Synthesis and structures of luminescent ladder-like lanthanide coordination polymers of 4-hydroxybenzenesulfonate†‡

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Reaction of sodium 4-hydroxybenzenesulfonate dihydrate ($NaL\cdot 2H_2O$) with $LnCl_3\cdot 6H_2O$ (3 : 1) in refluxing methanol gives the novel isomorphous 1-D framework compounds $\{[LnL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (Ln = Tb, Er and Yb) in 46–60% yields; the structures of the compounds have been determined by X-ray crystallography and their luminescence properties determined.

The construction of metal–organic framework (MOF) or metal–organic coordination polymers containing lanthanide ions is currently of interest due to their potential application in materials science.[1] A common strategy is to employ a variety of organic ligands as spacers and lanthanide ions as nodes. A drawback here is that lanthanide ions generally display variable and high coordination numbers and the energy differences between the various coordination geometries are small.[2] Many lanthanide systems reported have involved the use of multidentate oxygen containing ligands such as carboxylates, amino acidates and pyridones.[3] Although alkylsulfonate groups $R–SO_3^-$ can adopt a variety of coordination modes, the coordination chemistry of this class of ligand has remained relatively unexplored, perhaps because sulfonate anions are often regarded as poorly interacting or even non-coordinating ligands for transition metals.[4,5] More recently studies involving Ag^+, Ba^{2+} or d-block transition metals and organosulfonates as spacers have been reported.[6] In these studies sulfonate groups were shown to coordinate to metal ions and in some cases both rigid and flexible frameworks were found. In contrast there are relatively few reports on the coordination of sulfonate groups with lanthanide ions.[7] In some cases alkylsulfonate groups have been introduced, not to coordinate with metal ions, but to increase the solubility of complexes in water or to form supramolecular structures through weak intermolecular interactions.[8]

As part of our interest in polynuclear lanthanide complexes,[9] we describe here the synthesis, structures and photophysical properties of three 1-D coordination polymers $\{[LnL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (Ln = Tb (**1**), Er (**2**) and Yb (**3**)), prepared using 4-hydroxybenzenesulfonate anion (L) as ligand. To the best of our knowledge, this is the first report of benzenesulfonate coordination polymers containing lanthanide ions. Interestingly, **1–3** show ladder-like 1-dimensional supramolecular structures in the solid state.

Reaction of sodium 4-hydroxybenzenesulfonate dehydrate ($NaL\cdot 2H_2O$) with the lanthanide salts $LnCl_3\cdot 6H_2O$ in a 3 : 1 molar ratio in refluxing MeOH provided the isomorphous 1-D framework materials $\{[LnL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (Ln = Tb (**1**), Er (**2**) and Yb (**3**)) in 46–60% yields. Crystalline samples of these colorless materials were obtained by slow diffusion of diethyl ether into the filtered reaction solutions over several weeks. Single crystal X-ray diffraction studies were employed to reveal the structures in the solid state.‡ Crystallographic data for **1–3** are presented in Table 1 and selected bond lengths and angles are given in Tables 2–4. The three complexes are isomorphous and crystallize in the orthorhombic space group *Imm*2 (no. 44, $Z = 4$) with half a lanthanide ion, one and half 4-hydroxybenzenesulfonate anions and one coordinated H_2O molecule per asymmetric unit. A view of the metal coordination environment in **1** is shown in Fig. 1. In this structure, the lanthanide complex has crystallographically imposed *m*-symmetry with Tb1 and two water molecules (O1w and O2w) on the mirror plane. The Tb atom is 8-coordinate, surrounded by

