−Ln(2)−O(16)	79.04(19)	77.1(2)	78.2(2)	77.9(2)	79.3(3)	77.60(9)	74.1(3)
O(10)−Ln(2)−N(4)	82.03(16)	76.24(19)	77.18(19)	82.4(2)	77.6(3)	81.59(8)	81.6(3)
O(6)−Ln(2)−N(2)	66.47(18)	65.76(19)	67.6(2)	64.3(2)	67.9(3)	66.88(8)	65.4(3)

(III) complexes, there are no coordinated water molecules bound to the metal ions in the solid state.[27] The two ligands in **1**−**8** are not coplanar, and there is a twist of approximately 68° (range = 67.3° (**2**) to 70.5° (**8**)) between the two aromatic rings. Remarkably, the seven complexes are isostructural and no great deviations in geometry arising from a structural change around gadolinium are observed as the lanthanide series is traversed. The intermetallic separations are short, vary across the series in accordance with the reduction in eight-coordinate ionic radius (3.8546(7) Å (Sm) to 3.73 Å (Yb)),[28] and are similar to the range of Ln−Ln′ distances found in the dimeric tris-β-diketonate series (range 4.138−3.784 Å)[29] and other homobinuclear lanthanide-containing compounds.[30] For example, in the bis-dysprosium complex of the macrobicyclic phenolic cryptand $N[(CH_2)_2N{=}CH{-}R{-}CH{=}N(CH_2)_2]_3$ ($R = m\text{-}C_6H_2OH\text{-}2\text{-}Me\text{-}5$) the inter-Dy distance is shorter at 3.48 Å.[18]

2.2. ^{1}H NMR Spectroscopic Studies; Solution Speciation and Stability. Proton NMR spectra of aqueous solutions of crystalline samples of the samarium and europium complexes of 5-Me-HXTA (**2** and **3**) show the presence of a single, pseudo-C_2-symmetric solution species, in which the chelating iminodiacetic acid arms are chemically distinct on the NMR time scale. Proton NMR spectra of crude samples of the neodymium complex (**1**) also show a single paramagnetic species along with some diamagnetic impurities (uncomplexed 5-Me-HXTA), suggesting that the complexation reaction is not complete. In contrast to those of the solid-state structures, the relative simplicity of the NMR spectra for aqueous solutions suggests that the complexes may not be conformationally rigid on the time scale of the experiment. By comparison, the corresponding proton NMR spectra of the Dy, Tb, Er, Ho, and Yb complexes generally exhibit fewer resonances and are considerably paramagnetically broadened and shifted.

In order to probe the solution speciation of the complexes, we have performed a series of ^{1}H NMR titration experiments. The addition of between 0.25 and 4 equiv of Na_4•5-Me-HXTA (a in Figure 2) to 10^{-3} M solutions of $Eu(OTf)_3$ in D_2O (298 K) results in the evolution of a single paramagnetically shifted species; the ^{1}H NMR spectrum (b in Figure 2) corresponds to that of the isolated dimeric M_2L_2 complex. The addition of greater than 1 equiv of ligand affords ^{1}H NMR spectra that are a combination of **3** and uncomplexed Na_4•5-Me-HXTA (c in Figure 2). The coexistence of these two species in solution suggests that any intermolecular exchange processes between complexed and uncomplexed ligand are absent in this system on the NMR time scale. No other solution species corresponding to 2:1 L/M or M/L complexes are observed under the experimental conditions employed. In agreement with the stability constants of the terbium benzoyl analogues previously determined (log β_{12} = 29.8),[31] when **3** is challenged with an equimolar solution of diethylene triamine pentaacetic acid (DTPA), no evidence of ligand displacement and concomitant formation of Eu(DTPA) is observed (log $K = 22.8$);[32] after 6 months, the spectrum remains unchanged.

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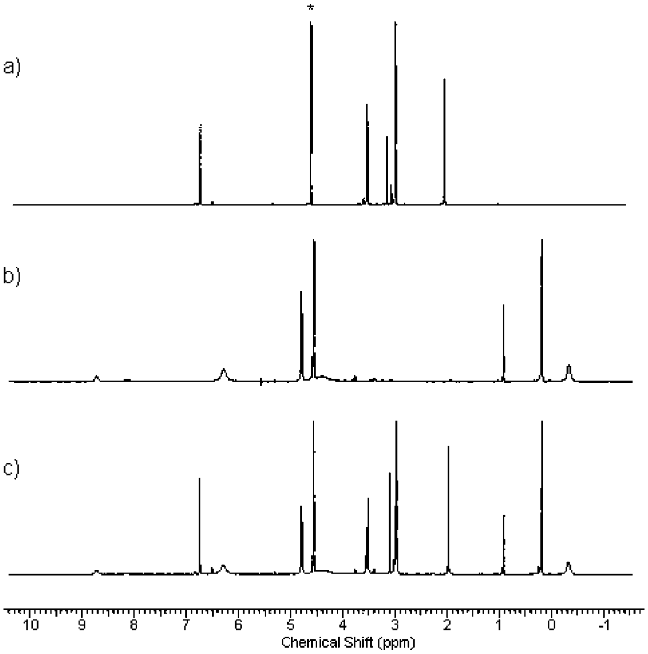

Figure 2. ^{1}H NMR spectra at 298 K of 3.0 × 10^{-3} M D_2O solutions of (a) Na_4•5-Me-HXTA, pD = 11.5; (b) **2** and 1:1 solutions of Na_4•5-Me-HXTA and $Eu(OTf)_3$, pD = 3.3; and (c) 2:1 solutions of Na_4•5-Me-HXTA and $Eu(OTf)_3$, pD = 9.4; the asterisk denotes diamagnetic solvent resonances.

