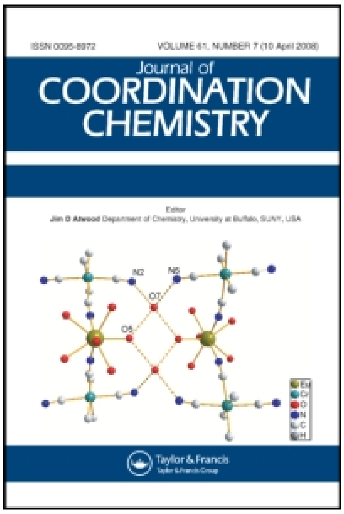

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Synthesis, crystal structure, and characterization of two lanthanide coordination polymers based on isonicotinate ligand

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Synthesis, crystal structure, and characterization of two lanthanide coordination polymers based on isonicotinate ligand

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Two new europium complexes [Eu(inic)$_3$(H$_2$O)] (**1**) and [Eu(inic)$_3$] (**2**) [inic = isonicotinate] have been structurally determined by single-crystal X-ray diffraction and characterized by elemental analysis, infrared spectroscopy, fluorescence, and thermogravimetric analysis. In the two complexes, bifunctional isonicotinate ligands interlink europium metal ions to construct 2-D (for **1**) and 3-D (for **2**) coordination polymeric networks.

Keywords: Europium complexes; Isonicotinic acid; Luminescence; Thermal behavior; Crystal structure

1. Introduction

There has been intense research on design and synthesis of intriguing architectures and functional lanthanide complexes [1–3]. Their capacities for gas storage [4], luminescence [5], magnetism [6], and other potential applications have been widely investigated. Their light-harvest units can act as antennas for collecting light and transferring energy to the lanthanide metal centers, resulting in extensive photoluminescence [7].

Lanthanide ions possess high coordination numbers and strong coordination tendency with oxygen donors, so a ligand with carboxylate groups is good for constructing lanthanide–organic coordination polymers [8–13]. Pyridine-carboxylic acids and analogs, such as 3-hydroxypicolinic acid (HpicOH) [14], pyridine-2,5-dicarboxylic acid (PYDC) [15], 5-nitroisophthalic acid (H$_2$Nip) [16], pyridine-3,5-dicarboxylic acid (H$_2$PDA) [17], 4-hydroxypyridine-2,6-dicarboxylic (chelidamic) acid (H$_3$Chel) [18], 2,2-bipyridine-3,3-dicarboxylic acid (BPDC) [19], pyrazine-2-carboxylate (PYZC) [20], and 1,3,5-tri(carboxymethyl)benzene (TCMB) [21] provide various coordination modes to form lanthanide–organic coordination polymers under appropriate synthetic conditions. Other pyridine carboxylic acids, such as isonicotinic (Hinic) acid, used in this work, and nicotinic (Hnic) acid are potential chelates with

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interesting possibilities of having bifunctional bridging ligands with oxygen and nitrogen donors [22].

Herein, we report two new europium complexes [Eu(inic)$_3$(H$_2$O)] (**1**) and [Eu(inic)$_3$] (**2**), which were synthesized and structurally characterized by elemental analysis, infrared (IR) spectroscopy, fluorescent spectra, and thermogravimetric analysis (TGA), as well as single crystal X-ray diffraction. In the two complexes, bifunctional isonicotinate ligands interlink europium ions to construct 2-D (for **1**) and 3-D (for **2**) coordination polymers.

2. Experimental

2.1. *Materials and methods*

The materials and reagents were obtained commercially and used as purchased. Elemental (C, H, N) analyses were performed on a Perkin-Elmer 240 element analyzer. FT-IR spectra were recorded from KBr pellets from 400 to 4000 cm^{-1} on a Nicolet 5DX spectrometer. TGA experiments were carried out on a Perkin-Elmer TGA 7 TG analyzer with a heating rate of 10°C min^{-1} from room temperature to 750°C under nitrogen. The luminescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

2.2. *Hydro(solvo)thermal synthesis*

2.2.1. [Eu(inic)$_3$(H$_2$O)] (1). A mixture of isonicotinic acid (0.123 g, 1 mmol), Eu(NO$_3$)$_3$ (0.176 g, 0.5 mmol), AgSCN (0.087 g, 0.5 mmol), KSCN (0.05 g, 0.5 mmol), and H$_2$O (10 mL) was sealed in a 20 mL Teflon-lined stainless-steel autoclave and heated at 160°C for 50 h, then cooled to room temperature at 10°C h^{-1} to obtain colorless block crystals of **1** (yield: 55% based on Eu). Anal. Calcd for $EuC_{18}H_{14}N_3O_7$ (%): C, 40.30; H, 2.60; N, 7.80. Found (%): C, 40.27; H, 2.52; N, 7.78. IR frequencies (KBr, cm^{-1}): νs (OH) 3412 s; νs (COO) 1637 s, 1618 s, 1562 s, 1437 s; νs (CH) 1131 s, 773w, 621 s, 479 m.