Table 1 Crystal data structure refinement for complexes **1–3**

	1	**2**	**3**
Formula	$C_{18}H_{23}O_{16}S_3Tb$	$C_{18}H_{23}O_{16}S_3Er$	$C_{18}H_{23}O_{16}S_3Yb$
Fw	750.46	758.80	764.58
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Imm*2	*Imm*2	*Imm*2
a/Å	19.336(4)	19.219(4)	19.244(4)
b/Å	24.529(5)	24.277(5)	24.149(5)
c/Å	5.4514(11)	5.4250(11)	5.4176(11)
V/Å^3	2585.5(9)	2531.2(9)	2517.7(9)
Z	4	4	4
D_{calc}/g cm^{-3}	1.928	1.991	2.017
Temperature/K	153(1)	153(1)	153(1)
$F(000)$	1488	1500	1508
μ, mm^{-1}	3.053	3.641	4.041
θ range/°	3.27–25.00	3.29–25.00	3.29–25.00
Reflns measured	2266	6935	2209
Reflns used	2266	2102	2209
Parameters	205	199	205
R^a $(I > 2\sigma(I))$	$R1 = 0.0439$ $wR2 = 0.1157$	$R1 = 0.0735$ $wR2 = 0.1366$	$R1 = 0.0528$ $wR2 = 0.1293$
R^a (all data)	$R1 = 0.0506$ $wR2 = 0.1193$	$R1 = 0.1940$ $wR2 = 0.1746$	$R1 = 0.0741$ $wR2 = 0.1411$
S	1.132	0.957	1.094

[a] $R1 = \Sigma|F_o| - |F_c|\Sigma|F_o|$. $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. $w = 1/[\Sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

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Table 2 Selected bond lengths (Å) and angles (°) for **1**. Symmetry code: #1: $1 - x, y, z$; #2: $x, y, 1 + z$; #3: $1 - x, y, 1 + z$

Tb(1)–O(6)	2.338(4)	O(2)–Tb(1)–O(4) #2	145.33(16)
Tb(1)–O(2)	2.351(4)	O(6)–Tb(1)–O(4) #3	71.85(17)
Tb(1)–O(4)	2.379(5)	O(2)–Tb(1)–O(4) #3	81.20(15)
Tb(1)–O(2W)	2.424(5)	O(6)–Tb(1)–O(2W)	72.83(14)
Tb(1)–O(1W)	2.490(5)	O(2)–Tb(1)–O(2W)	69.86(13)
O(6)–Tb(1)–O(6) #1	80.05(18)	O(4) #2–Tb(1)–O(2W)	137.08(13)
O(6)–Tb(1)–O(2)	80.97(14)	O(6)–Tb(1)–O(1W)	137.95(10)
O(6) #1–Tb(1)–O(2)	141.67(15)	O(2)–Tb(1)–O(1W)	74.67(14)
O(2)–Tb(1)–O(2) #1	94.1(2)	O(4) #2–Tb(1)–O(1W)	70.96(17)
O(6)–Tb(1)–O(4) #2	123.06(17)	O(2W)–Tb(1)–O(1W)	126.81(19)

Table 3 Selected bond lengths (Å) and angles (°) for **2**. Symmetry code: #1: $1 - x, y, z$; #2: $x, y, 1 + z$; #3: $1 - x, y, 1 + z$

Er(1)–O(2)	2.256(9)	O(6)–Er(1)–O(4) #2	125.1(3)
Er(1)–O(6)	2.280(7)	O(2)–Er(1)–O(4) #3	82.1(3)
Er(1)–O(4)	2.352(9)	O(6)–Er(1)–O(4) #3	71.7(3)
Er(1)–O(2W)	2.356(10)	O(2)–Er(1)–O(2W)	68.4(3)
Er(1)–O(1W)	2.445(9)	O(6)–Er(1)–O(2W)	71.9(3)
O(2) #1–Er(1)–O(2)	89.9(5)	O(4) #2–Er(1)–O(2W)	135.9(2)
O(2)–Er(1)–O(6) #1	139.9(3)	O(2)–Er(1)–O(1W)	75.6(3)
O(2)–Er(1)–O(6)	81.1(3)	O(6)–Er(1)–O(1W)	137.40(19)
O(6) #1–Er(1)–O(6)	81.3(3)	O(4) #2–Er(1)–O(1W)	70.1(3)
O(2)–Er(1)–O(4) #2	145.8(3)	O(2W)–Er(1)–O(1W)	128.2(4)

