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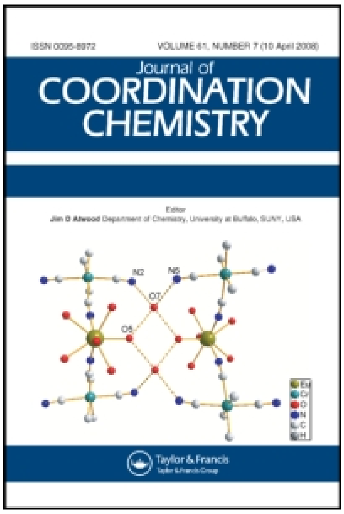

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Hydrothermal synthesis and crystal structure of a novel luminescent europium complex of 2,5-pyridinedicarboxylic acid

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A novel europium complex, Eu(Hdinic)(dinic)$(H_2O)_5 \cdot 4H_2O$ (dinic = 2,5-pyridinedicarboxylic acid), has been synthesized under hydrothermal conditions and characterized structurally by X-ray diffraction methods. The complex has a mononuclear molecular structure, is monoclinic, space group $C2/c$, with $a = 13.877(5)$, $b = 9.632(3)$, $c = 32.991(11)$ Å, $\beta = 93.414(4)°$, $V = 4402(2)$ Å^3, $D_c = 1.948$ Mg m^{-3}, $Z = 8$, $F(000) = 2576$, $R_1 = 0.0320$. Its photophysical properties are reported.

Keywords: Europium; Mononuclear; 2,5-Pyridinedicarboxylic acid; Molecular structure; Photophysical properties

1. Introduction

Over the past few years, considerable attention has been devoted to the design and synthesis of luminescent lanthanide complexes because of their interesting photophysical properties and their potential application in sensors, liquid crystalline materials, optical fiber lasers and amplifiers, luminescent labels for biomolecular interactions, and magnetic molecular and electroluminescent materials [1–6]. Several classes of ligand have been used for the preparation of these complexes, including cryptands [7–9], podands [10, 11], calixarenes [12–15], macrocyclic ligands [16–18], β-diketones [19–21], carboxylic acid derivatives [7, 22–24], and other ligands [25, 26] and proteins [27].

To prepare the lanthanide compounds, the use of rigid, multifunctional carboxylic acids containing hybrid atoms is one of the best of several choices. The pyridinedicarboxylic acids form 1 : 1, 2 : 3 and 1 : 2 metal derivatives that exhibit various coordination geometries [28]. The relative positions of the coordinating atoms lead to molecular

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solids, as with some 2,4-, 2,5- and 2,6-pyridinedicarboxylates derivatives, or two- or three-dimensional structures. Liang and coworkers [29] have discussed the coordination behavior of 2,5-pyridinedicarboxylate, which possesses many possible coordination modes; 14 have been found in its coordination complexes.

The hydrothermal method is effective for the crystal growth of many coordination polymers. Under hydrothermal conditions, properties of reactants and interactions between organic and inorganic partners are very different from those observed under conventional conditions in aqueous solution [23, 30, 31]. Recently, the method has been applied successfully to the syntheses of lanthanide complexes, and a large number of lanthanide complexes with one-dimensional chain-like, two-dimensional layer-like or three-dimensional net-like open framework structures have been prepared and characterized [32–40]. Taking account of these, we have chosen 2,5-pyridinedicarboxylates as reactants to synthesize europium compounds under hydrothermal conditions. It is surprising that the complex reported here has a mononuclear molecular structure, rarely found for other lanthanide carboxylates complexes produced under hydrothermal conditions.

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2. Experimental

2.1. *Synthesis of Eu(Hdinic)(dinic)$(H_2O)_5\cdot 4H_2O$*

$Eu(NO_3)_3\cdot 6H_2O$ was prepared by dissolving its oxide in concentrated nitric acid followed by evaporation. 2,5-Pyridinedicarboxylic acid (dinic) was purchased from Aldrich and used without further purification. All other reagents were commercially available and used as received.