2.2.1. Two-Dimensional Diffusion-Ordered NMR Spectroscopic Studies. ^{1}H diffusion-ordered correlation spectroscopy (DOSY) has proved useful in the virtual or spectroscopic separation of complex mixtures, where compounds differing in molecular weight are clearly separated into individual components.[33] In our hands, DOSY NMR spectroscopy has been applied to both probe and consequently determine the solution nuclearity of the complexes; the ^{1}H DOSY NMR spectrum of the samarium derivative **2** (D_2O, 295 K) is shown in Figure 3, and the spectra corresponding to the NMR titration of **3** are listed in the Supporting Information. Consistent with the 1D experiment, the ^{1}H DOSY NMR spectra of both **1** and **2** and **3** show the existence of a single paramagnetic species; these display translational diffusion coefficients (D) relative to HOD/D_2O of 2.28×10^{-10} m^2 s^{-1} (**1**), 2.25×10^{-10} m^2 s^{-1} (**2**), and 2.28×10^{-10} m^2 s^{-1} (**3**) ($D_{\mathrm{HOD/D_2O}} = 16.24 \times 10^{-10}$ m^2 s^{-1}), with an error estimated from the diffusion signal of ±10%. The hydrodynamic radii (R_H) of the binuclear complexes **1**−**3** determined from the diffusion coefficients using the Stokes−Einstein equation[33] are 8.50 Å (**1** and **3**) and 8.62 Å (**2**) and compare well to the radii of the unsolvated complexes measured from the largest crystallographic dimensions of the molecules found as 6.75 Å (**2**) and 6.72 Å (**3**). The corresponding molecular volumes are calculated as 1288 and 1271 Å^3 and relate to those determined from the unit cell parameters of 2748 and 2732 Å^3, which include the sodium counterions and a large number of waters of crystallization (∼15). By comparison, the solution molecular volumes ascertained from the hydrodynamic radii are 2575 Å^3 (**1** and **3**) and 2679 Å^3 (**2**), reflecting a smaller degree of solvation and higher local ordering of solvent molecules in the solution phase with respect to the solid state and that the solution dynamics of the hydrated molecules may deviate somewhat from assumed spherical behavior.

The diffusion coefficients of all three complexes are significantly smaller than that of the uncomplexed ligand Na_4•5-Me-HXTA (2.90×10^{-10} m^2 s^{-1}, $R_H = 6.68$ Å, and $V = 1249$ Å^3) and those anticipated for any mononuclear M/L complexes or higher M_2L_2 oligomers that may form based on molecular volume differences, providing strong evidence that all the complexes retain their dinuclear structure in aqueous solution. For example, a $\{Sm_2(HXTA)_2\}_2$ species, which exists crystallographically, possesses a considerably larger molecular volume of 5496 Å^3. Since we were unsuccessful in obtaining suitable single crystals of the Nd^{3+} derivative (**1**) for a structural study, these DOSY NMR experiments further corroborate the solution isonuclearity of the lighter lanthanides of the series. For the remaining paramagnetic complexes, the line widths of the proton resonances were too large to obtain structurally informative DOSY NMR spectra. Furthermore, the negative electrospray mass spectra of the complexes demonstrate the formation of both uninegative and dinegative molecular ion peaks, respectively, following the loss of one and two sodium counterions associated with the dimer (Figure S4, Supporting Information).

2.3. Photophysical Properties of 5-Me-HXTA Lanthanide Derivatives. 2.3.1. Emission Properties of Tb(III) and Eu(III) Complexes. Luminescence spectroscopy is an informative and noninvasive tool with which to probe the local environment of the metal ions. In particular, the number of inner-sphere solvent molecules (q) can be derived from lifetime measurements in protonated and deuteriated solvents, using the relationship $q = A[(k_H - k_D) - B]$ (Tb^{3+} and Yb^{3+}) and $q = A[(k_H - k_D)] - B$ (Nd^{3+}), where k_H and k_D are the observed luminescent decay rate constants in H_2O and D_2O and A and B are correction factors that account for proximate primary and secondary sphere O−H oscillator, respectively ($A = 5$ and $B = 0.06$ ms for Tb^{3+}, $A = 1$ and $B = 0.1$ μs for Yb^{3+}, and $A = 130$ and $B = 0.4$ ns for Nd^{3+}).[34,12b]

Excitation into the phenolic absorption manifold of 5-Me-HXTA of the terbium complex **4** in H_2O and D_2O (300 nm) results in a typical Tb(III) emission spectrum (Figure 4), comprised of two intense peaks at 490 and 545 nm corresponding to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions and two weaker bands at 587 and 624 nm arising from the $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions, respectively. The

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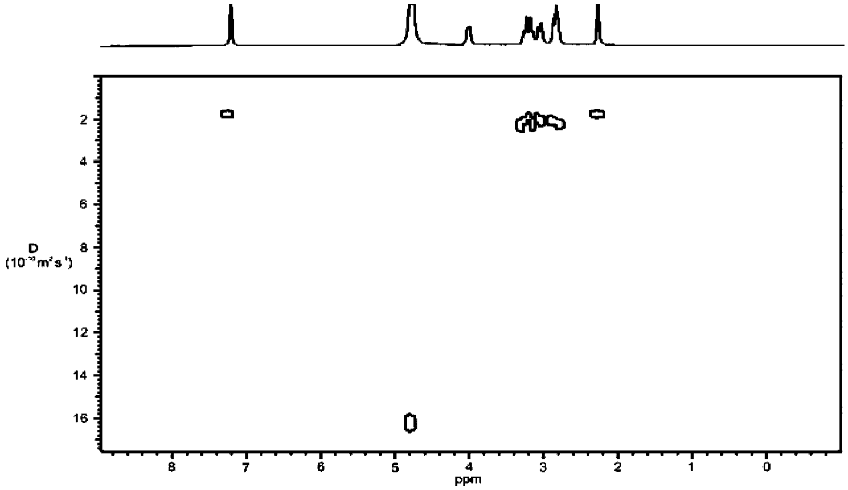

Figure 3. ^{1}H DOSY NMR spectrum of **3** (D_2O/295 K).