Table 4 Selected bond lengths (Å) and angles (°) for **3**. Symmetry code: #1: $1 - x, y, z$; #2: $x, y, 1 + z$; #3: $1 - x, y, 1 + z$

Yb(1)–O(2)	2.235(7)	O(6)–Yb(1)–O(2W)	71.82(19)
Yb(1)–O(6)	2.284(5)	O(2)–Yb(1)–O(4) #2	145.9(2)
Yb(1)–O(2W)	2.300(7)	O(6)–Yb(1)–O(4) #2	124.0(2)
Yb(1)–O(4)	2.346(7)	O(2W)–Yb(1)–O(4) #2	135.23(18)
Yb(1)–O(1W)	2.442(6)	O(2)–Yb(1)–O(4) #3	81.8(2)
O(2) #1–Yb(1)–O(2)	90.0(4)	O(6)–Yb(1)–O(4) #3	70.7(2)
O(2) #1–Yb(1)–O(6)	141.0(2)	O(2)–Yb(1)–O(1W)	75.44(19)
O(2)–Yb(1)–O(6)	82.1(2)	O(6)–Yb(1)–O(1W)	137.27(14)
O(6)–Yb(1)–O(6) #1	80.7(2)	O(2W)–Yb(1)–O(1W)	129.7(2)
O(2)–Yb(1)–O(2W)	69.6(2)	O(4) #2–Yb(1)–O(1W)	70.5(2)

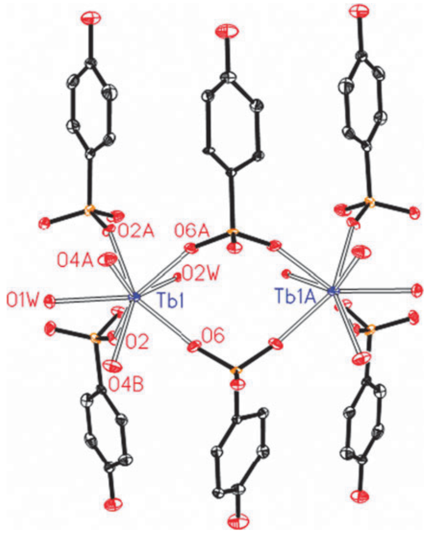

Fig. 1 Crystal structure of **1**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 25% probability level. Symmetry operator: $(x, -y, z)$ is used to generate Tb1A; $(x, y, 1 + z)$ for O4B; $(1 - x, y, 1 + z)$ for O4A and $(1 - x, y, z)$ for O2A and O6A.

eight oxygen atoms, six from six L ligands, two from two water molecules. Each Tb atom is connected to three other Tb atoms by six bridged L^- anions, forming an extended ladder-like structure (Fig. 2). In this 1-D structure, one Tb atom (node) is located at the junction position of the ladder and two bridged L^- ligands (spacer) are then located along each rung or edge. The distances between each rung and each edge are 5.451 Å and 5.958 Å, respectively. Each L^- anion bridges two Tb atoms through two oxygen atoms of the SO_3^- group. The Ln–O (SO_3^-) distances range from 2.338 to 2.490 Å (**1**), 2.256 to 2.445 Å (**2**) and 2.235 to 2.443 Å (**3**). Adjacent ladders are further linked by $O\cdots H_2O$ hydrogen bonds between the SO_3^- groups and un-coordinated water molecules ($O\cdots O$ distances: 2.335 to 3.015 Å (**1**), 2.425 to 2.990 Å (**2**) and 2.394 to 3.004 Å (**3**)). The resulting 3-dimensional structure has extended channels running along the *c*-axis (Fig. 3). As shown in Fig. 1 two oxygen atoms of each SO_3 group are bridging and one is terminal. All three complexes show similar infrared spectra. A strong band near 1027 cm^{-1} can be assigned to ν(S–O) stretching modes of the SO_3 groups but provide no additional structural information.[10]