$Eu(NO_3)_3\cdot 6H_2O$ (0.2281 g, 0.5 mmol) and dinic acid (0.1671 g, 1.0 mmol) were mixed in 10 cm^3 of deionized water. After stirring for 30 min, the mixture was placed in a 25 cm^3 Teflon-lined reactor, heated at 160°C for 3 days, then cooled slowly to room temperature. Colorless columnar crystals of the complex suitable for X-ray diffraction analysis were obtained. Anal. Calcd for $C_{14}H_{25}EuN_2O_{17}$(%): C, 26.03; H, 3.87; N, 4.34. Found: C, 25.89; H, 3.91; N, 4.24. IR spectra show $\nu_s(COO^-)$ at 1411 cm^{-1} and $\nu_{as}(COO^-)$ at 1546 cm^{-1}.

2.2. *X-ray crystallography*

Diffraction data for a crystal with dimensions $0.15\times 0.10\times 0.05$ mm were collected with graphite-monochromated Mo Kα radiation on a CCD area detector four-circle diffractometer using the ω–2θ scan technique. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [41, 42]. A summary of crystallographic data and refinement parameters is given in table 1. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 258492. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement details for the complex.

Complex	Eu(Hdinic)(dinic)$(H_2O)_5 \cdot 4H_2O$
Formula	$C_{14}H_{25}EuN_2O_{17}$
Relative molecular weight	645.32
Color	Colorless
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	Mo Kα
Space group	$C2/c$
Unit cell dimensions	$a = 13.877(5)$ Å $b = 9.632(3)$ Å $c = 32.991(11)$ Å $\beta = 93.414(4)^\circ$
Volume	4402(2) Å^3
Z	8
Calculated density	1.948 Mg m^{-3}
Absorption coefficient	2.938 mm^{-1}
$F(000)$	2576
Crystal size	$0.15 \times 0.10 \times 0.05$ mm
θ range for data collection	1.24 to 25.01°
Reflections collected/unique	8991/3866 [R(int) = 0.0256]
Completeness to $\theta = 25.01$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3866/0/379
Goodness-of-fit on F^2	1.199
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0320$, $wR2 = 0.0629$
Largest diff. peak and hole	0.660 and −0.701 e Å^{-3}

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2.3. *Physical measurements*

Elemental analyses (C, H, N) were determined on an Elementar Cario EL instrument. IR spectra (KBr pellets) were recorded on a Nexus 912 AO446 FTIR spectrophotometer in the range 4000–400 cm^{-1}. Luminescence excitation and emission spectra of an aqueous solution of the complex were obtained with a Perkin Elmer LS-55 spectrophotometer.

3. Results and discussion

3.1. *Description of the structure*

Final atomic coordinates for the nonhydrogen atoms of Eu(Hdinic)(dinic)$(H_2O)_5 \cdot 4H_2O$ are listed in table 2. Figure 1 shows the coordination geometry and the atom labeling scheme. The complex consists of one Eu ion, two dinic ligands, five coordinated water molecules and four lattice water molecules. The central Eu ion is nine-coordinated by seven oxygen atoms and two nitrogen aroms; the coordination geometry can be described as a distorted square antiprism. Two oxygen atoms from the two dinic molecules have bond distances of 2.388(3) [Eu(1)–O(1)] and 2.449(3) Å [Eu(1)–O(5)]. Two pyridine nitrogen atoms from the two dinic molecules have bond distances of 2.638(3) [Eu(1)–N(2)] and 2.625(4) Å [Zn(1)–N(1)]. Five oxygen atoms of the coordinated water molecules have bonds ranging from 2.378(4) to 2.485(4) Å. The average Eu–O distance is 2.435 Å. It is noteworthy that the bond to O(5) is the largest observed for lanthanide carboxylate complexes.

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($10^4\,\text{Å}^2$) for the complex.

