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PAPER

Construction of 1-D 4f and 3d–4f coordination polymers with flexible Schiff base ligands†

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Three new lanthanide 1-D coordination polymers ($\{[\text{Ln}_2(\text{H}_2\text{L})(\text{OAc})_6]\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Eu}$ (**1**), Er (**2**)) and $\{\text{YbNiLCl}(\text{OAc})_2(\text{H}_2\text{O})\}_n$ (**3**)) and a heterobinuclear complex $[\text{YbNiLCl}_3(\text{H}_2\text{O})_3]$ (**4**) are reported which are formed from salen type Schiff-base ligands H_2L ($\text{H}_2\text{L} = \text{N},\text{N}'\text{-bis(3-methoxysalicylidene)butane-1,4-diamine}$). The polymeric structures are formed by bridging H_2L units in the case of **1** and **2**, and by acetate groups in **3**. The structures of **1–4** were determined by single crystal X-ray crystallographic studies and their luminescence properties in MeCN solution were determined.

Introduction

Construction and characterization of coordination polymers continue to attract much attention owing to their potential application in catalysis, separations, photochemistry and electromagnetism.¹ Lanthanide (4f) homometallic and d-block transition metal–lanthanide (3d–4f) heterometallic coordination frameworks are currently of great interest for the potential to develop new optical, electrical and magnetic materials.² However, control over both the lanthanide coordination environment and the overall framework is often problematic due to the adoption of high coordination numbers and flexible geometries adopted by $\text{Ln}(\text{III})$ ions. Structures are often influenced by a variety of factors such as ligand geometries, ionic radius and the nature of counter ions.³ Compared with the growth of studies on 3d metal-based MOFs,^{1,4} reports of 4f or 3d–4f coordination polymers have been far fewer.^{2,5} Lanthanide ions behave as hard acids and they prefer oxygen to nitrogen donors, while d-block metal ions can coordinate to both N and O donors. One approach for the construction of 4f and 3d–4f frameworks is self-assembly of selected metal ions using ligands containing a mixed-donor atom set. The majority of 4f and 3d–4f coordination polymers reported so far have employed polydentate rigid ligands, such as multicarboxylic acids, pyridinecarboxylate, carbonyl, $\text{N}(\text{CN})_2^-$, macrocyclic and oxydiacetic ligands. A number of reports have been focused on the $[\text{Ln}–\text{Fe}/\text{Cu}]$ system in order to study magnetic properties.^{2,5,6}

Compartmental Schiff bases with two dissimilar metal-binding sites, one specific for 3d metal ions and another for 4f-block metal ions, have been employed for the synthesis of heterometallic 3d–4f complexes.⁷ However, most of these compounds are heterobinuclear or polynuclear complexes and there are very few reports of 4f and even fewer 3d–4f coordination polymers.⁸ Our recent studies have focused on the use of a variety of salen style Schiff base ligands with two dissimilar metal-binding sites (N_2O_2 and O_2O_2 , Scheme 1) for the synthesis of heterometallic 3d–4f complexes.⁹ For example, we recently reported five 1-D lanthanide coordination polymers which feature the flexible Schiff base ligand $\text{H}_2\text{L}'$ and $\text{H}_2\text{L}''$ (Scheme 1).^{9a} As part of our continuing studies focused on the assembly of lanthanide coordination frameworks we describe here the synthesis, structures and photophysical properties of three 1-D polymeric compounds $\{[\text{Ln}_2(\text{H}_2\text{L})(\text{OAc})_6]\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}\}_n$ ($\text{Ln} = \text{Eu}$ (**1**), Er (**2**)) and $\{\text{YbNiLCl}(\text{OAc})_2(\text{H}_2\text{O})\}_n$ (**3**) ($\text{H}_2\text{L} = \text{N},\text{N}'\text{-bis(3-methoxysalicylidene)butane-1,4-diamine}$). In the 4f homometallic polymers **1** and **2**, the flexible Schiff base ligands act as neutral bridging ligands between the metal centers resulting in the formation of 1-D coordination polymers, while the 1-D Ni–Yb coordination framework in **3** is created by the presence of bridging acetate (OAc^-) units. Interestingly, the formation of **3** appears to be OAc^- anion-dependent since the absence of OAc^- anion under similar reaction conditions results in the formation of a typical heterobinuclear complex $[\text{YbNiLCl}_3(\text{H}_2\text{O})_3]$ (**4**).