There is considerable interest in the photophysical properties of lanthanide complexes since Ln^{3+} ions are capable of long-lived emissions with narrow band widths in the visible and near-infrared (NIR) regions. The photophysical properties of **1–3** were studied at 298K in solution. Complex **1** shows a visible emission typical of the Tb^{3+} ion, while either no fluorescence or only very weak NIR emissions due to Ln^{3+} ions were observed for **2** and **3**. The UV-Vis spectra of NaL and **1** are shown in Fig. 4. The free L^- anion exhibits absorption bands at 230, 275 and 282 nm, which are red-shifted upon coordination to the metal ion in **1**. The excitation and emission spectra of NaL and **1** are shown in Fig. 5. Excitation at the absorption band at 287 nm for the free L^- anion results in a broad emission band at $\lambda_{max} = 590$ nm. Excitation of the analogous ligand-centered absorption band of **1** ($\lambda_{ex} = 286$ nm), results in a typical emission band of Tb^{3+} ion ($^5D_4 \rightarrow {}^7F_n$ transitions, n = 6, 5, 4 and 3). It is noteworthy that the excitation spectrum of **1** is similar to that of NaL and

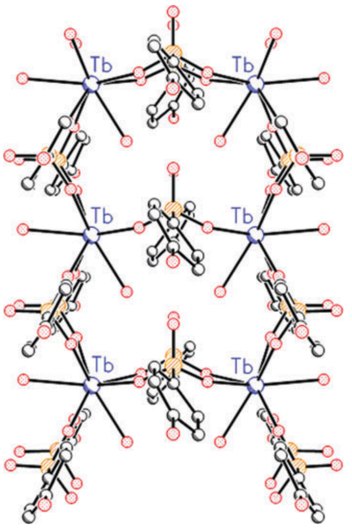

Fig. 2 A view of the ladder-like structure of **1** along the *a*-axis.

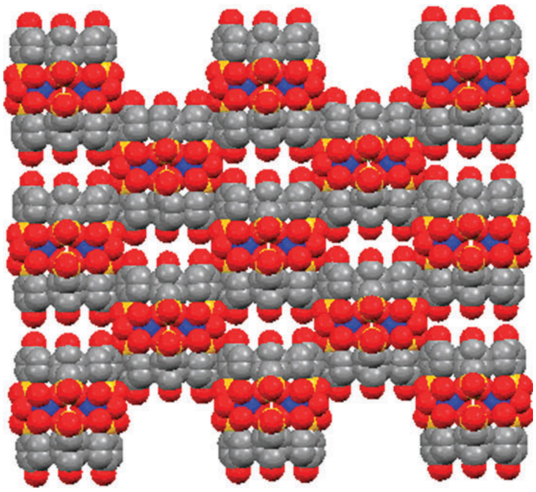

Fig. 3 A view of the 3-D network of **1** along the *c*-axis.

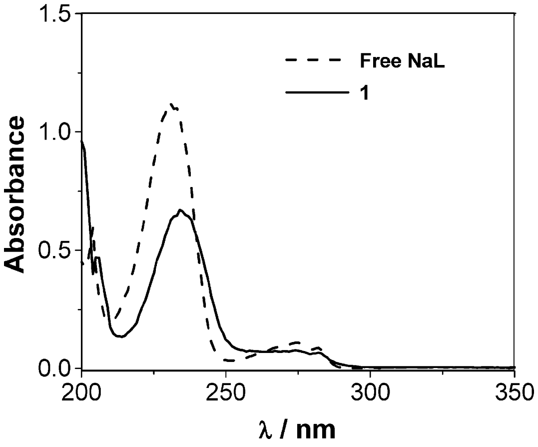

Fig. 4 Absorption spectra of sodium 4-hydroxybenzenesulfonate (NaL, --), and **1** (—).