Atom	x/a	y/b	z/c	U(eq)
Eu(1)	8973(1)	1815(1)	3812(1)	20(1)
N(1)	10221(2)	1444(3)	4438(1)	21(1)
N(2)	8767(2)	797(3)	3074(1)	22(1)
O(1)	9784(2)	−372(3)	3847(1)	28(1)
O(2)	10738(2)	−1990(3)	4134(1)	29(1)
O(3)	11018(3)	4350(3)	5320(1)	37(1)
O(4)	11732(3)	2717(3)	5707(1)	37(1)
O(5)	8893(2)	3487(3)	3252(1)	28(1)
O(6)	8716(3)	4097(3)	2603(1)	35(1)
O(7)	8810(3)	−3391(3)	2811(1)	37(1)
O(8)	8488(3)	−2991(3)	2158(1)	38(1)
O(9)	9272(3)	4131(4)	4035(1)	32(1)
O(10)	7844(3)	−141(4)	3903(1)	34(1)
O(11)	8134(3)	2196(5)	4441(1)	35(1)
O(12)	7292(3)	2573(4)	3628(2)	34(1)
O(13)	10555(3)	2098(4)	3568(1)	33(1)
O(14)	6471(3)	1345(5)	4789(2)	45(1)
O(15)	2244(3)	767(5)	3708(2)	59(2)
O(16)	1311(3)	4488(4)	3315(2)	42(1)
O(17)	9930(3)	6225(4)	3564(1)	40(1)
C(1)	10379(3)	−799(4)	4119(1)	23(1)
C(2)	10678(3)	218(4)	4452(1)	21(1)
C(3)	11376(3)	−107(5)	4751(1)	30(1)
C(4)	11599(3)	835(5)	5054(1)	31(1)
C(5)	11128(3)	2097(4)	5049(1)	22(1)
C(6)	10455(3)	2357(4)	4730(1)	24(1)
C(7)	11315(3)	3128(5)	5389(1)	27(1)
C(8)	8795(3)	3218(4)	2885(1)	24(1)
C(9)	8755(3)	1694(4)	2767(1)	22(1)
C(10)	8727(4)	1288(5)	2368(1)	30(1)
C(11)	8704(3)	−117(5)	2280(1)	29(1)
C(12)	8711(3)	−1062(4)	2595(1)	24(1)
C(13)	8744(3)	−561(4)	2986(1)	23(1)
C(14)	8660(3)	−2582(5)	2500(1)	23(1)

Bond angles involving Eu, oxygen and nitrogen atoms of the chelate rings are 63.71(10)° [O(1)–Eu(1)–N(1)] and 63.12(10)° [O(5)–Eu(1)–N(2)]. Selected bond distances and angles are listed in table 3.

In one unit of the complex there are two dinic molecules; one (dinic) is dianionic and the other one (Hdinic) must be monoprotonated to maintain electroneutrality. The presence of many water molecules in the complex leads to numerous hydrogen-bonding interactions, which consolidate a stacked arrangement leading to a three-dimensional supramolecular architecture. Coordinated and lattice water molecules act as donors and coordinated water molecules and oxygen atoms of the carboxylate groups act as acceptors.

3.2. *Luminescent properties*

The excitation spectrum of the complex shows that effective energy absorption mainly takes place in the far ultraviolet region, 350–400 nm and strong emission is observed at 379 nm. Emission of the complex mainly ranges from 400 to 600 nm (weak) with a