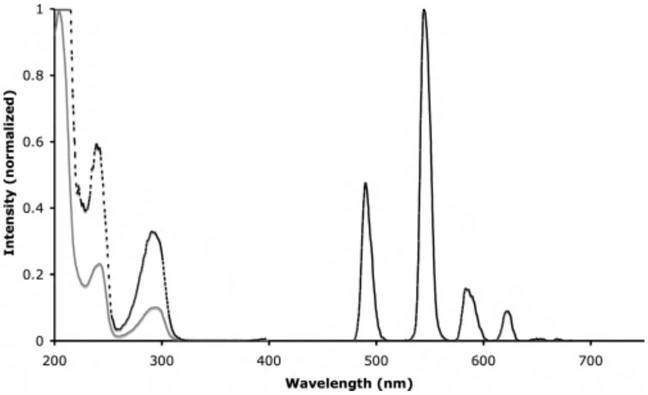

Figure 4. Normalized absorption (gray line), excitation λ_{em} 545 nm (dashed line), and steady-state emission λ_{exc} 300 nm (solid line) spectra of Na_4·$[Tb(5\text{-}Me\text{-}HXTA)]_2$·$15H_2O$ (**4**) in H_2O. Parameters: slit widths of 5 nm, delay time = 0.1 ms, and gate time = 10 ms.

Table 2. Photophysical Properties of the Complexes

complex	λ_{exc}/nm	λ_{em}/nm	$\tau_{H_2O}/\mu s$	$\tau_{D_2O}/\mu s$	q_{H_2O}	ϕ_{H_2O}/%
$[Nd(HXTA)]_2$·Na_4[a]	337	1055	0.10	0.32	0.51[a]	
$[Tb(HXTA)]_2$·Na_4	300	545	2620	2910	0.00	50
$[Yb(HXTA)]_2$·Na_4	337	980	2.14	7.51	0.23	

[a] The calculated *q* value for Nd^{3+} complexes is subject to a high degree of uncertainty due to quenching by ligand C−H oscillators.

absorption and excitation spectra (Figure 4) overlap well, indicating that efficient phenol-sensitized emission is occurring. Indeed, following irradiation, the sample luminesces with a strong green color, which is easily visible by the naked eye.

The luminescence lifetimes of **4** (Table 2) in aqueous solution and deuterated water are long at 2.62 and 2.91 ms, respectively, allowing the number of inner-sphere coordinated water molecules (*q*) to be calculated as 0 (uncertainty ±10%).[18] The observed decays fit well to monoexponential decay functions (Figure 5), indicative of the presence of a single emissive solution species in agreement with the ^{1}H NMR data; no significant improvement in fit was observed on applying a secondary exponential component to the decay profile.

Solution speciation was also examined by luminescence spectroscopy. The luminescence lifetimes over the concentration range of 10^{-7} to 10^{-3} M are constant within error (2.62 ms) and in agreement with the presence of a single emissive species in which the number of bound inner-sphere solvent molecules approximates to 0. Similarly, lifetime measurements close to and at physiological pH are consistent with the above and imply that under these conditions, the complexes are kinetically stable with respect to dissociation on the millisecond time scale.

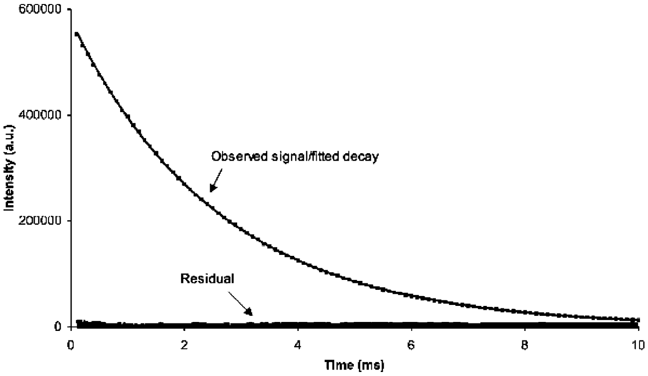

Figure 5. Fitted kinetic trace for $[Tb(HXTA)]_2$·Na_4 (**4**) in H_2O (λ_{exc} = 300 nm, λ_{em} = 545 nm, τ_{H2O} = 2.62 ms).

The quantum yield (ϕ)[35] of **4** was measured relative to the terbium complex of the Lehn cryptand[36] $[Tb(N(CH_2(bipy)CH_2)_3N)]^{3+}$ and to terbium(tris-2,6-dipicolinate)·Na_3 ($[Tb(dpa)_3]^{3-}$)[37] in 0.1 M tris(hydroxymethyl)aminomethane (Tris) buffer and found to be 49 and 57% in aqueous solution at room temperature, respectively; a value of 54% in methanolic solution was also obtained relative to the Lehn cryptand $[Tb(N(CH_2(bipy)CH_2)_3N)]^{3+}$. This quantum yield is among the highest reported to date[38] and results from a

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combination of an extremely efficient energy transfer from the ligand chromophore and lack of nonradiative deactivation pathways (possible back energy transfer from the metal to the chromophore)[39] combined with almost complete exclusion of solvent oscillators from the inner coordination sphere. The uncertainty in Φ is in line with an experimental error of around 10%. Accordingly, time-gated terbium emission can be detected at exceptionally low concentrations down to 1.0×10^{-12} M.