2.2.2. [Eu(inic)$_3$] (2). A mixture of isonicotinic acid (0.123 g, 1 mmol), Eu(NO$_3$)$_3$ (0.176 g, 0.5 mmol), AgNO$_3$ (0.087 g 0.5 mmol), KSCN (0.10 g, 1 mmol), and CH$_3$CN (10 mL) was sealed in a 20 mL Teflon-lined stainless-steel autoclave and heated at 150°C for 72 h, then cooled to room temperature at 10°Ch^{-1} to obtain colorless block crystals of **2** (yield: 51% based on Eu). Anal. Calcd for $EuC_{18}H_{12}N_3O_6$ (%): C, 41.70; H, 2.30; N, 8.10. Found (%): C, 41.68; H, 2.31; N, 8.11. IR frequencies (KBr, cm^{-1}): νs (COO) 1629 s, 1620 s, 1614 s, 1443 s; νs (CH) 1222 s, 774w, 616 s, 501 m.

2.3. *X-ray crystallography*

Single crystal X-ray diffraction data for **1** and **2** were collected at room temperature on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Data collection and reduction were

Table 1. Crystallographic data for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{18}H_{14}EuN_3O_7$	$C_{18}H_{12}EuN_3O_6$
Formula weight	536.28	518.27
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
Unit cell dimensions (Å, °)		
a	19.7562(12)	10.6883(8)
b	9.6058(6)	9.6931(7)
c	10.2118(6)	17.4922(13)
α	90	90
β	97.6320(10)	101.3260(10)
γ	90	90
Volume (Å^3), Z	1920.77, 4	1776.95, 4
Calculated density (g cm^{-3})	1.855	1.937
Absorption coefficient (mm^{-1})	3.312	3.572
Crystal size (mm^3)	0.20 × 0.15 × 0.10	0.20 × 0.15 × 0.10
F(000)	1048	1008
Parameters	268	253
Goodness-of-fit	1.048	1.036
R_1 $[I > 2\sigma(I)]^a$	0.0163	0.0216
wR_2 (all data)^b	0.0392	0.0461

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b\ wR = \left[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\right]^{1/2}$.

performed using SMART and SAINT software [17]. A multi-scan absorption correction was applied using SADABS [23]. The two structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package [23]. Hydrogens were located from difference Fourier maps and refined using a riding model. Crystal parameters and details of data collection and refinement are summarized in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single-crystal X-ray diffraction revealed that [Eu(inic)$_3$(H$_2$O)] (**1**) belongs to a monoclinic system with space group *Cc*, representing a 2-D layered network. As illustrated in figure 1(a), **1** contains one Eu(III), three inic ligands, and one-coordinated water molecule in the asymmetric unit. The Eu(III) is eight-coordinate by six oxygen donors from five inic ligands, one nitrogen from a inic, and one water molecule. Eu(III) has a bicapped trigonal prismatic coordination sphere with Eu–O bond lengths from 2.309(3) to 2.506(3) Å and O–Eu–O bond angles 52.57(9)–156.65(9)° (table 2). The Eu–O(chelating) distances are longer than the Eu–O (bridging) distance, due to the bidentate chelating mode, where the small bite angle O(3)–Eu(1)–O(4) weakens the Eu–O bonding interactions. Meanwhile, the Eu(1)–N(2) distance is 2.655(3) Å, longer than any Eu–O distances.

