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Transformation of a Luminescent Benzimidazole-Based Yb₃ Cluster into a One-Dimensional Coordination Polymer

Xiaoping Yang,[†] Richard A Jones,^{*,†} Michael J. Wiester,[†] Michael M. Oye,[†] and Wai-Kwok Wong^{*,‡}

[†]Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165 and [‡]Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, P. R. China

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ABSTRACT: Reaction of the benzimidazole-based ligand 2-(1H-benzoimidazol-2-yl)-4-bromo-6-methoxy-phenol (HL) with $LnCl_3 \cdot 6H_2O$ in a 4:3 mol ratio in refluxing EtOH gave the trinuclear complexes $[Ln_3L_4Cl_4(H_2O)_2] \cdot Cl \cdot H_2O \cdot EtOH(1)$ (Ln = Tb (a), Er (b), Yb (c)) in 40-59% yields. Under similar conditions, but with the subsequent addition of $Zn(OAc)_2 \cdot 2H_2O$ to the reaction mixture, complex { $[Yb_3L_4(OAc)_4] \cdot Cl \cdot EtOH$ }, (2) can be isolated in 48% yield. 2 has a one-dimensional coordination structure in the solid state. All complexes display intramolecular $\pi - \pi$ stacking and hydrogen bonded interactions in the solid state as well as lanthanide ion based luminescence in both solution and the solid.

Introduction

There is currently considerable interest in metal—organic coordination polymers or framework materials (MOF) from both a structural standpoint and for potential application in, for example, catalysis, molecular recognition, and storage devices.¹ The "node and spacer" methodology has proven to be a very successful strategy for the design of many metal—organic architectures including chain, ladder, grid, brick wall, honeycomb, diamondoid, rutile, and α -polonium structures.² Most of this work has been focused on coordination polymers of d-block transition metals. Coordination polymers based on lanthanides would be of interest for the potential to develop new optical, electrical, and magnetic materials.³ However, lanthanide ions generally display high and variable coordination numbers and their use as nodes for the construction of coordination polymers is currently of interest.

As part of a general program aimed at the synthesis of multinuclear lanthanide complexes, we recently reported the use of an unusual benzimidazole ligand (H_2L') which was used to stabilize a range of Ln-Cu heterobimetallic complexes (Scheme 1).^{4a} We have also recently reported the construction of several different polynuclear lanthanide framework materials based on 1,4-benzenedicarboxylate and 4-hydroxybenzene sulfonate linker units.^{4b-4e} We were therefore interested in the possibility of constructing a coordination polymer from benzimidazole-based lanthanide units and carboxylate linkers. Lanthanide complexes with benzimidazole-based ligands are of interest since they have the potential to exhibit ligand-to-metal energy transfer (LMCT) processes as well as supramolecular architectures based on $\pi - \pi$ stacking and hydrogen bonded interactions.⁵ In this paper, we describe the synthesis, structures, and photophysical properties of Ln₃ clusters stabilized with the simplified benzimidazole ligand HL (Scheme 2). In the case of the Yb₃ complex 1c we were able to replace the H₂O and Cl⁻ ions with acetate (OAc⁻) by

Scheme 1. The Structure of Benzimidazole Ligand H₂L'



treatment of the reaction mixture with $Zn(OAc)_2 \cdot 2H_2O$. The resulting compound has an unusual one-dimensional (1-D) coordination polymeric structure in the solid state in which Yb_3L_4 clusters are linked by double OAc^- bridges. We chose $Zn(OAc)_2 \cdot 2H_2O$ for this conversion on the basis that it was reasonably soluble in EtOH. At present we do not know if the reaction is dependent on Zn^{2+} , although it seems reasonable to assume that other metal acetates would be capable of producing the same result.