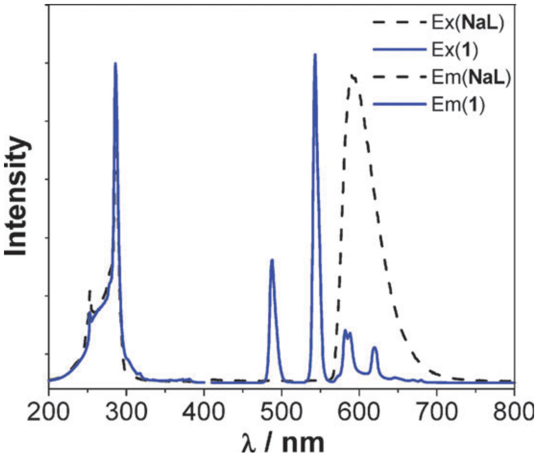

Fig. 5 Excitation and emission spectra of sodium 4-hydroxybenzenesulfonate (NaL, --), and **1** (—).

does not show the typical Tb^{3+} ion excitation bands. Meanwhile, no ligand-centered luminescence is found in the emission spectrum of **1**. These observations indicate that the ligand-to-metal energy transfer takes place efficiently in **1**.[11]

Experimental

All reactions were performed under dinitrogen atmospheres using standard Schlenk techniques. Metal salts, sodium 4-hydroxybenzenesulfonate dihydrate and solvents were purchased from Aldrich and used directly without further purification. Infrared (IR) spectra from 4000 to 400 cm^{-1} were recorded on a Nicolet IR 200 FTIR spectrometer. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Melting points were obtained in sealed glass capillaries and are uncorrected.

$\{[TbL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (1)

Sodium 4-hydroxybenzenesulfonate dihydrate ($NaL\cdot 2H_2O$, 0.070 g, 0.3 mmol) was added to a solution of $TbCl_3\cdot 6H_2O$ (0.037 g, 0.1 mmol) in MeOH (20 ml). The mixture was stirred and heated under reflux (6 h), cooled to room temperature, and filtered. Diethyl ether was allowed to diffuse slowly into the solution in a closed vessel at room temperature. Colorless single crystals of **1** were formed after two weeks. Yield: 0.045 g (60%). Mp >320 °C (dec). Anal. Found: C, 30.32; H, 3.10. Calc. for $C_{18}H_{19}O_{14}S_3Tb$ (M − $2H_2O$): C, 30.26; H, 2.68%. IR (MeOH, cm^{-1}): 3460(s), 2941(s), 2618(w), 2598(w), 2517(w), 2067(w), 1442(m), 1417(m), 1118(m), 1029(s), 668(m).

$\{[ErL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (2)

The procedure was the same as that for **1** except that $ErCl_3\cdot 6H_2O$ (0.038 g, 0.1 mmol) was used instead of $TbCl_3\cdot 6H_2O$. Colorless single crystals of **2** were formed after two weeks. Yield: 0.040 g (53%). Mp > 320 °C (dec). Anal. Found: C, 30.10; H, 3.05. Calc. for $C_{18}H_{19}O_{14}S_3Er$ (M − $2H_2O$): C, 29.91; H, 2.65%. IR (MeOH, cm^{-1}): 3342(s), 2942(s), 2831(s), 2594(w), 2517(w), 2043(w), 1446(m), 1417(m), 1115(m), 1025(s), 670(m).

$\{[YbL_3(H_2O)_2]\cdot 2H_2O\}_\infty$ (3)

The procedure was the same as that for **1** except that $YbCl_3\cdot 6H_2O$ (0.039 g, 0.1 mmol) was used instead of $TbCl_3\cdot 6H_2O$. Colorless single crystals of **3** were formed after two weeks. Yield: 0.035 g (46%). Mp > 320 °C (dec). Anal. Found: C, 29.80; H, 3.00. Calc. for $C_{18}H_{19}O_{14}S_3Yb$ (M − $2H_2O$): C, 29.67; H, 2.63%. IR (MeOH, cm^{-1}): 3336(s), 2941(s), 2833(s), 2598(w), 2520(w), 2230(w), 2043(w), 1658(w), 1442(m), 1414(m), 1111(m), 1029(s), 657(m).

X-Ray crystallography‡

Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[12] The 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.[13]

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