In the polymeric structure of **1**, the carboxylates of inic link europiums to form a chain running along the *a*-axis. The chains are further interconnected by carboxylates of

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Eu(1)–O(6)#1	2.309(3)	O(6)–Eu(1)–O(1)	93.40(15)
Eu(1)–O(1)	2.344(5)	O(6)–Eu(1)–O(5)	86.93(15)
Eu(1)–O(5)	2.349(5)	O(6)–Eu(1)–O(2)	149.15(12)
Eu(1)–O(2)#2	2.355(3)	O(6)–Eu(1)–O(1w)	140.31(11)
Eu(1)–O(1w)	2.437(3)	O(6)–Eu(1)–O(3)	78.65(11)
Eu(1)–O(3)	2.506(3)	O(6)–Eu(1)–O(4)	78.29(11)
Eu(1)–O(4)	2.479(3)	O(5)–Eu(1)–O(2)	95.82(15)
Eu(1)–N(2)#3	2.655(3)	O(5)–Eu(1)–O(1w)	86.72(15)
O(6)–Eu(1)–N(2)	72.73(11)	O(5)–Eu(1)–O(4)	73.05(15)
O(1)–Eu(1)–O(5)	156.65(9)	O(5)–Eu(1)–O(3)	125.41(15)
O(1)–Eu(1)–O(2)	95.75(15)	O(5)–Eu(1)–N(2)	78.15(16)
O(1)–Eu(1)O(1w)	78.16(15)	O(1w)–Eu(1)–O(4)	136.09(11)
O(1)–Eu(1)–O(4)	129.88(16)	O(1w)–Eu(1)–O(3)	134.71(12)
O(1)–Eu(1)–O(3)	77.31(15)	O(1w)–Eu(1)–N(2)	67.61.71(12)
O(1)–Eu(1)–N(2)	79.66(17)	O(4)–Eu(1)–O(3)	52.57(9)
O(2)–Eu(1)O(1w)	70.52(12)	O(4)–Eu(1)–N(2)	139.84(11)
O(2)–Eu(1)–O(4)	76.25(11)	O(3)–Eu(1)–N(2)	141.80(11)
O(2)–Eu(1)–O(3)	74.78(11)	O(2)–Eu(1)–N(2)	137.94(12)
Eu(1)–O(3)#1	2.316(2)	O(2)–Eu(1)–O(6)	73.16(8)
Eu(1)–O(2)#2	2.331(2)	O(3)–Eu(1)–O(6)	126.77(8)
Eu(1)–O(1)#3	2.334(2)	O(4)–Eu(1)–O(5)	78.67(8)
Eu(1)–O(4)	2.369(2)	O(1)–Eu(1)–O(5)	136.22(8)
Eu(1)–O(5)	2.464(2)	O(2)–Eu(1)–O(5)	111.37(8)
Eu(1)–O(6)	2.479(2)	O(3)–Eu(1)–O(5)	77.95(8)
Eu(1)–N(3)#4	2.628(3)	O(1)–Eu(1)–O(4)	144.33(8)
Eu(1)–N(1)	2.695(3)	O(2)–Eu(1)–O(4)	78.65(8)
O(3)–Eu(1)–O(2)	154.33(8)	O(3)–Eu(1)–O(4)	80.01(8)
O(3)–Eu(1)–O(1)	110.16(8)	O(2)–Eu(1)–O(1)	80.26(8)
O(1)–Eu(1)–O(6)	95.44(8)	O(4)–Eu(1)–O(6)	105.45(8)
O(5)–Eu(1)–O(6)	52.85(8)	O(2)–Eu(1)–N(3)	80.46(9)
O(3)–Eu(1)–N(3)	80.61(9)	O(1)–Eu(1)–N(3)	72.57(8)
O(4)–Eu(1)–N(3)	75.79(8)	O(5)–Eu(1)–N(3)	149.02(8)
O(6)–Eu(1)–N(3)	152.61(9)	O(3)–Eu(1)–N(1)	75.60(8)
O(2)–Eu(1)–N(1)	129.40(8)	O(1)–Eu(1)–N(1)	66.44(8)
O(4)–Eu(1)–N(1)	147.13(8)	O(5)–Eu(1)–N(1)	74.97(9)
O(6)–Eu(1)–N(1)	73.36(9)	N(3)–Eu(1)–N(1)	120.63(9)

Symmetry codes: Complex **1**: #1 x, $1-y$, $0.5+z$; #2 x, $1-y$, $-0.5+z$; #3 x, $y-1$, z; Complex **2**: #1 $-x$, $1-y$, $-z$; #2 x, $0.5-y$, $-0.5+z$; #3 $1-x$, $0.5+y$, $0.5-z$; #4 x, $1+y$, z.

inic to form a 2-D layered network (figure 1b). Intermolecular interactions play a significant role in the formation and stability of the complex; as shown in table 3, there are two hydrogen bonds in **1**, O(1W)–H(1A)···N(3) and O(1W)–H(1B)···O(3), which result in formation of a 3-D supramolecular network (figure 1c), and enhance the stability of **1**.