Experimental Section

General Methods. All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Solvents and starting materials were purchased from Aldrich and used without further purification unless noted. ¹H NMR spectra were recorded on a Varian-500 NMR spectrometer with SiMe₄ as an internal standard, infrared spectra from 4000 to 400 cm^{-1} on a Bruker EQINOX 55 FT-IR, and ESI-MS mass spectra on a Finnigan MAT TSQ 700. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Melting points were in sealed capillaries under nitrogen and are uncorrected. The solvents used for the photophysical investigations were dried and freshly distilled under nitrogen. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter. Near-infrared (NIR) emission spectra were measured with a 1-m SPEX 1704 spectrometer and a liquid-nitrogen cooled Ge detector, using an argon ion laser as the excitation source.

X-ray Crystallography. Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and



^{*}To whom correspondence should be addressed. (R.A.J.) Tel: (512)471-1706. E-mail: rajones@mail.utexas.edu; (W.-K.W.) tel: 852-3411-7011. E-mail: wkwong@hkbu.edu.hk.

Scheme 2. Formation of Lanthanide Complexes 1a-c and 2



Table 1. Crystal Data and Structure Refinement for the Free Ligand HL, 1a-c and 2

	HL	1 a	1b	1c	2
formula	C ₁₄ H ₁₁ BrN ₂ O ₂	C ₅₈ H ₅₂ Br ₄ Cl ₅ N ₈ O ₁₂ Tb ₃	C ₅₈ H ₅₂ Br ₄ Cl ₅ N ₈ O ₁₂ Er ₃	C ₅₈ H ₅₂ Br ₄ Cl ₅ N ₈ O ₁₂ Yb ₃	C64H52Br4ClN8O16Yb3
fw	319.16	2026.68	2051.70	2069.04	2063.35
cryst syst	triclinic	tetragonal	tetragonal	tetragonal	tetragonal
space group	$P\overline{1}$	P4/ncc	P4/ncc	P4/ncc	P4/ncc
a, Å	7.2664(15)	25.992(4)	25.943(4)	25.902(4)	25.912(4)
b, Å	11.972(2)	25.992(4)	25.943(4)	25.902(4)	25.912(4)
<i>c</i> , Å	14.604(3)	23.403(5)	23.312(5)	23.203(5)	22.760(5)
α, deg	75.96(3)	90	90	90	90
β , deg	89.72(4)	90	90	90	90
γ , deg	86.96(3)	118.08(3)	90	90	90
$V, Å^3$	1230.8(4)	15810(4)	15689(4)	15567(4)	15281(4)
Z	4	8	8	8	8
$D_{\rm calc}, {\rm g \ cm^{-3}}$	1.722	1.698	1.732	1.761	1.794
temp, K	153(1)	153(1)	153(1)	153(1)	153(1)
F(000)	640	7728	7800	7848	7896
μ , mm ⁻¹	3.338	4.900	5.442	5.855	5.833
θ range, deg	2.98 - 25.00	2.93-25.00	3.14-25.00	3.17-25.00	2.96-25.00
reflns meas	5950	35599	24665	24214	64718
reflns used	4283	6804	6907	6856	6653
params	343	426	426	426	434
$\hat{R}^a (I > 2\sigma(I))$	R1 = 0.0378	R1 = 0.0962	R1 = 0.0615	R1 = 0.0563	R1 = 0.0958
	wR2 = 0.0894	wR2 = 0.2024	wR2 = 0.1563	wR2 = 0.1461	wR2 = 0.1656
R^a (all data)	R1 = 0.0515	R1 = 0.1879	R1 = 0.1026	R1 = 0.0897	R1 = 0.1578
	wR2 = 0.0976	wR2 = 0.2334	wR2 = 0.1864	wR2 = 0.1716	wR2 = 0.2484
S	1.072	1.026	1.050	1.077	0.989

 ${}^{a}\mathrm{R1} = \Sigma |F_{o}| - |F_{c}|/\Sigma |F_{o}|. \ w\mathrm{R2} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]]^{1/2}. \ w = 1/[\sigma^{2}(F_{o}^{2}) + (mP)^{2} + nP], \ \text{where} \ P = (F_{o}^{2} + 2F_{c}^{2})/3.$

refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.⁶ Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.⁷