Scheme 1 Schiff-base ligands H_2L , $\text{H}_2\text{L}'$ and $\text{H}_2\text{L}''$.

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Experimental section

General considerations

Metal salts and solvents were purchased from Aldrich and used directly without further purification in the preparation of the free ligand and complexes. The solvents used for the photophysical investigations were dried and distilled under nitrogen. All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. The Schiff-base ligand H_2L was prepared according to well-established procedures.¹⁰ Physical measurements: NMR: VARIAN UNITY-plus 600 spectrometer (1H , 600 MHz) at 298 K; mass spectrometry: HRESI, Finnigan MAT TSQ 700; IR: Nicolet IR 200 FTIR spectrometer. Melting points were obtained in sealed glass capillaries under N_2 on an Electrothermal melting point apparatus and are uncorrected. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer. Excitation and visible emission spectra were recorded on a QuantaMaster PTI fluorimeter.

Synthesis of complexes 1–4

$\{[Eu_2(H_2L)(OAc)_6] \cdot EtOH \cdot 2H_2O\}_n$ (**1**). The compound $Eu(OAc)_3 \cdot 4H_2O$ (0.165 g, 0.5 mmol) was added to a solution of H_2L (0.178 g, 0.5 mmol) in $CH_3CN/EtOH$ (1 : 3, 20 mL). The mixture was stirred and heated under reflux (20 min). The mixture was then cooled to room temperature and filtered. Diethyl ether was allowed to diffuse slowly into the filtrate in a closed vessel at room temperature and yellow crystals were obtained after two weeks. The crystals were filtered off and washed with $EtOH$ (5 mL). Yield (based on $Eu(OAc)_3 \cdot 4H_2O$): 0.102 g (37%). mp > 220 °C (dec.). C, H and N microanalytical data on all compounds proved to be unreliable, possibly due to variable loss of solvent molecules while under vacuum. HRESI-MS (MeOH) m/z : 967 $[Eu_2(H_2L)(OAc)_4(H_2O)_3OH]^+$, 1000 $[Eu_2(H_2L)(OAc)_5EtOH]^+$, 1059 $[Eu_2(H_2L)(OAc)_6EtOH + H]^+$. IR (CH_3OH , cm^{-1}): 3391(m), 2981 (s), 1652 (s), 1557 (s), 1540 (s), 1456 (s), 1400 (m), 1253 (w), 1215 (w), 1063 (s), 1053 (s), 1031 (w), 1009 (w), 800 (m).

$\{[Er_2(H_2L)(OAc)_6] \cdot EtOH \cdot 2H_2O\}_n$ (**2**). The procedure was the same as that for **1** using $Er(OAc)_3 \cdot 4H_2O$ (0.172 g, 0.5 mmol). Yellow crystals of **2** were formed after two weeks. Yield (based on $Er(OAc)_3 \cdot 4H_2O$): 0.154 g (55%). mp > 222 °C (dec.). HRESI-MS (MeOH) m/z : 818 $[Er_4(H_2L)(OAc)_{10}H_2O]^+$, 997 $[Er_2(H_2L)(OAc)_4(H_2O)_3OH]^+$, 1049 $[Er_2(H_2L)(OAc)_5(EtOH)H_2O]^+$, 1089 $[Er_2(H_2L)(OAc)_6 \cdot EtOH + H]^+$. 1H NMR (600 MHz, CD_3OD): δ (ppm) –36.817 (2H), –31.455 (2H), –25.856 (2H), –23.374 (6H), –20.118 (2H), –15.917 (2H), –15.145 (2H), –11.219 (2H), 1.166 (3H), 3.593 (2H), 6.800 (2H), 27.074 (2H), 31.657 (2H), 36.789 (2H), 50.444 (2H), 59.138 (2H), 65.944 (2H), 68.061 (2H), 76.607 (6H). IR (CH_3OH , cm^{-1}): 3179 (w), 2943 (w), 1643 (m), 1541 (s), 1446 (s), 1415 (m), 1340 (m), 1212 (m), 1175 (w), 1047 (m), 1004 (s), 857 (w), 732 (m).