In contrast to the case for the terbium complex **4**, direct (397 nm) or indirect excitation of the chromophore in the europium complex **3** (270−300 nm) affords only very weak metal-based emission; the spectrum is dominated by the electric dipole-allowed $\Delta J = 2$ ($^5D_0 \rightarrow {}^7F_2$) band in addition to the $\Delta J = 1$ transition, centered respectively at 617 and 594 nm. This emission is very short-lived (<0.2 ms),[40] precluding the determination of a luminescence lifetime and suggesting that competitive nonradiative decay processes are operative at room temperature. Indeed, the UV−vis absorption spectrum of **3** in H_2O shows, in addition to the $\pi \rightarrow \pi^*$ phenolic transitions, the presence of a weak band centered at 362 nm ($\epsilon = 210$ M cm^{-1}) characteristic of a lower energy LMCT transition[41] facilitated by strong chelation of the phenolic oxygen atoms to the metal centers. In the related europium benzoyl-HXTA complex investigated by Latva, a lower-lying $n \rightarrow \pi^*$ ligand-triplet excited state (22 600 vs 26 600 cm^{-1} in 5-Me-HXTA)[42] mediates the Eu(III) emission, while the carbonyl group acts as an electron acceptor, thus impeding competitive population of the nonradiative phenolic LMCT state. In **3**, the chromophore has no such electron-withdrawing group, and consequently we observe only very weak emission from the europium center.

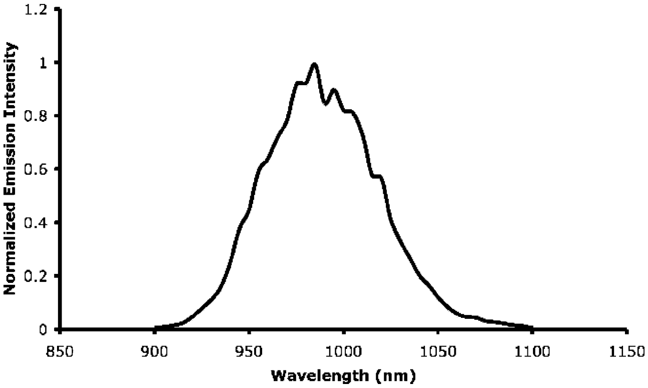

Figure 6. Total emission spectrum of $[Yb(HXTA)]_2 \cdot Na_4$ (**8**) in D_2O (λ_{exc} = 337 nm and λ_{em} = 980 nm).

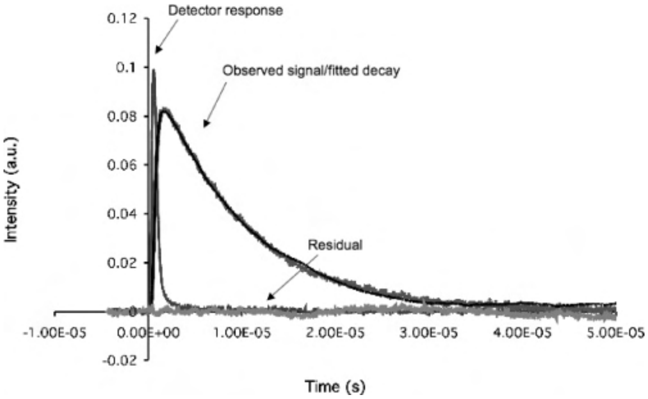

Figure 7. Fitted time-resolved decay profile of **8** in D_2O solution (λ_{exc} = 337 nm and λ_{em} = 980 nm, τ_{D_2O} = 7.51 μs).

2.3.2. Time-Resolved NIR Luminescence of Nd(III) and Yb(III) Derivatives. For $Na_4 \cdot [Nd(HXTA)]_2$ (**1**) and $Na_4 \cdot [Yb(HXTA)]_2$ (**8**), excitation into the low-energy intraligand absorption band at 337 nm using a pulsed nitrogen laser gives rise to characteristic emission in the NIR of the spectrum, at 1055 and 980 nm, respectively (Figure 6). Luminescent lifetime were measured in both H_2O and D_2O at the emission maxima, and for both complexes, the lifetime values were acquired by iterative reconvolution of the detector response with a single-exponential decay component.[6]

Similar to the case of the terbium complex **4**, the determined luminescent lifetimes are long for eight-coordinate metal complexes. For comparison, in the related bis DO3A-macrocyclic 4-methyl phenol bimetallic ytterbium complex (DO3A = 1,4,7,10-tetraazacyclododecane triacetic acid), the lifetimes for the octa-coordinated metal ions are considerably shorter (1.67 and 4.95 μs in H_2O and D_2O).[43] For the ytterbium complex **8**, the LMCT state is likely to be involved in the energy transfer process; this is borne out to some extent by the fact that the energy transfer is complete within the envelope of the laser pulse (as judged by the rise time of the fitted decay (Figure 7). Similarly, for electrochemically generated NIR luminescence of the same compound, it has been proposed that the oxidation−reduction excitation pathway is the dominant mechanism by which energy transfer occurs.[42]