Preparation of the Ligand HL. The new benzimidazole ligand (HL) was synthesized with 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 0.01 mol) and o-phenylenediamine (1.08 g, 0.01 mol) in nitrobenzene (30 mL) according to well-established procedures.^{8,8b} A solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 0.01 mol) in nitrobenzene (10 mL) was dropwise added to a solution of o-phenylenediamine (1.08 g, 0.01 mol) in nitrobenzene (20 mL) over a period of 30 min. The mixture was heated under reflux (12 h). During this time, the color changed from yellow to dark red. The reaction mixture was then allowed to cool to room temperature and volatile materials were removed under vacuum. The residue was treated with EtOH (20 mL), and the mixture was stirred (30 min) and then filtered. The colorless residue (HL) that remained was washed with ethanol (15 mL). Yield 2.39 g, 75%. Anal. Found: C, 52.60; H, 3.34; N, 8.84. Calc. for C₁₄H₁₁BrN₂O₂: C, 52.69; H, 3.47; N, 8.78. FABMS: *m*/*z* 320 ([M + H]⁺). mp 230-1 °C. ¹H NMR (400 MHz, CD₃CN): δ (ppm) 3.924 (s, 3H), 7.204 (d, 1H), 7.350-7.381 (m, 2H), 7.628-7.657 (m, 2H), 7.647 (d, 1H). IR (CH₃CN, cm⁻¹): 3348 (br), 1621 (m), 1589 (m), 1525 (m), 1490 (m), 1463 (s), 1444 (m), 1398 (m), 1250 (m), 1052 (w) and 745 (m).



Figure 1. Crystal structure and packing of the free ligand HL: $C(4c) \cdots C(10a)$: 3.575 Å. $C(2c) \cdots C(13a)$: 3.387 Å. $N(1a) \cdots C(4e)$: 3.355 Å. $N(2a) \cdots C(2e)$: 3.503 Å. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 25% probability level.

Colorless single crystals for X-ray crystallography were obtained from an EtOH solution in air at room temperature.

Synthesis of $[Ln_3L_4Cl_4(H_2O)_2] \cdot Cl \cdot H_2O \cdot EtOH (1) (Ln = Tb (a), Er (b), Yb (c))$. A solution of $LnCl_3 \cdot 6H_2O (0.03 \text{ mmol})$ in EtOH

Table 2.	Selected Bond Lengths (Å) and Angles (°) for the Free Ligand
	HL, 1a-c and 2