$\{YbNiLCl(OAc)_2(H_2O)\}_n$ (**3**). The compound $Ni(OAc)_2 \cdot 4H_2O$ (0.124 g, 0.5 mmol) was added to a solution of H_2L (0.178 g, 0.5 mmol) in $CH_3CN/EtOH$ (20 mL, 1 : 3). The mixture was stirred and heated under reflux (10 min). The reaction mixture was allowed to cool briefly, $YbCl_3 \cdot 6H_2O$ (0.194 g, 0.5 mmol) was added and the mixture was again heated under reflux (15 min), cooled and then filtered. Diethyl ether was allowed to diffuse slowly

into the filtrate in a closed vessel at room temperature and blue crystals were obtained after two weeks. The crystals were filtered off and washed with $EtOH$ (5 mL). Yield: 0.227 g (60%). mp > 202 °C (dec.). HRESI-MS (MeOH) m/z : 704 $[YbNiL_2(OAc)_2]^+$, 646 $[Yb_2NiL_2(OAc)_3 + H]^{2+}$. IR (CH_3OH , cm^{-1}): 3360 (m), 1624 (s), 1558 (s), 1471 (s), 1415 (s), 1302 (s), 1223 (s), 1168 (m), 1078 (m), 960 (m), 854 (m), 739 (s).

$[YbNiLCl_3(H_2O)_3]$ (**4**). The procedure was the same as that for **3** using $NiCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol). Blue crystals of **4** were formed after two weeks. Yield 0.193 g (52%). mp > 180 °C (dec.). IR (CH_3OH , cm^{-1}): 3330 (m), 1625 (s), 1468 (s), 1298 (s), 1223 (s), 1099 (w), 957 (m), 852 (m), 738 (s).

X-Ray crystallography

Data were collected on a Rigaku MiniFlex II CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 223 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. The structures were solved by direct methods and refined anisotropically using the full-matrix least-squares methods with the SHELX 97 program package.¹¹ 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.¹²

Results and discussion

Reactions of the Schiff-base ligand H_2L with $Ln(OAc)_3 \cdot 4H_2O$ ($Ln = Eu$ and Er) in refluxing $MeCN/EtOH$ (1 : 3) produced yellow solutions from which the 1-D polymers **1** and **2** were isolated as yellow crystalline solids in 37% and 55% yields, respectively. Reaction of H_2L with $YbCl_3 \cdot 6H_2O$ and $Ni(OAc)_2 \cdot 4H_2O$ gave the 1-D polymer **3**, while when $Ni(OAc)_2 \cdot 4H_2O$ was replaced by $NiCl_2 \cdot 6H_2O$ it gave the heterobinuclear complex **4**. The solid state structures of **1–4** were determined by single crystal X-ray crystallographic studies. Crystallographic data for all polymers are presented in Table 1 and selected bond lengths and angles are given in Tables 2–5. Complexes **1** and **2** are isomorphous and have the general formula $\{[Ln_2(H_2L)(OAc)_6] \cdot EtOH \cdot 2H_2O\}_n$ ($Ln = Eu$ (**1**) and Er (**2**)). The compounds crystallize in the triclinic space group $P\bar{1}$ with one Ln^{3+} ion, half an H_2L ligand and three coordinated OAc^- units per asymmetric unit. A view of the central Eu_2 unit of **1** is shown in Fig. 1a. Two Eu atoms are crystallographically equivalent and have coordination numbers of 9. Each Eu atom is coordinated to one bidentate OAc^- anion and they are bridged by four other OAc^- anions with a $Eu-Eu$ separation of 3.985 Å. The 1-D polymeric framework is completed by neutral Schiff base ligands (H_2L) which link the Eu_2 units *via* phenolic and methoxy oxygen atoms (Fig. 1b). The $Eu-Eu$ distance between two Eu atoms linked by H_2L is 11.199 Å. In complexes **1** and **2**, the distances for $Ln-O$ (phenolic) (2.379 Å (**1**), 2.327 Å (**2**)) and $Ln-O$ (methoxy) (2.699 Å (**1**), 2.678 Å (**2**)) are comparable to those found in the literature.^{7,9}

The reaction of H_2L with $YbCl_3 \cdot 6H_2O$ and $Ni(OAc)_2 \cdot 4H_2O$ in refluxing $MeCN/EtOH$ produces the 1-D polymeric material **3**. The compound crystallizes in the monoclinic space group $P2_1/c$ with two metal ions Yb^{3+} and Ni^{2+} , one L^{2-} ligand, two OAc^-

