Synthesis and Crystal Structure of 1-D Coordination Polymer: $\{\text{Na}[\text{Eu}(\text{2,6-PDA})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}\}_n$ (2,6-PDA=2,6-Pyridinedicarboxylate)

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Received February 22, 2011, Accepted March 10, 2011

Key Words : Eu(III) complex, X-ray crystal structure, 2,6-Pyridinedicarboxylate complex, Luminescence

Many attentions have been paid to the metal organic coordination polymers, which have been an active research area in supramolecular chemistry. The applications of such materials in the areas of gas storage, ion-exchange, catalytic, fluorescence, and magnetic properties greatly depend on the coordination nature of metals, as well as the functionality and symmetry of organic ligands.¹ For the construction of coordination polymers with metals, the selection of organic ligands is very important. One of the appropriate organic ligands for the network geometries of the coordination polymers is the series of multidentate ligands containing such as oxygen and nitrogen atoms to have a great possibility for the design of multifunctional chemical architectures.² Lanthanide complexes with organic ligands with conjugate groups have been widely studied because of the characteristic luminescent properties. Luminescent metal complexes with *N*-containing ligands have been reported in the investigation of their interesting photophysical properties and various coordination modes.³ However the studies on the lanthanide complexes are more difficult than those of transition metal complexes because of high coordination number of lanthanide ions.

Pyridine carboxylates have been extensively used to prepare and design lanthanide complexes because nitrogen and oxygen atoms, which have high affinity to lanthanide ions, could be coordinated to and transfer energy to lanthanide ions.⁴ As an extension of our work on luminescent complexes,⁵ herein, we report the X-ray single crystal structure of Eu(III) complex with 2,6-pyridinedicarboxylic acid (2,6-H₂PDA).

Experimental Section

Synthesis. Europium trichloride solution was prepared by dissolving EuCl₃·6H₂O (0.37 g, 1.0 mmol; Aldrich) in absolute ethanol (20 mL) at room temperature with stirring. The ligand solution was prepared by dissolving 2,6-pyridinedicarboxylic acid (0.33 g, 2.0 mmol; Aldrich) in absolute ethanol (30 mL) at room temperature. The pH of the ligand solution was adjusted to about 6.0 with 2 N NaOH solution. The europium trichloride solution was added dropwise slowly to the ligand solution. The reaction mixture was stirred for 2 hours at room temperature and then the white product was filtered through a plastic membrane of 0.45 μm

pore size. The powder product was recrystallized from the mixture of distilled water and absolute ethanol solution to obtain colorless crystals for four weeks. Infrared spectra were recorded by the KBr pellet method on a Bio-Rad Lab. FTS-175C between 4,000–400 cm⁻¹. The product was thermally decomposed at 320 °C. FT-IR (KBr, cm⁻¹) 3068, 2919 (C-H), 1633, 1576 (C=O), 1374, 1285, 1251 (C=C, C=N).

Determination and Refinement of the X-ray Structure.

X-ray intensity data were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo *K*α radiation ($\lambda = 0.71073$ Å) at 233 K. The data frames were integrated and scaled using Bruker package.^{6a} Structure was solved by applying the direct method using a SHELXS-97 and refined by a full-matrix least-squares calculation on *F*² using SHELXL-97.^{6b} All non-hydrogen atoms were refined anisotropically. The H atoms on water molecules were located in a difference map and refined freely. The other hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms (*B*_{iso} = 1.2 *B*_{eq}).

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-813815). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The crystallographic data and structure refinement parameters of complex **1**, $\{\text{Na}[\text{Eu}(\text{2,6-PDA})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}\}_n$ (2,6-PDA = 2,6-pyridinedicarboxylate) is given in Table 1. An ORTEP diagram for complex **1** is shown in Figure 1 with the atom-numbering scheme. The structural feature of an asymmetric unit is that two 2,6-PDA and two water ligands are coordinated directly to the Eu atom in the inner coordination sphere forming the complex anion, while one Na atom as counter cation is bound to the complex anion. And there are three water molecules in the outer sphere.

In the anionic part of complex **1**, $[\text{Eu}(\text{2,6-PDA})_2(\text{H}_2\text{O})_2]^{1-}$, the Eu(III) atom is nine-coordinated in a slightly distorted monocapped square antiprismatic geometry defined by four carboxylate O atoms, two pyridine N atoms, two water O atoms, and one more O atom (O24^b) from the neighboring

Table 1. Crystal data and structure refinement for **1**

Empirical formula	C ₁₄ H ₁₆ EuN ₂ NaO ₁₃
Formula weight	595.24
Temperature	233(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 13.978(2) Å α = 90° <i>b</i> = 11.2055(19) Å β = 102.513(3)° <i>c</i> = 12.789(2) Å γ = 90°
Volume	1955.6(6) Å ³
Z, Calculated density	4, 2.022 Mg/m ³
Absorption coefficient	3.303 mm ⁻¹
<i>F</i> (000)	1168
Crystal size	0.22 × 0.21 × 0.13 mm ³
θ range for data collection	2.35 to 26.00°
Reflections collected	16707
Independent reflections	3839 [<i>R</i> _{int} = 0.0260]
Completeness to θ = 26.00	100.0 %
Data / restraints / parameters	3839 / 1 / 316
Goodness-of-fit on <i>F</i> ²	1.071
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0226, <i>wR</i> ₂ = 0.0554
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0281, <i>wR</i> ₂ = 0.0588
Largest diff. peak and hole	0.622 and -1.076 e Å ⁻³

Figure 1. (a) Molecular structure of complex **1** showing the atom-numbering scheme and 30% probability ellipsoids. (b) Simple schematic drawing of asymmetric unit.

carboxylate ligand (Fig. 2). The four O atoms (O11, O20, O23, and O26) and other four atoms (N1, O8, O25, and O24ⁱ) are constructed to be the distorted square antiprism

Figure 2. The coordination sphere of Eu atom in complex **1**. Square antiprism is indicated by dashed lines. [Symmetry code: (i) *x*, -*y*+3/2, *z*-1/2].

geometry and the other N13 atom lies on the capped position.