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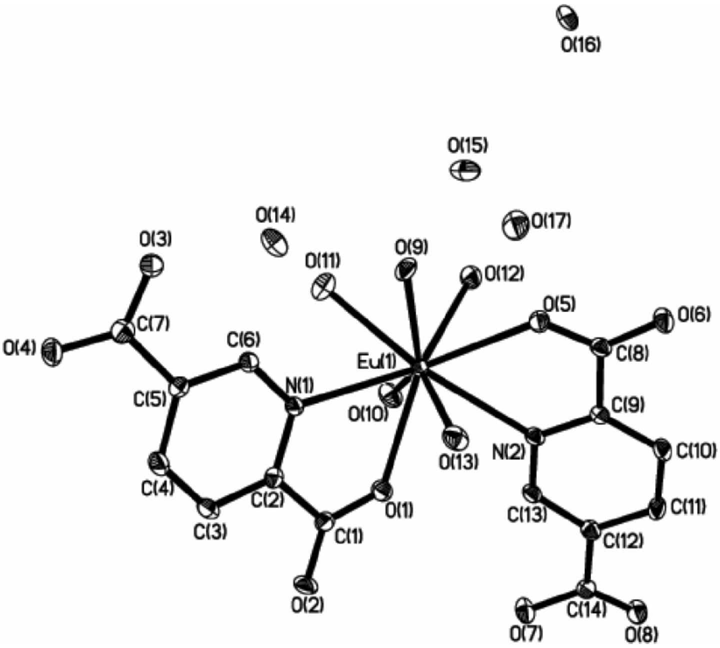

Figure 1. An ORTEP drawing of the complex with the atom labeling scheme.

Table 3. Selected bond distances (Å) and angles (°) for the complex.

Eu(1)–O(9)	2.378(4)	Eu(1)–O(10)	2.480(4)
Eu(1)–O(1)	2.388(3)	Eu(1)–O(12)	2.485(4)
Eu(1)–O(13)	2.398(4)	Eu(1)–N(2)	2.625(4)
Eu(1)–O(5)	2.449(3)	Eu(1)–N(1)	2.638(3)
Eu(1)–O(11)	2.468(4)		
O(9)–Eu(1)–O(1)	137.70(12)	O(5)–Eu(1)–O(12)	67.86(13)
O(9)–Eu(1)–O(13)	81.43(15)	O(11)–Eu(1)–O(12)	71.25(15)
O(1)–Eu(1)–O(13)	71.22(13)	O(10)–Eu(1)–O(12)	70.22(14)
O(9)–Eu(1)–O(5)	67.42(12)	O(9)–Eu(1)–N(2)	130.16(13)
O(1)–Eu(1)–O(5)	128.06(11)	O(1)–Eu(1)–N(2)	74.95(10)
O(13)–Eu(1)–O(5)	70.93(13)	O(13)–Eu(1)–N(2)	77.44(12)
O(9)–Eu(1)–O(11)	71.47(16)	O(5)–Eu(1)–N(2)	63.12(10)
O(1)–Eu(1)–O(11)	109.59(12)	O(11)–Eu(1)–N(2)	143.65(14)
O(13)–Eu(1)–O(11)	138.81(15)	O(10)–Eu(1)–N(2)	78.09(12)
O(5)–Eu(1)–O(11)	122.33(12)	O(12)–Eu(1)–N(2)	80.47(13)
O(9)–Eu(1)–O(10)	140.81(14)	O(9)–Eu(1)–N(1)	77.92(12)
O(1)–Eu(1)–O(10)	67.88(12)	O(1)–Eu(1)–N(1)	63.71(10)
O(13)–Eu(1)–O(10)	136.43(14)	O(13)–Eu(1)–N(1)	72.94(13)
O(5)–Eu(1)–O(10)	126.16(13)	O(5)–Eu(1)–N(1)	132.67(11)
O(11)–Eu(1)–O(10)	71.23(15)	O(11)–Eu(1)–N(1)	71.48(13)
O(9)–Eu(1)–O(12)	86.79(14)	O(10)–Eu(1)–N(1)	101.09(13)
O(1)–Eu(1)–O(12)	134.73(12)	O(12)–Eu(1)–N(1)	142.52(14)
O(13)–Eu(1)–O(12)	138.56(15)	N(2)–Eu(1)–N(1)	134.86(11)

maximum at 468 nm. Emission of the free dinicH_2 molecule occurs at 395 nm and emission of the Eu^{3+} ion ranges from 480 to about 700 nm. This indicates that the lower energy band may be assigned to ligand-to-metal charge transfer and the observed luminescence of the complex is attributed to the coordinated dinic ligands.

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