	Free Lig	gand HL					
$\overline{\operatorname{Br}(1)} - C(4)$	1 807(4)	N(1) = C(8)	1 315(5)				
DI(1) = C(4) N(1) = C(0)	1.097(4) 1.278(5)	N(1) = C(0) O(1) = C(2) = C(7)	1.313(3)				
N(1) = C(9) N(2) = C(8)	1.376(3) 1.276(5)	C(5) = C(4) = Pr(1)	120.3(3)				
N(2) = C(0) N(2) = C(14)	1.370(3) 1.380(5)	C(3) = C(4) = Br(1)	120.3(3) 117.5(3)				
O(1) - C(2)	1.339(3) 1.371(4)	O(2) - C(7) - C(2)	118.0(3)				
O(1) - C(2) O(1) - C(1)	1.371(4) 1.426(5)	O(2) = C(7) = C(2)	122 6(2)				
O(1) - C(1) O(2) - C(7)	1.420(3) 1.255(4)	V(1) - C(8) - V(2)	122.0(3)				
C(2) = C(7) C(3) = N(1) = C(0)	1.333(4) 107.0(3)	N(1) = C(8) = N(2) N(1) = C(8) = C(6)	112.0(3) 122.5(3)				
C(8) = N(1) = C(9) C(8) = N(1) = H(1A)	107.0(3)	N(1) = C(8) = C(0) N(2) = C(8) = C(6)	122.3(3) 125.6(3)				
C(0) = N(1) = H(1A) C(0) = N(1) = H(1A)	120.5	N(2) = C(0) = C(0)	123.0(3) 120.0(2)				
$C(9) = N(1) = \Pi(1A)$ C(8) = N(2) = C(1A)	120.3 106.4(3)	N(1) = C(9) = C(10) N(1) = C(0) = C(14)	108 6(2)				
C(0) = N(2) = C(14) C(2) = O(1) = C(1)	100.4(3)	$\Gamma(1) = C(9) = C(14)$ C(12) = C(14) = N(2)	122 2(2)				
C(2) = O(1) = C(1) O(1) = C(2) = C(2)	110.0(3) 124.4(2)	V(13) - C(14) - N(2)	152.2(5) 105.0(2)				
0(1)=C(2)=C(3)	124.4(3)	N(2) = C(14) = C(9)	105.9(5)				
1a							
Tb(1) - O(2')	2.260(13)	O(2')-Tb(1)-N(1')	74.1(5)				
Tb(1) - O(1W)	2.285(17)	O(2) - Tb(1) - N(1')	134.9(5)				
Tb(1) - O(2)	2.334(13)	O(2')-Tb(1)-O(1)	120.3(5)				
Tb(1)-N(1')	2.449(17)	O(2) - Tb(1) - O(1)	65.2(5)				
Tb(1)-O(1)	2.474(15)	N(1')-Tb(1)-O(1)	159.8(6)				
Tb(1)-Cl(1)	2.556(8)	O(2') - Tb(2) - O(2)	70.0(5)				
Tb(1)-Cl(2)	2.554(8)	O(2')-Tb(2)-N(1)	137.2(5)				
Tb(2) - O(2')	2.256(12)	O(2) - Tb(2) - N(1)	75.1(5)				
Tb(2) - O(2)	2.260(13)	O(2') - Tb(2) - O(1')	65.9(5)				
Tb(2) - N(1)	2.369(16)	O(2) - Tb(2) - O(1')	112.9(5)				
Tb(2) - O(1')	2.529(13)	N(1) - Tb(2) - O(1')	154.1(5)				
O(2') - Tb(1) - O(2)	68.7(4)						
	1	b					
Er(1) = O(2')	2 235(7)	Er(1) = O(1)	2 455(8)				
Er(1) = O(1W)	2.255(9)	Er(1) - Cl(2)	2 549(4)				
Er(1) - O(2)	2.235(7)	Er(1) - Cl(1)	2 595(4)				
Er(1) - N(1')	2.515(1) 2 416(10)	Er(2) - O(2)	2.393(1) 2.242(8)				
Fr(2) = O(2')	2.110(10) 2.247(7)	N(1') - Fr(1) - O(1)	160.2(3)				
Er(2) = O(2) Er(2) = N(1)	2.247(7) 2 364(9)	O(2) - Er(2) - O(2')	69 6(3)				
Fr(2) = O(1')	2.504(9) 2 510(8)	O(2) - Er(2) - N(1)	75 7(3)				
O(2') - Er(1) - O(2)	68 5(2)	O(2) = Er(2) = N(1) O(2') = Fr(2) = N(1)	137 7(3)				
O(2') - Er(1) - N(1')	745(3)	O(2) - Er(2) - O(1')	113 8(3)				
O(2) - Er(1) - N(1')	1350(3)	O(2) = Er(2) = O(1')	66 2(3)				
O(2') - Er(1) - O(1)	119.2(3)	N(1) - Fr(2) - O(1')	153 7(3)				
O(2) - Er(1) - O(1)	64.7(3)	11(1) 21(2) 0(1)	100.7(0)				
	1	c					
$Vb(1) = O(2^{1})$	2 224(6)	O(2') = Vb(1) = N(1')	74 5(2)				
$V_{b(1)} = O(1W_{b(1)})$	2.234(0)	O(2) = Vb(1) = N(1)	125 1(2)				
10(1) - O(1W) Vb(1) $O(2)$	2.247(7)	O(2) = I D(1) = N(1)	110.8(2)				
10(1) = O(2) Vb(1) N(1')	2.319(0) 2.207(8)	O(2) = I O(1) = O(1)	(119.0(2))				
$V_{b(1)} = N(1)$	2.37/(0)	N(1') = Vb(1) = O(1)	150 0(2)				
10(1) = O(1) Vb(1) $C1(2)$	2.430(7)	N(1) = 10(1) = O(1)	139.0(3)				
$V_{b(1)} = C_{1(1)}$	2.3+3(3)	O(2) = Vb(2) = O(2)	75 5(2)				
10(1) - CI(1) Vb(2) $O(2)$	2.367(3)	O(2) = I O(2) = N(1) O(2') = N(2) = N(1)	127.5(2)				
10(2) = O(2) Vb(2) = O(2')	2.233(0) 2.243(6)	O(2) = I O(2) = I(1) O(2) = Vb(2) = O(1')	137.0(2)				
10(2) = O(2) Vb(2) N(1)	2.243(0) 2.254(7)	O(2) = I D(2) = O(1)	113.4(2) 66 2(2)				
10(2) = N(1) Vb(2) $O(1/)$	2.334(7) 2.406(7)	V(2) = I U(2) = O(1)	152.7(2)				
O(2') - Vb(1) - O(2)	68.5(2)	N(1) = 10(2) = O(1)	155.7(2)				
		2					
Y b(1) = O(3)	2.207(15)	Y b(2) - O(2')	2.288(13)				
Yb(1) - O(2')	2.279(14)	Y b(2) - N(2)	2.371(18)				
Yb(1) - N(2')	2.44(2)	Y b(2) - O(1')	2.510(16)				
Yb(1) - O(1)	2.444(15)	O(2') - Yb(1) - O(2)	68.2(5)				
Yb(1) - O(5)	2.439(18)	O(2') - Yb(1) - N(2')	72.4(6)				
Yb(1) - O(2)	2.370(14)	O(2) - Yb(1) - N(2')	133.3(5)				
Yb(1) - O(6)	2.40(2)	O(2') - Yb(1) - O(1)	119.0(5)				
Yb(2) - O(2)	2.270(14)	O(2) - Yb(1) - O(1)	64.5(5)				
N(2')-Yb(1)-O(1)	161.7(5)	O(2) - Yb(2) - O(1')	111.4(5)				
O(2) - Yb(2) - O(2')	69.8(5)	O(2') - Yb(2) - O(1')	65.8(6)				
O(2) - Yb(2) - N(2)	75.6(5)	N(2) - Yb(2) - O(1')	152.8(6)				
O(2') - Yb(2) - N(2)	137.8(6)						