Table 1 Crystal data and structure refinement for complexes 1–4

	1	2	3	4
Formula	C ₃₄ H ₄₆ N ₂ O ₁₉ Eu ₂	C ₃₄ H ₄₆ N ₂ O ₁₉ Er ₂	C ₂₄ H ₃₀ ClN ₂ O ₉ NiYb	C ₂₀ H ₂₂ Cl ₃ N ₂ O ₇ NiYb
Fw	1090.65	1121.25	757.70	740.50
Cryst syst.	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Pba</i> 2
<i>a</i> /Å	8.815(5)	8.788(5)	10.064(2)	16.493(3)
<i>b</i> /Å	12.074(5)	11.889(4)	29.115(6)	35.431(7)
<i>c</i> /Å	13.158(4)	13.115(5)	9.1293(18)	8.6771(17)
α /°	108.260(5)	107.873(5)	90	90
β /°	90.776(4)	91.001(5)	96.85(3)	90
γ /°	98.218(5)	98.201(3)	90	90
<i>V</i> /Å ³	1313.7(10)	1288.1(9)	2656.1(9)	5070.8(17)
<i>Z</i>	1	1	4	8
<i>D_c</i> /g cm ^{−3}	1.379	1.445	1.895	1.940
<i>T</i> /K	153(1)	153(1)	153(1)	153(1)
<i>F</i> (000)	542	552	1500	2888
μ /mm ^{−1}	2.426	3.298	4.363	4.767
θ range/°	1.63–25.00	1.63–25.00	1.40–25.00	3.01–25.00
reflns meads	11 444	11 268	13 521	8296
reflns used	4626	4529	4656	8296
params	281	281	344	614
<i>R</i> ^a (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0566 <i>wR</i> ₂ = 0.1595	<i>R</i> ₁ = 0.0721 <i>wR</i> ₂ = 0.1821	<i>R</i> ₁ = 0.0483 <i>wR</i> ₂ = 0.1270	<i>R</i> ₁ = 0.0505 <i>wR</i> ₂ = 0.1106
<i>R</i> ^a (all data)	<i>R</i> ₁ = 0.0701 <i>wR</i> ₂ = 0.1857	<i>R</i> ₁ = 0.0962 <i>wR</i> ₂ = 0.2330	<i>R</i> ₁ = 0.0660 <i>wR</i> ₂ = 0.1672	<i>R</i> ₁ = 0.0762 <i>wR</i> ₂ = 0.1222
<i>S</i>	1.190	1.186	1.204	1.099

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum w[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}, w = 1/[\sigma^2(F_o^2) + (0.075P)^2], \text{ where } P = [\max(F_o^2, 0) + 2F_c^2]/3.$$

Fig. 1 (a) A view of the crystal structure of **1**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 30% probability level. (b) A view of the 1-D polymeric chain in **1**.

groups, one Cl[−] anion and one coordinated H₂O molecule per asymmetric unit. A view of the crystal structure of **3** is shown in Fig. 2a. The Ni²⁺ and Yb³⁺ ions in **3** are located in the inner N₂O₂ and O₂O₂ cavities of the Schiff-base ligand, respectively. Within each Yb–Ni–L moiety the Ni²⁺ and Yb³⁺ ions are bridged by a single bidentate OAc[−] group in addition to the phenolic oxygen atoms of the Schiff base ligand. The Ni–Yb separation is 3.356 Å.

The Ni²⁺ ion has bi-pyramidal geometry with one chlorine anion and one oxygen atom from the bidentate OAc[−] anion occupying the axial positions. The 1-D polymeric framework is formed by OAc[−] units which link the Yb–Ni–L moieties (Fig. 2b). The Yb–Yb distance between two Yb–Ni–L moieties is 5.871 Å. The Yb³⁺ ion is 8-coordinate, surrounded by eight oxygen atoms, four from the Schiff base ligand, three from OAc[−] anions and one from H₂O molecule. The average distances for Ni–O (phenolic), Ni–N, Ln–O (phenolic) and Ln–O (methoxy) are 2.049 Å, 2.059 Å, 2.251 Å and 2.479 Å, respectively.

It appears that the use of Ni(OAc)₂·4H₂O for the preparation of **3** is critical to the formation of the 1-D polymeric complex. The reaction of H₂L with YbCl₃·6H₂O and NiCl₂·6H₂O under similar conditions produces the heterobinuclear complex **4**. A view of the crystal structure of **4** is shown in Fig. 3. The compound crystallizes in the orthorhombic space group *Pba*2. The Ni²⁺ and Yb³⁺ ions are bound to the inner N₂O₂ and O₂O₂ cores of the Schiff base ligand, respectively, and have a separation of 3.554 Å. The Ni²⁺ ion has a bi-pyramidal geometry with two chlorine anions occupying axial positions. The Yb³⁺ ion is 8-coordinate from the four-oxygen atoms of the Schiff base ligand, one Cl[−] anion and three H₂O molecules. The average distances for Ni–O (phenolic) (2.062 Å), Ni–N (2.063 Å), Ln–O (phenolic) (2.326 Å) and Ln–O(methoxy) (2.455 Å) are comparable to those found in **3**.