The numbers of coordinated water molecules (q) were determined to be 0.5 (**1**) and 0.2 (**8**) (Table 2), possibly reflecting the contraction in ionic radius across the series, although the lowest $^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition in Nd^{3+} is more susceptible to vibronic quenching by C−H oscillators (in addition to O−H),[44] which results in a larger discrepancy in

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quoted values. Near-infrared emission from the Er(III) analogue (**7**) was very weak, both in solution and in the solid state, preventing lifetime measurements from being recorded. This is also likely to result from facile quenching by ligand C−H oscillators and has been observed in many systems.[45]

3. Conclusions

The septadentate chelate 5-Me-HXTA forms hydrolytically stable 2:2 dimeric complexes with all lanthanide(III) ions investigated. X-ray crystallographic analyses show that the complexes are unusually isostructural across the entire lanthanide series and that the phenolate bridges the two metals, affording short interatomic Ln−Ln′ distances. Diffusion-ordered NMR spectroscopy has proved a valuable technique in verifying the solution nuclearity of the complexes, whereas luminescence spectroscopy demonstrates that the bimetallic structure is retained over a concentration range amenable to analytical time-resolved applications. The complexes display efficient phenol-sensitized visible and near-infrared emission, affording particularly long luminescent lifetimes for carboxylate-containing compounds and, in the case of the Tb^{3+} complex (**4**), a quantum yield of lanthanide luminescence which is among the highest reported to date. Luminescence spectroscopy additionally suggests that both metal ions in the dimer behave as isolated entities, which renders this family of complexes good candidates for time-resolved assay in the visible and near-infrared spectral region.

4. Experimental Section

General Details. All chemical reagents and lanthanide salts used were purchased from AldrichCo. and were used without any further purification. The compounds 5-Na_3·Me-HXTA,[21] $[Tb(N(CH_2(bipy)CH_2)_3N)]^{3+}$,[46] and Na_3·Tb(dpa)$_3$[47] were synthesized according to published procedures. Fourier-transform infrared (FT-IR) spectra were recorded on a Mattson series FT-IR instrument using pressed KBr discs. Mass spectrometry was performed on a Fisons Instruments Autospec with a 0−650 °C temperature range. Elemental analyses were performed by the microanalytical services at the University of Manchester.

Absorption and Luminescence Spectroscopy. Absorption spectra were recorded in H_2O on a T60U spectrometer (PG Instruments, Ltd.) using luminescence quartz cells with a path length of 1 cm. Steady-state and time-resolved luminescence properties of the terbium and europium derivatives were measured on a Perkin-Elmer LS55 fluorimeter at 298 K in phosphorescence mode. The quantum yield of luminescence of Na_4·[Tb(HXTA)]$_2$ was measured relative to two terbium standards with a known quantum yield; the Lehn cryptand $[Tb(N(CH_2(bipy)CH_2)_3N)]^{3+}$ ($\phi = 3\%$)[36] by measuring a series of absorption intensities at the excitation wavelength and integration of the resultant emission spectra[35] and to Na_3·terbium(tris-2,6-dipicolinate) (Na_3·[Tb(dpa)$_3$])[37] in 0.1 M tris-(hydroxymethyl)aminomethane (Tris) buffer ($\phi = 26.5\%$), using solutions of the sample and standard with the same absorbance value (between 0.18 and 0.22); quoted values are the result of at least six independent measurements. Concentrations higher or lower than this gave erroneous results due to solution speciation of the Na_3·[Tb(dpa)$_3$] complex. The details of these approaches are described in detail in the above references. Time-resolved luminescence decay profiles of the ytterbium and neodymium complexes were acquired by exciting the sample with a pulsed nitrogen laser (PTI-3301, 337 nm). Light emitted at right angles to the excitation beam was focused onto the slits of the monochromator (PTI-120, resolution 0.5 nm), which was used to select the appropriate emission wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to the computer for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatter) with exponential components for growth and decay of the metal-centered luminescence, using a spreadsheet running in Microsoft *Excel*.[6] The time-resolved emission spectra for the complexes were obtained by measuring the growth and decay of the luminescence at 10 nm steps over the appropriate wavelength range.

NMR Spectroscopy. All 1D NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating frequency 400 MHz (^{1}H), 101 MHz (^{13}C), variable temperature unit at 300 K. DOSY NMR spectra were recorded using a Varian Innova 400 spectrometer at room temperature (295 K) using an in-house-developed one-shot pulse sequence.[48] The spectra were processed by applying a nonlinear function, and the diffusion coefficients (D) were calibrated to the diffusion coefficient of the HOD/D_2O signal at 295 K of 16.24 10^{-10} m^2 s^{-1} ± 2.0% from the known value at 298 K (19.02 × 10^{-10} m^2 s^{-1}).[49] Chemical shifts are reported in parts per million and referenced to residual proton resonances in D_2O, calibrated externally to TMS.

Preparation of Na_4·5-Me-HXTA. The ligand Na_4·5-Me-HXTA was synthesized by modification of a published procedure.[50] To a methanolic solution of *p*-cresol (3.0 g, 27.7 mmol, 130 mL) was added 2 equiv of disodium iminodiacetate (Na_2-IDA) (9.82 g, 55.5 mmol) in portions as a solid. The resulting slurry was stirred at ambient temperature for 30 min and then cooled to 0 °C, and 2 equiv of solid *p*-formaldehyde (1.67 g, 55.5 mmol) was added to the reaction mixture. The reaction mixture was warmed slowly to room temperature, stirred for 24 h, then heated to reflux temperature for a further 12 h. After this time, the solution was filtered while hot and the collected solids were washed with MeOH (3 × 20 mL) and Et_2O (2 × 20 mL) and dried under vacuum suction to afford 13.5 g of Na_4·5-Me-HXTA as a white powder (92%).