Figure 2. Crystal structure of **1a**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 25% probability level. (a) View showing intramolecular $\pi - \pi$ stacking interactions: X1A···X1B: 3.958 Å, X1C···X1D: 3.872 Å, X1E···X1F: 3.891 Å, X1G···X1H: 3.891 Å. (b) View showing the crossed ligand configuration.

(5 mL) was added to a solution of HL (0.013 g, 0.04 mmol) in EtOH (5 mL) and the mixture was stirred and heated under reflux (2 h). The reaction mixture was then allowed to cool to room temperature and filtered. Diethylether was allowed to diffuse slowly into the filtrate at room temperature and yellow crystalline 1a-c was obtained

(1 month). The product was isolated by filtration. For **1a**, Yield 0.008 g (40%). ESI-MS (CH₃CN) m/z: 1906 ([M-Cl-2H₂O-EtOH]⁺). IR (CH₃CN, cm⁻¹): 3458 (br), 1620 (s), 1609 (s), 1566 (s), 1525 (m), 1462 (m), 1398 (m), 1202 (m), 1050 (w), 956 (m) and 745 (m). For **1b**, Yield 0.009 g (45%). ESI-MS (CH₃CN) m/z: 1915 ([M-Cl-3H₂O-EtOH]⁺). mp > 245 °C (dec). IR (CH₃CN, cm⁻¹): 3500 (br), 1621 (s), 1607 (s), 1567 (m), 1512 (s), 1456 (m), 1410 (m), 1200 (m), 1048 (w), 957 (m) and 742 (m). ¹H NMR (500 MHz, CD₃-CN): δ (ppm) –18.953 (3H), –11.520 (1H), –10.687 (2H), –9.907 (1H), 6.692 (2H), 14.402 (2H), 25.387 (2H), 42.151 (3H), 54.313 (1H), 59.711 (1H). For **1c**, Yield 0.012 g (59%). ESI-MS (CH₃CN) m/z: 1966 ([M-Cl-H₂O-EtOH]⁺). IR (CH₃CN, cm⁻¹): 3469 (br),