It is noteworthy that, in complexes **1** and **2**, the neutral Schiff base ligand links Ln₂ centers forming 1-D coordination polymers and shows a “stretched” configuration (Fig. 1a). However, in complexes **3** and **4**, the deprotonated Schiff base ligand coordinates with Ni and Yb atoms forming a Yb–Ni–L moiety and exhibits an “enclosed” configuration (Fig. 2a and Fig. 3).

Table 2 Selected bond lengths (Å) and angles (°) for **1**. Symmetry operator (− *x*, − *y*, − *z*) generates equivalent atoms marked with “#”

Eu(1)–O(6)#	2.376(6)
Eu(1)–O(8)#	2.376(6)
Eu(1)–O(2)	2.379(6)
Eu(1)–O(5)	2.393(7)
Eu(1)–O(4)	2.460(7)
Eu(1)–O(7)	2.481(6)
Eu(1)–O(3)	2.518(7)
Eu(1)–O(8)	2.652(6)
Eu(1)–O(1)	2.699(6)
O(6)#–Eu(1)–O(8)#	76.5(2)
O(6)#–Eu(1)–O(2)	134.0(2)
O(8)#–Eu(1)–O(2)	148.0(2)
O(6)#–Eu(1)–O(5)	135.9(2)
O(8)#–Eu(1)–O(5)	76.5(2)
O(2)–Eu(1)–O(5)	82.6(2)
O(6)#–Eu(1)–O(4)	82.6(2)
O(8)#–Eu(1)–O(4)	84.2(3)
O(2)–Eu(1)–O(4)	89.8(3)
O(5)–Eu(1)–O(4)	128.7(3)
O(6)#–Eu(1)–O(7)	86.7(2)
O(8)#–Eu(1)–O(7)	125.5(2)
O(2)–Eu(1)–O(7)	73.8(2)
O(5)–Eu(1)–O(7)	81.4(2)
O(4)–Eu(1)–O(7)	144.2(2)
O(6)#–Eu(1)–O(3)	128.9(2)
O(8)#–Eu(1)–O(3)	76.9(2)
O(2)–Eu(1)–O(3)	74.8(2)
O(5)–Eu(1)–O(3)	76.7(2)
O(4)–Eu(1)–O(3)	52.6(3)
O(7)–Eu(1)–O(3)	143.6(2)
O(6)#–Eu(1)–O(8)	69.5(2)
O(8)#–Eu(1)–O(8)	75.3(2)
O(2)–Eu(1)–O(8)	119.9(2)
O(5)–Eu(1)–O(8)	70.3(2)
O(4)–Eu(1)–O(8)	148.3(3)
O(7)–Eu(1)–O(8)	50.3(2)
O(3)–Eu(1)–O(8)	140.8(2)
O(6)#–Eu(1)–O(1)	72.6(2)
O(8)#–Eu(1)–O(1)	143.3(2)
O(2)–Eu(1)–O(1)	61.9(2)
O(5)–Eu(1)–O(1)	140.2(2)
O(4)–Eu(1)–O(1)	72.0(2)
O(7)–Eu(1)–O(1)	72.2(2)
O(3)–Eu(1)–O(1)	108.1(2)
O(8)–Eu(1)–O(1)	110.8(2)

Table 3 Selected bond lengths (Å) and angles (°) for **2**. Symmetry operator (− *x*, − *y*, − *z*) generates equivalent atoms marked with “#”