NMR/D_2O: δ_H 6.98 (s, 2H, Ar−H), 3.70 (s, 4H, CH_2−N), 3.17 (s, 8H, CH_2CO_2), 2.22 (s, 3H, Ar−CH_3). NMR (D_2O): δ_C 179.14 ($CH_2CO_2^-$), 153.23, 128.84, 123.29 (Ar−C), 131.49 (Ar−CH), 58.24 (CH_2CO_2), 51.82 (N−CH_2), 19.41 (Ar−CH_3). DOSY NMR/D_2O: $D = 2.90 \times 10^{-10}$ m^2 s^{-1}. FT-IR υ(cm^{-1}): 2919 (s, υ(O−H)), 1595 (br, $\upsilon_{asym}(CO_2)$), 1409 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 224 (6380), 289 (3090). Anal. Calcd for $C_{17}H_{18}N_2O_9Na_4 \cdot 2.5H_2O$: C 38.43, H 4.36, N 5.27, Na 17.31. Found: C 38.30, H 4.21, N 5.17, Na 17.71.

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Table 3. Data Collection and Structural Refinement for Complexes **2**−**8**

	7.5q**2**	**3**	**4**	**5**	**6**	**7**	**8**
diffractometer type	Bruker AXS CCD	Bruker AXS CCD	Bruker AXS CCD	Bruker AXS CCD	Bruker AXS CCD	Bruker AXS CCD	Oxford Diffraction
chemical formula	$C_{34}H_{45}$ N_4Na_4 - $O_{23.50}Sm_2$	$C_{35.50}$ $H_{51.50}Eu_2$ - N_4Na_4 $O_{31.75}$	C_{34} H_{64} N_4 Na_2- $O_{32.25}Tb_2$	C_{34} $H_{33.75}$ Dy_2- N_4Na_4 $O_{31.13}$	C_{34} $H_{44.75}$ Ho_2- $N_4Na_4O_{23.75}$	C_{34} $H_{48.25}$ Er_2 N_4 - Na_4O_{24}	C_{34} $H_{74.50}Yb_2$- $N_4Na_4O_{29.50}$
M_r	1278.40	1438.19	1408.71	1413.36	1311.31	1323.50	1449.52
cell setting, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, C_2/c	triclinic, $P\bar{1}$
a, *b*, *c* (Å)	17.003(3), 17.453(3), 20.335(3)	16.9434(8), 17.4122(8), 20.3917(9)	16.8750(10), 17.3103(11), 20.2441(13)	16.9031(8), 17.4094(8), 39.6714(18)	16.865(3), 17.4715(19), 39.741(9)	21.0999(7), 20.5791(7), 25.8866(8)	16.9226(10), 17.0690(10), 20.2256(15)
α, *β*, *γ* (deg)	99.286(3), 99.113(3), 108.721(3)	99.5200(10), 99.0500(10), 108.9950(10)	99.182(2), 97.809(2), 108.543(2)	94.8640(10), 99.3070(10), 108.6030(10)	95.086(12), 99.109(11), 108.664(12)	90, 98.688(2), 90	99.758(6), 98.158(6), 108.341(3)
V (Å^3)	5495.9(14)	5464.4(4)	5423.6(6)	10801.9(9)	10832(3)	11111.4(6)	5344.8(6)
Z	4	4	4	2	8	8	4
D_x (Mg·m^{-3})	1.545	1.748	1.725	1.738	1.608	1.582	1.801
radiation type	Mo Kα	Mo Kα	synchrotron	Mo Kα	Mo Kα	synchrotron	Mo Kα
θ range (deg)	1.30−28.34	1.79−28.41	1.76−25.00	1.30−28.45	1.05−28.28	2.75−30.97	2.54−31.97
μ (mm^{-1})	2.222	2.402	2.699	2.871	1.608	3.106	3.603
T (K)	150(2)	150(2)	123(2)	150(2)	150(2)	150(2)	150(2)
crystal form, color	block, colorless	block, colorless	block, colorless	block, colorless	block, colorless	needle, pink	needle, colorless
crystal size (mm)	0.24 × 0.19 × 0.13	0.20 × 0.20 × 0.20	0.01 × 0.01 × 0.01	0.45 × 0.30 × 0.17	0.12 × 0.09 × 0.09	0.25 × 01.5 × 0.03	0.20 × 0.10 × 0.08
data collection method	ϕ and ω	ϕ and ω	ω with narrow frames	ϕ and ω	ϕ and ω	ϕ and ω	ϕ and ω
T_{min} (K)	0.801	0.171	1.000	0.801	1.05	0.5106	0.895
T_{max} (K)	0.683	0.212	0.890	0.528	28.28	0.9264	1.066
no. of measured, independent, and observed reflections	36826, 25371, 17417	36 584, 25 228, 17 477	43 219, 20 506, 15 641	72 357, 49 671, 31 749	89 537, 38 984, 20 214	70 700, 19 436, 17 041	50 944, 31 023, 12 157
R_{int}	0.0423	0.0416	0.0316	0.0301	0.0657	0.0375	0.0595
θ_{max} (deg)	28.3	28.4	25.0	27.5	27.5	31.05	31.97
$R[F^2 > 2\sigma(F^2)]$, $R_w(F^2)$, *S*	0.0571, 0.163, 1.02	0.0537, 0.1357, 1.019	0.0540, 0.1618, 1.078	0.0647, 0.1787, 1.018	0.0605, 0.1579, 0.922	0.0323, 0.0884, 1.111	0.0694, 0.1883, 0.944
no. of reflections	25 371	25 228	20 506	20 802	38 984	19 346	31 023
no. of parameters	1235	1453	1355	1115	2456	614	1337
$(\Delta/\sigma)_{max}$	0.004	0.017	0.000	0.009	0.000	0.004	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	3.56, −1.64	2.077, −1.980	3.483, −1.810	1.50, −1.55	2.844, −1.340	2.068, −1.350	4.012, −3.577