Figure 3. View of Cl···H-O hydrogen bonded interactions between the coordinated Cl⁻ ion and H₂O in 1a, which result in a 1-D wave-like strand: Cl(1)···O(1w): 2.839 Å.

1620 (s), 1606 (s), 1567 (s), 1515 (s), 1465 (s), 1407 (m), 1201 (m), 1046 (w), 959 (m) and 741 (m).

Synthesis of {[**Yb**₃**L**₄(**OAc**)₄]·**Cl**·**EtOH**}_{*n*} (2). A solution of YbCl₃·6H₂O (0.012 g, 0.03 mmol) in EtOH (5 mL) was added to a solution of HL (0.013 g, 0.04 mmol) in EtOH (5 mL) and the mixture was stirred and heated under reflux (2 h). The mixture was allowed to cool to room temperature. A solution of Zn(OAc)₂· 2H₂O (0.110 g, 0.50 mmol) in EtOH (5 mL) added and the mixture was heated under reflux (1 h). The mixture was then allowed to cool to room temperature. A solution of Zn(OAc)₂· 2H₂O (0.110 g, 0.50 mmol) in EtOH (5 mL) added and the mixture was heated under reflux (1 h). The mixture was then allowed to cool to room temperature and filtered. Diethylether was allowed to cool to room temperature and pale yellow single crystals of 2 were obtained after two weeks. Yield 0.010 g (48%). ESI-MS (CH₃CN) *m/z*: 636 ([Yb₃L₄(OAc)₂]³⁺). mp > 272 °C (dec). IR (CH₃CN, cm⁻¹): 3488 (br), 1626 (s), 1606 (s), 1597 (s), 1560 (s), 1515 (s), 1483 (s), 1465 (s), 1436 (m), 1410 (m), 1202 (m), 1040 (w), 958 (m) and 740 (m).

Results and Discussion

A view of the molecular structure of the free benzimidazole ligand HL along with a view of its packing in the solid state is shown in Figure 1. Details of crystallographic parameters, data collection, and refinements are listed in Table 1, and selected bond lengths and angles are given in Table 2. In the solid state, the molecule packs in an offset head-to-head fashion with the five-membered ring of the imidazole moiety stacked closest to the phenylene ring of its nearest neighbor, resulting in a herringbone effect (Figure 1). As described below this kind of π - π stacking interaction is also found in the lanthanide complexes 1a-c and 2.

Reactions of the substituted benzimidazole (HL) with $LnCl_3 \cdot 6H_2O$ in a 4:3 molar ratio in refluxing EtOH produce the trinuclear lanthanide complexes 1a-c in ca. 40–60% yield