Er(1)–O(7)	2.288(9)
Er(1)–O(5)	2.304(9)
Er(1)–O(2)	2.327(8)
Er(1)–O(6)#	2.341(9)
Er(1)–O(8)#	2.421(9)
Er(1)–O(4)	2.435(10)
Er(1)–O(3)	2.460(10)
Er(1)–O(7)#	2.624(9)
Er(1)–O(1)	2.678(9)
O(7)–Er(1)–O(5)	76.7(3)
O(7)–Er(1)–O(2)	148.0(3)
O(5)–Er(1)–O(2)	133.8(3)
O(7)–Er(1)–O(6)#	77.3(3)
O(5)–Er(1)–O(6)#	136.0(4)
O(2)–Er(1)–O(6)#	82.0(3)
O(7)–Er(1)–O(8)#	125.8(3)
O(5)–Er(1)–O(8)#	85.4(3)
O(2)–Er(1)–O(8)#	74.0(3)
O(6)#–Er(1)–O(8)#	81.9(3)
O(7)–Er(1)–O(4)	84.8(4)
O(5)–Er(1)–O(4)	82.1(4)
O(2)–Er(1)–O(4)	90.1(4)
O(6)#–Er(1)–O(4)	129.7(4)
O(8)#–Er(1)–O(4)	142.9(4)
O(7)–Er(1)–O(3)	76.0(3)
O(5)–Er(1)–O(3)	130.2(3)
O(2)–Er(1)–O(3)	75.4(3)
O(6)#–Er(1)–O(3)	75.4(4)
O(8)#–Er(1)–O(3)	143.9(3)
O(4)–Er(1)–O(3)	54.7(4)
O(7)–Er(1)–O(7)#	74.7(4)
O(5)–Er(1)–O(7)#	69.1(3)
O(2)–Er(1)–O(7)#	120.4(3)
O(6)#–Er(1)–O(7)#	70.2(3)
O(8)#–Er(1)–O(7)#	51.2(3)
O(4)–Er(1)–O(7)#	147.6(4)
O(3)–Er(1)–O(7)#	138.6(3)
O(7)–Er(1)–O(1)	142.6(3)
O(5)–Er(1)–O(1)	71.9(3)
O(2)–Er(1)–O(1)	62.5(3)
O(6)#–Er(1)–O(1)	140.0(3)
O(8)#–Er(1)–O(1)	71.5(3)
O(4)–Er(1)–O(1)	71.3(3)
O(3)–Er(1)–O(1)	109.9(3)
O(7)#–Er(1)–O(1)	111.2(3)

We have probed the nature of these coordination polymers in solution using ^1H NMR and high resolution ESI mass spectrometry studies. The ^1H NMR spectrum of **2** in CD_3OD at room temperature shows the presence of 15 slightly broadened peaks ranging from -40 to $+80$ ppm (see Fig. S1, Supporting Information†). These peaks correspond to the 21 C-H protons from one half of the half Schiff base ligand and three coordinated OAc^- groups which corresponds to the formula determined by the crystallographic analysis. The ESI mass spectra of both complexes **1** and **2** in MeOH show some $[\text{Ln}_2(\text{H}_2\text{L})]^+$ fragments such as $[\text{Ln}_2(\text{H}_2\text{L})(\text{OAc})_4(\text{H}_2\text{O})_3\text{OH}]^+$, $[\text{Ln}_2(\text{H}_2\text{L})(\text{OAc})_5\text{EtOH}]^+$ and $[\text{Ln}_2(\text{H}_2\text{L})(\text{OAc})_6\text{EtOH} + \text{H}]^+$. Meanwhile, two fragments $[\text{YbNiL}(\text{OAc})_2]^+$ and $[\text{Yb}_2\text{NiL}_2(\text{OAc})_3 + \text{H}]^{2+}$ were observed in the ESI mass spectrum of **3**. This data indicates that in solution the 1-D polymeric structures of the complexes break down into more soluble subunits which appear to retain the same metal:ligand stoichiometry as that found in the solid state.

Luminescence studies

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.¹³ The photophysical properties of the Eu(III) complex **1** were studied in MeCN. The free ligand H_2L exhibits absorption bands at 222, 261, 327, and 422 nm which are all red-shifted upon co-ordination to metal ions in **1** (Fig. 4). The emission spectrum of the free ligand H_2L and the excitation and emission spectra of **1** are shown in Fig. 5. Excitation of the absorption band at 316 nm of the free ligand H_2L produces a broad emission band at $\lambda_{\text{max}} = 490$ nm. Upon excitation of the ligand centered absorption bands, **1** shows typical visible emission bands of the Eu^{3+} ion ($^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions, $j = 0, 1, 2, 3$ and 4), while the ligand centered $^1\pi-\pi^*$ emission was not detected. The appearance of the symmetry-forbidden emission $^5\text{D}_0 \rightarrow ^7\text{F}_0$ at 579 nm indicates that the Eu^{3+} ions in **1** occupy sites with low symmetry and have no inversion center.¹⁴ This is further confirmed by the intensity ratio of 3.0 for $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$, which is a good measure of the

Table 4 Selected bond lengths (Å) and angles (°) for **3**. Symmetry operator ($x, -y, \frac{1}{2} + z$) generates equivalent atoms marked with “#”