As synthesized by solvothermal method, [Eu(inic)$_3$] (**2**) is a monoclinic system with space group $P2_1/c$. Single-crystal X-ray diffraction reveals an open 3-D coordination framework constructed by inic ligands and europium. In the asymmetric unit, there is one Eu(III) and three inic ligands (figure 2a). Each europium is coordinated by six oxygens from five different inic ligands and two nitrogens from two inic ligands, displaying a bicapped trigonal prismatic geometry. The Eu–O bond distances and O–Eu–O bond angles vary from 2.316(2) to 2.479(2) Å and 52.85(8) to 154.33(8)°, respectively. The mean Eu–O bond distance of 2.382(2) Å is comparable with that found in **1** (2.397(3) Å) and another similar structure (2.423(3) Å) [17]. The Eu(1)–N(1)

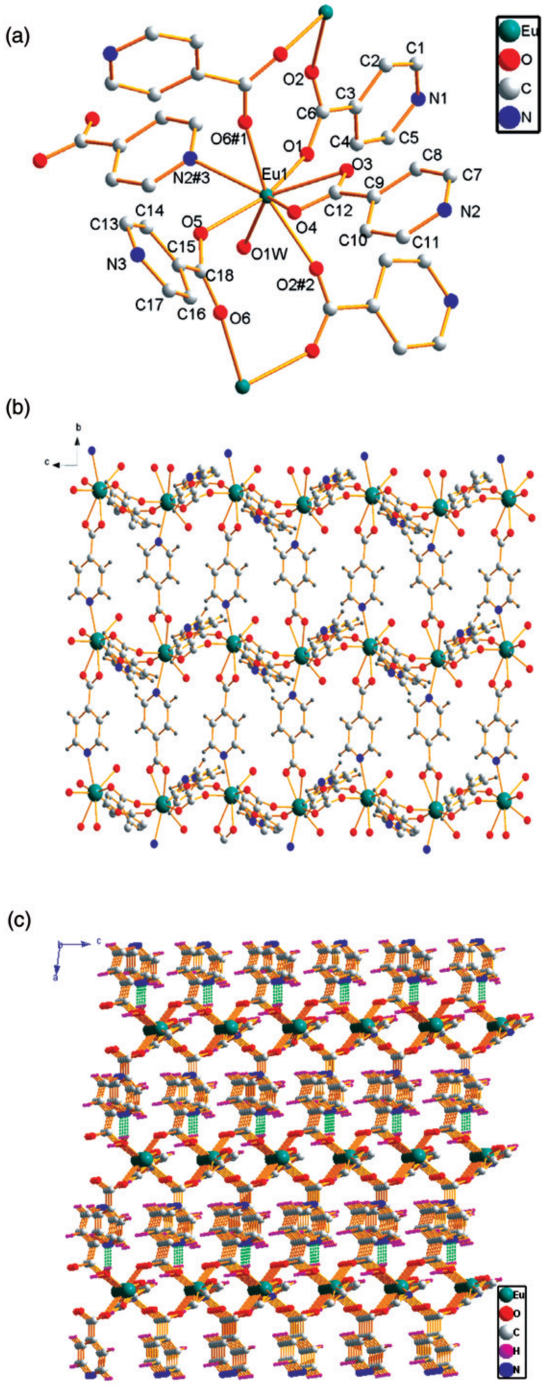

Figure 1. (a) The expanded asymmetric unit of **1**. For clarity hydrogens were omitted. Symmetry codes: #1 x, $1-y$, $0.5+z$; #2 x, $1-y$, $-0.5+z$; #3 x, $y-1$, z. (b) View of the layer structure of **1** along the *a*-axis. (c) View of a 3-D supramolecular network of **1** with hydrogen bonding O–H···N (represented by green bonds) along the *b*-axis.

Table 3. Distances (Å) and angles (°) of hydrogen bonds for **1**.

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠(D–H···A)
O(1W)–H(1A)···N(3)#1	0.850(4)	2.002(4)	2.779(7)	153(4)
O(1W)–H(1B)···O(3)#2	0.850(3)	1.851(3)	2.686(4)	169(4)

Symmetry codes: #1 $-0.5+x$, $-0.5+y$, z; #2 x, $1-y$, $-0.5+z$.

and Eu(1)–N(3) distances are 2.695(3) and 2.628(3) Å, respectively, also similar to the Eu–N distance of **1**, and the N(3)–Eu(1)–N(1) bond angle is 120.69(3)°. There are two obvious differences between **1** and **2**: (1) For **2**, there are two nitrogens connected to europium, while only one for europium in **1** (figure 3); (2) the interlayer hydrogen bonds between nitrogens of inic and coordinated water of **1** result in the formation of a 3-D supramolecular network structure, but there are no classical hydrogen bonds in **2**.