Synthesis of Lanthanide Complexes. Na_4·[Nd(5-Me-HXTA)]$_2$ (1). A solution of Na_4·5-Me-HXTA (0.10 g, 0.21 mmol) and NaOH (0.008 g, 0.21 mmol) in 4 mL of H_2O was added dropwise to a stirred aqueous solution of $Nd(OTf)_3$ (0.12 g, 0.21 mmol, 3 mL). After 24 h, the solution was allowed to evaporate to dryness at ambient temperature and the resultant solid was triturated with MeCN and filtered to remove residual sodium triflate salts. The solids were then dissolved in 2 mL of H_2O and 3 mL of MeOH and 5 mL of EtOH and 10 mL of Et_2O and layered onto this solution. After diffusion was complete (2 weeks), **1** was isolated as the bis-NaOTf salt by filtration as a pale blue solid in 51% yield (0.103 g). NMR/D_2O: δ_H 8.05 (br, 1H), 6.41 (br, 2H), 5.47 (br, 1H), 4.47 (br, 1H), 3.03 (br, 2H), 1.93 (br, 1H), 1.34 (br, 1H). DOSY NMR/D_2O: $D = 2.28 \times 10^{-10}$ m^2 s^{-1}. FT-IR υ(cm^{-1}): 3430 (s, υ(O−H)), 1584 (s, $\upsilon_{asym}(CO_2)$), 1401 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 241 (9670), 296 (5490). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Nd_2Na_4$·13$H_2O$·MeCN·2NaOTf: C 24.87, H 3.55, N 3.92. Found: C 24.88, H 3.54, N 4.25.

Na_4·[Sm(5-Me-HXTA)]$_2$ (2). A solution of Na_3·5-Me-HXTA (0.87 g, 1 mmol) and sodium hydroxide (0.04 g, 1 mmol) in 10 mL of H_2O was added to an aqueous stirred solution of $Sm(NO_3)_3$·6H_2O (0.44 g, 1 mmol, 10 mL). After 24 h, the volume of the solution was reduced to approximately half by the slow evaporation of the solvent at room temperature. The layering of ethanol onto this aqueous solution afforded single colorless crystals suitable for X-ray diffraction after several weeks (0.23 g, 34%). NMR/D_2O: δ_H 7.18 (s, 2H, Ar−*H*), 4.18 (br, 4H, C*H*$_2$−N), 3.56, 3.12, 2.95, 2.70 (overlapping m, 8H, C*H*$_2CO_2$) 2.15 (s, 3H, Ar−CH_3). DOSY NMR/D_2O: $D = 2.25 \times 10^{-10}$ m^2 s^{-1}. ES$^-$MS: *m*/*z* 586 $[Sm_2HXTA_2Na_2]^{2-}$. FT-IR υ(cm^{-1}): 3415 (s, υ(O−H)), 1584 (s, $\upsilon_{asym}(CO_2)$), 1402 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 242 (16 510), 296 (7430). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Sm_2Na_4$·10$H_2O$: C 30.04, H 4.00, N 4.12. Found: C 29.90, H 3.70, N 4.42.

Na_4·[Eu(5-Me-HXTA)]$_2$ (3). Synthesized using the same procedure as above but with $Eu(NO_3)_3$·6H_2O, (0.52 g, 76%). NMR/D_2O: δ_H 8.73 (br, 1H), 6.40 (br, 2H), 4.95 (br, 2H), 4.65 (br, sh), 0.34 (s, 3H, Ar−C*H*$_3$), −5.11 (br, 1H), −2.5 (br). DOSY NMR/D_2O: $D = 2.28 \times 10^{-10}$ m^2 s^{-1}. ES$^-$MS: *m*/*z* 1159 $[Eu_2HXTA_2Na_3]^-$, 569 $[Eu_2HXTA_2Na_2]^{2-}$, ES$^+$MS: *m*/*z* 1182.9 $[Eu_2HXTA_2Na_4]^+$. IR (solid) υ_{max} (cm^{-1}): 3421 (s, υ(O−H)), 1585 (s, $\upsilon_{asym}(CO_2)$), 1402 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 243 (14 040), 297 (5950) 362 (sh, 210) nm. Anal. Calcd for $C_{34}H_{34}N_4O_{18}Eu_2Na_4$·10$H_2O$: C 29.97, H 3.99, N 4.11. Found: C 29.97, H 3.53, N 4.51.

Na_4·[Tb(5-Me-HXTA)]$_2$ (4). Synthesized using the same procedure as above but with $Tb(NO_3)_3$·6H_2O, (0.20 g, 29%). NMR (D_2O): δ_H 12.50 (br), 7.80 (br), −1.13 (br), −44.65 (br), −54.54 (br). ES$^-$MS: *m*/*z* 1173 $[Tb_2HXTA_2Na_3]^-$, 575 $[Tb_2HXTA_2Na_2]^{2-}$. IR (solid) υ_{max} (cm^{-1}): 3421 (m, υ(O−H)), 1585 (s, $\upsilon_{asym}(CO_2)$), 1402 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 241 (24 610), 295 (10 610) nm. Anal. Calcd for $C_{34}H_{34}N_4O_{18}Tb_2Na_4$·10$H_2O$: C 28.91, H 4.14, N 3.97. Found: C 28.30, H 4.44, N 3.92.