Yb(1)–O(2)	2.233(6)
Yb(1)–O(3)	2.268(6)
Yb(1)–O(8)	2.273(6)
Yb(1)–O(6)#	2.291(6)
Yb(1)–O(5)	2.329(6)
Yb(1)–O(9)	2.356(7)
Yb(1)–O(4)	2.465(7)
Yb(1)–O(1)	2.493(6)
Ni(1)–O(2)	2.038(6)
Ni(1)–N(2)	2.044(8)
Ni(1)–O(3)	2.058(6)
Ni(1)–N(1)	2.074(8)
Ni(1)–O(7)	2.121(6)
Ni(1)–Cl(1)	2.455(3)
O(2)–Yb(1)–O(3)	72.8(2)
O(2)–Yb(1)–O(8)	77.4(2)
O(3)–Yb(1)–O(8)	76.1(2)
O(2)–Yb(1)–O(6)#	115.8(2)
O(3)–Yb(1)–O(6)#	146.4(2)
O(8)–Yb(1)–O(6)#	74.6(2)
O(2)–Yb(1)–O(5)	143.7(2)
O(3)–Yb(1)–O(5)	122.6(2)
O(8)–Yb(1)–O(5)	135.5(2)
O(6)#–Yb(1)–O(5)	71.1(2)
O(2)–Yb(1)–O(9)	79.1(2)
O(3)–Yb(1)–O(9)	75.9(2)
O(8)–Yb(1)–O(9)	147.7(2)
O(6)#–Yb(1)–O(9)	136.5(2)
O(5)–Yb(1)–O(9)	74.5(2)
O(2)–Yb(1)–O(4)	135.7(2)
O(3)–Yb(1)–O(4)	66.0(2)
O(8)–Yb(1)–O(4)	77.7(2)
O(6)#–Yb(1)–O(4)	91.8(2)
O(5)–Yb(1)–O(4)	76.0(2)
O(9)–Yb(1)–O(4)	105.0(2)
O(2)–Yb(1)–O(1)	65.2(2)
O(3)–Yb(1)–O(1)	131.3(2)
O(8)–Yb(1)–O(1)	115.6(2)
O(6)#–Yb(1)–O(1)	77.2(2)
O(5)–Yb(1)–O(1)	83.4(2)
O(9)–Yb(1)–O(1)	73.1(2)
O(4)–Yb(1)–O(1)	158.9(2)
O(2)–Ni(1)–N(2)	169.9(3)
O(2)–Ni(1)–O(3)	81.4(2)
N(2)–Ni(1)–O(3)	89.1(3)
O(2)–Ni(1)–N(1)	89.9(3)
N(2)–Ni(1)–N(1)	99.6(3)
O(3)–Ni(1)–N(1)	171.3(3)
O(2)–Ni(1)–O(7)	87.0(2)
N(2)–Ni(1)–O(7)	95.9(3)
O(3)–Ni(1)–O(7)	86.7(2)
N(1)–Ni(1)–O(7)	93.1(3)
O(2)–Ni(1)–Cl(1)	89.69(18)
N(2)–Ni(1)–Cl(1)	86.9(2)
O(3)–Ni(1)–Cl(1)	89.89(19)
N(1)–Ni(1)–Cl(1)	89.9(2)
O(7)–Ni(1)–Cl(1)	175.53(19)