(Scheme 2). Single crystals of these complexes suitable for X-ray diffraction studies were obtained by allowing Et₂O to diffuse into the reaction mixture at room temperature. The compounds 1a-c are isomorphous and crystallize in the tetragonal space group P4/ncc with eight Ln₃L₄ units per unit cell. The view of the X-ray structure of the Tb complex 1a is shown in Figure 2. Crystallographic details are provided in Table 1, and selected bond lengths and angles are given in Table 2. The structure of 1a contains of three nonlinear Tb(III) ions (Tb-Tb-Tb angle 141.15°) bound by four deprotonated L⁻ ligands. Interestingly, the L⁻ ligands bind in two distinct ways. Two are arranged so that each pair of phenolic and methoxy O atoms is bound in a chelating fashion to the central Tb(2) ion. The imidazole nitrogen atoms from these groups are then bound to each of the terminal Tb ions. This pair of ligands is arranged so that the aromatic rings are roughly parallel with each other. The distances between rings are 3.958 Å (X1A····X1B) and 3.872 Å (X1C···X1D) (Figure 2a). The other two ligands are coordinated so that the imidazole nitrogen atoms are bound to the central Tb(2)with the O_2 binding set of each ligand being coordinated to the two terminal Tb ions. The phenolic oxygen atoms for all four ligands bind to the central Tb and also bridge the outer Tb ions. The latter pair of ligands is also roughly parallel to each other, and the distance between rings is 3.891 Å (Figure 2a). The molecule contains a C_2 rotation axis which passes through Tb(2), and so the two terminal Tb atoms are crystallographically equal. The unique Tb–Tb distance is 3.737 Å. This ligand configuration results in the central Tb ion having a coordination number of 8. The terminal Tb ions are each



Figure 4. View of Cl···H–N hydrogen bonded interactions between uncoordinated Cl⁻ ions and N–H groups of L⁻ ligands in **1a**, which result in a 3-D open network viewed along [110]: Cl(3)···N-(2): 3.178 Å, Cl(3)···N(2'): 3.111 Å.



Figure 5. Crystal structure of 1-D coordination polymer 2. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 25% probability level.

bound to two Cl⁻ groups and a water molecule in addition to the L⁻ ligands and are seven-coordinate. The pairs of L⁻ ligands are aligned in a criss-cross fashion with the angles



Figure 6. Space filling view of 2 along the *c*-axis showing the 3-D network.

between the least-squares planes of each being 66.8° and 89.5° (Figure 2b). The terminally bound Cl⁻ and H₂O groups appear to play a key role in the crystal packing of the Ln₃ clusters since there are close Cl···H–O interactions which link adjacent molecules (Cl···O 2.839 Å, Figure 3) forming 1-D structures. The structures are further connected by Cl···H–N hydrogen bonding between the uncoordinated Cl⁻ ion and the N–H group of the L ligand (Cl···N 3.178 Å and 3.111 Å). This results in a three-dimensional open network which has extended channels running along the *c*-axis (Figure 4). These channels measure approximately 7 × 7 Å and accommodate guest molecules of H₂O and EtOH. Hydrogen bonded interactions are present between the entrapped molecules and the surrounding supramolecular framework.

The addition of $Zn(OAc)_2 \cdot 2H_2O$ to the original reaction mixture obtained in the synthesis of 1c produces the acetate derivative { $[Yb_3L_4(OAc)_4] \cdot Cl \cdot EtOH$ }_n (2). The key difference between the structures 1a-c and 2 is that the coordinated Cl⁻ and H₂O units are now replaced with OAc⁻ groups. The acetates create a zigzag 1-D polymer by forming double (OAc⁻) bridges between Yb₃L₄ units (Figure 5). Interestingly, 2 crystallizes in the same space group as 1a-c (P4/ncc) and the 1-D structure exhibit similar crystal packing behavior in the solid state. Thus, **2** also has a $Cl \cdots H-N$ hydrogen bonding interaction between uncoordinated Cl⁻ and the N-H group of the imidazole ligand (Cl···N 3.215 and 3.305 Å). The resulting 3-D open network structure has extended channels running along the c-axis which are again approximately 7×7 Å in size and accommodate EtOH molecules (Figure 6). The overall structure of the Yb_3L_4 core of 2 is similar to that of 1a-c with the exception that each terminal Yb (III) ion now bears a chelating OAc⁻ group. This results in the terminal Yb (III) ions having a coordination number of 8. In previous studies of heteropolynuclear Zn₄Eu₂ cage complex, we discovered that aryl-Br units could engage in short intermolecular Br···O interactions resulting in interesting 3-D frameworks.⁹ However, in the complexes described in this paper no such interactions were observed.