Na_4·[Dy(5-Me-HXTA)]$_2$ (5). Synthesized using the same procedure as above but with $Dy(NO_3)_3$·6H_2O, (0.44 g, 64%). NMR (D_2O): δ_H 28.20 (br), 25.50 (br), 8.17 (br), −44.65 (br), 3.95 (br), 2.83 (br), 1.13 (br), −0.12 (br), −3.17 (br), −18.00 (br). ES⁻MS: *m/z* 1181 $[Dy_2HXTA_2Na_3]^-$, 579 $[Dy_2HXTA_2Na_2]^{2-}$. IR (solid) υ_{max} (cm^{-1}): 3423 (s, υ(O−H)), 1592 (s, $\upsilon_{asym}(CO_2)$), 1408 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 241 (6260), 295 (3520). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Dy_2Na_4\cdot 10H_2O$: C 29.51, H 3.93, N 4.05. Found: C 29.70, H 3.76, N 4.40.

$Na_4\cdot$[Ho(5-Me-HXTA)]$_2$ (6). Synthesized using the same procedure as above but with $HoCl_3\cdot 6H_2O$, (0.44 g, 63%). NMR (D_2O): δ_H 17.00 (br), 2.50 (br), 1.78 (br), −1.73 (br), 0.10 (br). IR (solid) υ_{max} (cm^{-1}): 3429 (s, υ(O−H)), 1610 (s, $\upsilon_{asym}(CO_2)$), 1408 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 241 (5660), 295 (14 230). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Ho_2Na_4\cdot 10H_2O$: C 29.41, H 3.92, N 4.03. Found: C 29.00, H 4.38, N 3.68.

$Na_4\cdot$[Er(5-Me-HXTA)]$_2$ (7). A solution of $Na_4\cdot$5-Me-HXTA (0.25 g, 0.51 mmol) and NaOH (0.021 g, 0.51 mmol) in 8 mL of H_2O was added dropwise to a stirred aqueous solution of $Er(OTf)_3$ (0.32 g, 0.51 mmol, 5 mL). After 24 h, the solution was allowed to evaporate to dryness at ambient temperature and the resultant solid was triturated with MeCN and filtered to remove residual sodium triflate salts. The solids were then dissolved in 4 mL of MeOH and 10 mL of Et_2O layered onto this solution to afford pale pink single crystals of **7**, which were isolated by filtration in 41% yield (0.156 g). NMR (D_2O): δ_H 3.51 (br), −0.33 (br), −8.50 (br), −18.75 (br). IR (solid) υ_{max} (cm^{-1}): 3429 (s, υ(O−H)), 1610 (s, $\upsilon_{asym}(CO_2)$), 1412 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 240 (15 800), 295 (7100). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Er_2Na_4\cdot 15H_2O$: C 27.53, H 4.35, N 3.78, Na 6.20, Er 22.55. Found: C 27.24 H 3.91, N 3.71, Na 6.18, Er 21.64.

$Na_4\cdot$[Yb(5-Me-HXTA)]$_2$ (8). A solution of $Na_4\cdot$5-Me-HXTA (0.20 g, 0.41 mmol) and NaOH (0.017 g, 0.41 mmol) in 6 mL of H_2O was added dropwise to a stirred aqueous solution of $YbCl_3\cdot 6H_2O$ (0.16 g, 0.41 mmol, 5 mL). After 24 h, the solution was allowed to evaporate to dryness at ambient temperature and the resultant solid was triturated with MeCN and filtered to remove residual sodium triflate salts. The solids were then dissolved in 2 mL of H_2O and 3 mL of MeOH and 5 mL of EtOH and 10 mL of Et_2O and layered onto this solution. After diffusion was complete (3 weeks), **8** was isolated as single colorless crystals in 30% yield (0.097 g). NMR (D_2O): δ_H 15.88 (br, 6H), 3.65 (sh, br), −0.55 (br, 2H), −4.84 (br, 2H), −10.35 (br, 1H). IR (solid) υ_{max} (cm^{-1}): 3420 (s, υ(O−H)), 1610 (s, $\upsilon_{asym}(CO_2)$), 1411 (m, $\upsilon_{sym}(CO_2)$). UV−vis (H_2O) λ_{max} (ϵ (M^{-1} cm^{-1})): 238 (13 550), 295 (6990). Anal. Calcd for $C_{34}H_{34}N_4O_{18}Yb_2Na_4\cdot 18H_2O$: C 26.36, H 4.55, N 3.62, Yb 22.34. Found: C 26.36, H 4.02, N 3.54, Yb 24.70.

Data Collection and Structural Refinement for Complexes 2−8 (Table 3). All the structures reported have large number of waters of crystallization, many of which are highly disordered. No H atoms have been included in the refinement for these atoms. This disorder has not been fully modeled, and *SQUEEZE* has been applied for compounds **2**, **3**, **6**, and **7**. For compound **4**, the application of *SQUEEZE* was not required, and for compound **8**, the refinement was not improved. Where no suitable model for the disordered solvent molecules could be found, they have been refined isotropically. In all cases, the structure of the anion is well defined.[51]

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Supporting Information Available: PDF and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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