The bond lengths lie within the range 2.384(3)-2.507(2) Å for the Eu-O bonds and 2.558(3)-2.562(3) Å for the Eu-N bonds which are significantly shorter than the sum of the covalent radii of the Eu-O (2.660 Å) and Eu-N (2.700 Å). And these values are within the range of those observed for other nine coordinated Eu(III) complexes.^{4a,5b} The selected bond lengths and angles are given in Table 2. And intermolecular hydrogen-bond geometry is summarized in Table 3. The dihedral angles between pyridine rings and the carboxylate groups are in the range of 2.77(8)-14.96(17)° which are

Table 2. The selected bond distances (Å) and angles (°) of **1**

Eu-O(26)	2.384(3)	Eu-O(23)	2.501(2)
Eu-O(25)	2.423(3)	Eu-O(11)	2.507(2)
Eu-O(24) ⁱ	2.433(2)	Eu-N(1)	2.558(3)
Eu-O(8)	2.441(2)	Eu-N(13)	2.562(3)
Eu-O(20)	2.459(2)		
O(11)-Eu-N(13)	65.41(8)	O(20)-Eu-O(23)	124.57(7)
O(20)-Eu-N(13)	62.88(8)	O(26)-Eu-O(11)	140.40(9)
O(23)-Eu-N(13)	62.34(8)	O(25)-Eu-O(8)	97.03(10)
O(26)-Eu-N(13)	75.29(9)	O(24) ⁱ -Eu-N(1)	118.96(8)

Symmetry code: (i) *x*, -*y*+3/2, *z*-1/2

Table 3. Hydrogen-bond geometry (Å, °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(25)-H(25A)...O(23) ⁱ	0.82(2)	1.94(3)	2.708(4)	155(5)
O(25)-H(25B)...O(9) ⁱⁱ	0.67(5)	2.07(5)	2.735(4)	177(6)
O(26)-H(26B)...O(28) ⁱⁱⁱ	0.79(5)	1.99(5)	2.731(4)	157(4)
O(28)-H(28B)...O(21) ^{iv}	0.82(6)	1.86(6)	2.678(4)	174(6)
O(29)-H(29B)...O(8)	0.73(7)	2.22(7)	2.943(4)	170(8)
O(30)-H(30A)...O(9)	0.83(6)	1.81(7)	2.637(5)	169(6)
O(30)-H(30B)...O(29)	0.85(7)	2.23(7)	2.798(6)	124(6)

Symmetry code: (i) *x*, -*y*+3/2, *z*-1/2; (ii) -*x*+1, *y*+1/2, -*z*+1/2; (iii) -*x*+2, -*y*+1, -*z*+1; (iv) *x*, -*y*+3/2, *z*+1/2

Figure 3. One-dimensional supramolecular chain along the *c* axis.

Figure 4. Three-dimensional network showing channels along the *b* axis.

also good evidence for the interactions between the O atoms and Eu ion.

As shown the simple schematic drawing of asymmetric unit in Fig. 1(b), one of the carboxylate ligands bridges the Eu ions, forming a one-dimensional coordination polymer along the *c* axis (Fig. 3). Symmetric O24 atom is directly coordinated to Eu(III) ions to form nine coordinated Eu complex with the bond distance of 2.433(2) Å. Several lanthanide complexes with pyridinecarboxylate ligands have been known to form a one-dimensional (1D) chainlike structure.^{5b,7}

In the crystal structure, intermolecular O–H···O hydrogen bonds (Table 3) link the uncoordinated water molecules to the coordinated carboxylate ligands and further link the molecules into a three dimensional network showing channels along the *b* axis (Fig. 4).

Complex **1** emits strong red luminescence characteristic originating from the f-f transition of Eu(III) ion. Complex **1** exhibits an emission at 617 nm upon 396 nm excitation in

PL spectra with 325 nm of He-Cd laser excitation wavelength. The strong emission band at 617 nm is corresponding to $^5D_0 \rightarrow ^7F_2$ transition which is electric dipole in origin and very sensitive to crystal fields.⁸

In summary, the X-ray single crystal structure of complex $\{Na[Eu(2,6\text{-PDA})_2(H_2O)_2] \cdot 3H_2O\}_n$ (**1**) is reported. This forms a one-dimensional (1D) coordination polymer of a chainlike structure. And in the crystal structure, weak hydrogen bonds make 3-D network frames. The coordination geometry on Eu(III) is the monocapped square antiprism with nine coordination. The luminescent studies show that the Eu complex emits strong red luminescence characteristic of the Eu^{3+} ion.

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