On the basis of the interesting connections of inic ligands, one sandwich-like polymeric-layered network is formed (figure 2b), and these layers are further interconnected by inic to form a 3-D network. By treating Eu as the nodes and bridging inic as links, an ideal 3-D framework with topology is obtained as illustrated in figure 2(c). Topological analysis indicates that **2** could be regarded as built from six-connected nodes (Eu) with Schläfli vertex symbols of $\{4^3.5^3.6^5.7^4\}$ and three-connected nodes (inic 3) with Schläfli symbols of {4.5.6}.

3.2. *IR spectra analysis*

The IR spectra of **1** and **2** are in accord with the structural data. The presence of water in **1** was proved by the strong and broad band at 3412 $\mathrm{cm^{-1}}$, ascribed to the stretching vibrations ν(O–H). The asymmetric mode ν_{as}(COO) and the symmetric mode ν_s(COO) of carboxylate is at 1618, 1437 $\mathrm{cm^{-1}}$ for **1**, and 1629, 1443 $\mathrm{cm^{-1}}$ for **2** [24].

3.3. *Thermogravimetric analysis*

The TGA curve for crystalline **1** showed two weight-loss steps accompanied by two endothermic peaks. The first weight loss (3.39%) from 100°C to 165°C can be attributed to the loss of one-coordinated water molecule (Calcd 3.35%). The major weight loss (50.15%) at 340–500°C corresponds to the complete decomposition of inic and the collapse of the framework. For **2**, TGA analysis indicated that the framework does not decompose until 300°C. These values agree very well with the elemental analysis results (Supplemental material).

3.4. *Luminescent properties*

Photoluminescence properties of **1** and **2** were investigated at room temperature. As the one-coordinated water molecule reduces the conjugation of **1**, the photoluminescence intensity of **1** is much weaker than **2**. However, the luminescence spectra of **1** and **2** were very similar. Therefore, only **1** is discussed in detail. The emission spectra of **1** excited at 395 nm are shown in figure 4. The emission peaks show moderately strong bands at 580,