The ¹H NMR spectrum of **1b** supports a structure in solution which is similar to that found in the solid state. The ¹H NMR spectra of the free ligand HL and **1b** at 298 K in



Figure 7. ¹H NMR spectra of the free ligand HL (a) and complex 1b (b) in CD₃CN at 298 K. In b, the peaks of solvent, H₂O and EtOH, together with the signal at 6.692 ppm of L^- , have been omitted for clarity.



Figure 8. Excitation and emission spectra of 1a in CH₃CN (5 \times 10⁻⁶ M) at 298 K.

CD₃CN are shown in Figure 7. The free ligand shows the presence of five peaks corresponding to nine C-H protons. In the ¹H NMR spectrum of **1b**, there are 10 reasonably sharp peaks which are assigned to the ligands bound in two different ways as described above. The spectra are unchanged after one month at room temperature indicating that 1b is thermally stable in solution under these conditions. A detailed analysis of the NMR data (2D-COSY) allows the assignment of these signals. Each L⁻ displays one signal for the three methoxy protons, two signals for the two benzyl protons, and two signals for the four benzimidazole protons. Mass spectroscopic studies (ESI-MS) for 1a-c support the presence of the Ln₃L₄ units in solution (experimental). For 2, ESI-MS data indicate that the 1-D polymeric structure in the solid state does not persist in solution $(m/z = 636, [Yb_3L_4(OAc)_2]^{3+})$. The photophysical properties of complexes 1a-c and 2 have been studied at 298 K both in the solid state and in solution. Upon excitation of the ligand-centered absorption band, all complexes show typical emission spectra of the Ln(III) ions. Complex 1a shows visible emission bands of Tb³⁺ ion ((${}^{5}D_{0} \rightarrow {}^{7}F_{i}$) transitions, j = 1, 2, 3, and 4, Figure 8), while **1b** shows the NIR



Figure 9. NIR emission spectra of 1b (5 \times 10⁻⁶ M) and 2 (2 \times 10⁻⁶ M) in CH₃CN at 298 K.

luminescence of the Er^{3+} ion assigned to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition at 1510 nm, and complexes 1c and 2 show that of the Yb³⁺ ion assigned to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition at about 978 nm (Figure 9). A similar luminescence is observed for each lanthanide complex in the solid state. The fluorescence quantum yield (Φ_{em}) of Tb³⁺ complex 1a in CH₃CN is 0.218,¹⁰ while the NIR luminescence quantum yields of 1b-c and 2 could not be measured due to instrumental limitations. The relative emission intensities of 1c and 2 were determined under the same experimental conditions. With the same absorbance value at 275 nm, the relative emission intensity at 978 nm was estimated to be 3.6 for 2:1c in CH₃CN, indicating that 2 has superior luminescence properties compared to 1c. The difference in luminescence properties may be because there are no coordinated H₂O molecules in 2 which can efficiently quench lanthanide luminescence.¹¹

Conclusions

A series of luminescent Ln_3 clusters of formula $[Ln_3L_4Cl_4-(H_2O)_2] \cdot Cl \cdot H_2O \cdot EtOH$ (1) (Ln = Tb (a), Er (b), Yb (c))

 $[Ln_3L_4Cl_4(H_2O)_2] \cdot Cl \cdot H_2O \cdot EtOH$ (1) (Ln = Tb (a), Er (b), Yb (c)) have been synthesized and characterized (HL=2-(1Hbenzoimidazol-2-yl)-4-bromo-6-methoxy-phenol). The Yb₃ cluster **1c** may be converted into a 1-D coordination polymer by treatment with Zn(OAc)₂·2H₂O. All complexes display intramolecular $\pi - \pi$ stacking and hydrogen bonded interactions in the solid state as well as lanthanide ion based luminescence in both solution and the solid.

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Supporting Information Available: X-ray crystallographic data for the free ligand HL and lanthanide complexes 1-4 (CIF). This material is available free of charge via the Internet at http://pubs. acs.org.

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