Table 5 Selected bond lengths (Å) and angles (°) for **4**

Yb(1)–O(3)	2.310(7)
Yb(1)–O(2)	2.342(7)
Yb(1)–O(1 W)	2.377(8)
Yb(1)–O(3 W)	2.395(10)
Yb(1)–O(2 W)	2.404(10)
Yb(1)–O(4)	2.450(6)
Yb(1)–O(1)	2.461(7)
Yb(1)–Cl(1)	2.795(2)
Ni(1)–N(2)	2.047(9)
Ni(1)–O(2)	2.062(7)
Ni(1)–O(3)	2.064(7)
Ni(1)–N(1)	2.079(10)
Ni(1)–Cl(3)	2.426(4)
Ni(1)–Cl(2)	2.716(4)
O(3)–Yb(1)–O(2)	66.8(2)
O(3)–Yb(1)–O(1 W)	75.3(3)
O(2)–Yb(1)–O(1 W)	79.6(3)
O(3)–Yb(1)–O(3 W)	77.7(3)
O(2)–Yb(1)–O(3 W)	76.7(3)
O(1 W)–Yb(1)–O(3 W)	149.3(3)
O(3)–Yb(1)–O(2 W)	127.1(3)
O(2)–Yb(1)–O(2 W)	136.8(3)
O(1 W)–Yb(1)–O(2 W)	68.3(3)
O(3 W)–Yb(1)–O(2 W)	141.6(2)
O(3)–Yb(1)–O(4)	66.3(2)
O(2)–Yb(1)–O(4)	131.9(3)
O(1 W)–Yb(1)–O(4)	98.2(3)
O(3 W)–Yb(1)–O(4)	83.7(4)
O(2 W)–Yb(1)–O(4)	82.2(3)
O(3)–Yb(1)–O(1)	129.8(2)
O(2)–Yb(1)–O(1)	64.8(2)
O(1 W)–Yb(1)–O(1)	83.6(3)
O(3 W)–Yb(1)–O(1)	103.3(3)
O(2 W)–Yb(1)–O(1)	83.1(3)
O(4)–Yb(1)–O(1)	163.3(3)
O(3)–Yb(1)–Cl(1)	140.28(19)
O(2)–Yb(1)–Cl(1)	125.93(17)
O(1 W)–Yb(1)–Cl(1)	139.6(2)
O(3 W)–Yb(1)–Cl(1)	71.0(2)
O(2 W)–Yb(1)–Cl(1)	72.6(2)
O(4)–Yb(1)–Cl(1)	86.28(15)
O(1)–Yb(1)–Cl(1)	81.79(18)
N(2)–Ni(1)–O(2)	166.9(3)
N(2)–Ni(1)–O(3)	90.1(3)
O(2)–Ni(1)–O(3)	76.8(3)
N(2)–Ni(1)–N(1)	101.6(4)
O(2)–Ni(1)–N(1)	91.4(3)
O(3)–Ni(1)–N(1)	166.6(3)
N(2)–Ni(1)–Cl(3)	90.7(3)
O(2)–Ni(1)–Cl(3)	90.9(2)
O(3)–Ni(1)–Cl(3)	98.8(2)
N(1)–Ni(1)–Cl(3)	87.6(3)
N(2)–Ni(1)–Cl(2)	91.0(3)
O(2)–Ni(1)–Cl(2)	88.1(2)
O(3)–Ni(1)–Cl(2)	84.3(2)
N(1)–Ni(1)–Cl(2)	89.0(3)
Cl(3)–Ni(1)–Cl(2)	176.48(1)

nature and symmetry of the first coordination sphere of Eu^{3+} ion.¹⁵ The emissive lifetime, $26.59 \pm 1.53 \mu\text{s}$ at room temperature, was obtained by fitting the data to a single-exponential decay curve. The overall quantum yield of **1** in MeCN was determined as 0.015 relative to $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ in water (bipy = 2,2'-bipyridine; $\Phi_{\text{em}} = 0.028$)¹⁶ and corrected for the refractive index of the solvent. This value is higher than that of 1-D coordination polymer **EuL'** but less than that of **TbL''**.^{9a} For complexes **2–4**, either no fluorescence or only very weak emissions in near-infrared (NIR) range due to Ln^{3+} ions were observed under the experimental conditions employed.

Conclusions

Three 1-D 4f and 3d–4f coordination polymers **1–3** and one heterobinuclear Ni–Yb complex **4** with Schiff-base ligand H_2L have been prepared and structurally characterized. In the lanthanide coordination polymers **1–2**, the flexible neutral salen ligand (H_2L) acts as a bridge or linker in the formation of 1-D coordination frameworks. In the Ni–Yb coordination polymer **3**, acetate (OAc^-) is employed as a linker in the formation of such framework, while the absence of acetate under similar reaction conditions results in

Fig. 2 (a) A view of the crystal structure of **3**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 30% probability level. Symmetry operator ($x, -y, \frac{1}{2} + z$) generates equivalent atoms marked with "A". Symmetry operator ($x, y, 1 + z$) generates equivalent atoms marked with "B". (b) A view of the 1-D polymeric chain in **3**.

Fig. 3 A view of the molecular structure of **4**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 30% probability level.

the formation of the heterobinuclear complex **4**. Complex **1** shows the typical visible emission of Eu^{3+} ions.

Fig. 4 Absorption spectra of the free H_2L and $\text{Eu}(\text{III})$ complex **1**.

Fig. 5 Excitation spectrum of **1** (.....) and emission spectra of the free ligand H_2L (---) and **1** (—) in CH_3CN .

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