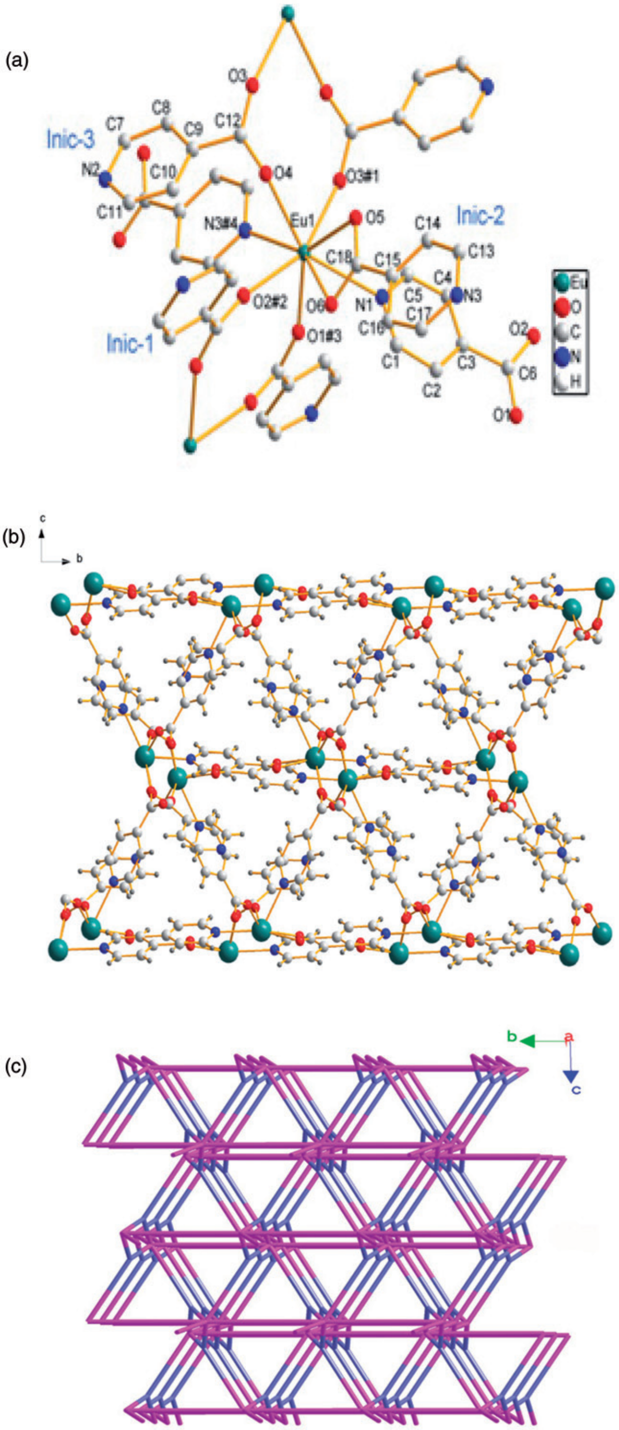

Figure 2. (a) The expanded asymmetric unit of **2**. Symmetry codes: #1 $-x$, $1-y$, $-z$; #2 x, $0.5-y$, $-0.5+z$; #3 $1-x$, $0.5+y$, $0.5-z$; #4 x, $1+y$, z. (b) View of the 2-D layer of **2** running along the *a*-axis. (c) Schematic view of the six-connected $4^3.5^3.6^5.7^4$ for Eu(red) and of three-connected 4.5.6 for inic 3(blue) and of a linear bridging line for inic 2(red) in **2**.

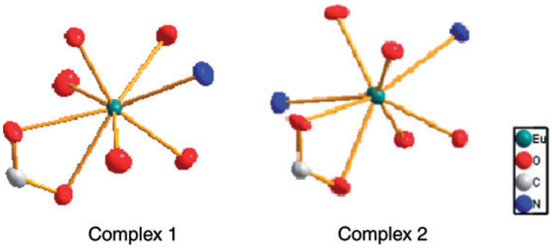

Figure 3. View of coordination environment to Eu^{3+} in **1** and **2**.

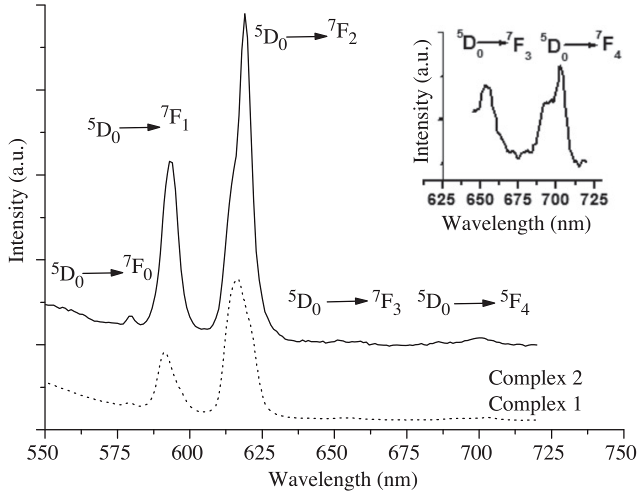

Figure 4. Emission spectra of **1** and **2** (excited at 395 nm).

593, and 619 nm corresponding to the electronic transition of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$, and two weak bands at 651 and 700 nm corresponding to $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ [25], respectively. These indicate a moderately efficient ligand-to-metal (europium) energy transfer (LMCT) [5a, 17, 26]. The symmetry-forbidden weak emission peak $^5D_0 \rightarrow {}^7F_0$ at 580 nm indicates that Eu(III) is located on a low symmetry site [27]. The emission peak $^5D_0 \rightarrow {}^7F_1$ at 593 nm is a magnetic dipole transition and its intensity should vary with the crystal field strength acting on Eu(III). The most intense emission band at 619 nm suggests that it is an electric dipole transition and that the ligand is suitable for red luminescence of Eu(III). The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ of *ca* 1.6 indicates that Eu(III) is in a low-symmetry coordination environment, consistent with the single-crystal X-ray analysis.

4. Conclusions

Two lanthanide complexes have been synthesized by Eu^{3+} and isonicotinates. Complex **1** is a 2-D polymer which extends to a 3-D supramolecular network through hydrogen bonding interactions, while **2** forms a sandwich-like polymeric network and further interconnects by inic ligands to form a 3-D network. Complexes **1** and **2** exhibit strong europium-centered luminescence, showing energy transfer from the inic to Eu^{3+}. This work shows the influence of coordination modes of inic on the structural topology.

Supplementary material

CCDC 716502 and 716503 contain the supplementary crystallographic data for **1** and **2**, respectively. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: int code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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