A Novel Synthesis Path to Luminescent Dimeric Dysprosium Complex Controlled by the Hydrolysis of Methyl Nicotinate

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A novel path to synthesize lanthanide complex of aromatic carboxyl group controlled by the hydrolysis of the corresponding ester of aromatic carboxylic acid has been found. According to this path, we achieved a dimeric dysprosium coordination compound of nicotinate (NIC) using methyl nicotinate as the starting ligand. With the hydrolysis of sodium hydroxide, a dimeric dysprosium complex forms slowly: $[Dy(NIC)_3(H_2O)_2]_2$ has been synthesized. X-Ray analysis reveals that it forms a novel dimeric structure through bridged oxygen atoms of carboxylate groups. The title complex crystallizes in the monoclinic system, space group $P2_1/c$, with lattice parameters $a = 9.575(2)$ Å, $b = 11.600(2)$ Å, $c = 17.758(5)$ Å, $\beta = 91.565(4)°$, $V = 1971.6(7)$ Å^3, $D_c = 1.903$ Mg/m^3, $Z = 2$, $F(000) = 1100$, GOF $= 1.144$, $R_1 = 0.0337$. The title complex exhibits strong luminescence of Dy^{3+}.

In recent years, much research work has been done on lanthanide coordination compounds with some organic ligands which have special chelated structures and exhibit photophysical properties for the application in luminescence probes for chemical or biological macromolecules [1, 2] and the active centre for molecular-based luminescent materials [3, 4]. Especially, lanthanide complexes with aromatic carboxylic acids show higher thermal or luminescent stability for practical applications than other lanthanide complex systems because they readily form the dimer or infinite chain polymeric structures [5—7]. Pyridinecarboxylic acids belong to heterocyclic acids with conjugated structures and in some papers the molecular or crystal structures for some lanthanide ions have been discussed [8, 9]. The basic compositions for these lanthanide complexes with pyridine-3(4)-carboxylic acids (L) correspond to $n(Ln):n(L):n(H_2O) = 1:3:1$ [10—15].

In this work, a new dimeric dysprosium complex of nicotinate (NIC) with the similar composition has been synthesized, but it shows a dimer structure: $[Dy(NIC)_3(H_2O)_2]_2$. Especially, the dimeric complex exhibits strong luminescence and the blue emission is much stronger than the yellow one. The detailed crystal structure and spectroscopic properties were reported earlier.

The typical hydrolysis process can be described as

$$C_5NH_4COOCH_3(MNIC) + NaOH \rightarrow$$

$$\rightarrow C_5NH_4COONa(NaNIC) + CH_3OH \qquad (A)$$
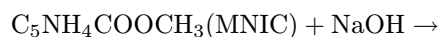
In the presence of NaOH to adjust the pH value of the mixed reaction solutions, methyl nicotinate hydrolyzes and reacts with NaOH. In the hydrolysis process, the chemical bond (O—C—O) between aryl (pyridine-3-carboxyl) and oxygen cleaves in the methyl nicotinate molecules and results in nicotinate (sodium salt) and methanol, then the coordination reaction between nicotinate and Dy^{3+} takes place. So the formation of the dimeric Dy complex of nicotinate is controlled by both hydrolysis process and coordination reaction.

Final atomic coordinates for nonhydrogen atoms are listed in Table 1. Fig. 1 shows the coordination geometry and atom labeling in the crystal structure of the title complex. X-Ray diffraction crystal structure analysis reveals that it leads to a dimeric formulation $[Dy(NIC)_3(H_2O)_2]_2$ with two equivalent structural units corresponding to one half of dimer related by a crystallographic inversion centre, which is similar to the structures of other lanthanide pyridine-3-carboxylates [10—15]. The two symmetry-related dysprosium ions are bridged by four carboxylate groups, with two additional carboxylate groups chelating to them. The coordination polyhedron is completed by two water molecules per dysprosium ion with coordination number of dysprosium of 8. The pyridine-3-carboxylate groups are coordinated to the two dysprosium ions by sole carboxylate oxygen atoms from four

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Table 1. Atomic Coordinates (10^4) of Equivalent Isotropic Displacement Parameters (10^3 $\AA^2$) for the Title Complex

Atom	x	y	z	U(eq)
Dy(1)	8105(1)	8953(1)	9948(1)	21(1)
N(1)	5165(6)	6580(5)	12816(3)	51(1)
N(2)	14716(5)	6483(4)	9466(3)	43(1)
N(3)	11588(6)	10641(5)	6745(3)	50(1)
O(1)	6069(4)	9071(3)	10755(2)	34(1)
O(2)	7481(4)	7617(3)	10995(2)	38(1)
O(3)	10202(3)	7930(3)	9951(2)	36(1)
O(4)	12073(4)	9067(3)	10114(2)	37(1)
O(5)	8938(4)	9182(4)	8734(2)	43(1)
O(6)	10703(4)	10353(4)	9003(2)	48(1)
O(7)	7445(4)	7195(3)	9369(2)	36(1)
O(8)	6065(4)	9331(3)	9187(2)	33(1)
C(1)	6383(5)	8175(4)	11123(3)	28(1)
C(2)	5445(5)	7761(4)	11728(3)	31(1)
C(3)	4081(6)	8130(6)	11765(4)	44(1)
C(4)	3268(6)	7704(6)	12336(4)	52(2)
C(5)	3840(6)	6934(6)	12835(3)	54(2)
C(6)	5936(6)	6992(5)	12268(3)	41(1)
C(7)	11484(5)	8140(4)	9938(3)	27(1)
C(8)	12411(5)	7165(4)	9686(3)	23(1)
C(9)	11858(6)	6146(4)	9404(4)	39(1)
C(10)	12730(7)	5304(5)	9169(4)	50(2)
C(11)	14158(6)	5507(5)	9196(4)	48(2)
C(12)	13833(5)	7288(4)	9705(3)	34(1)
C(13)	9975(5)	9762(4)	8561(3)	31(1)
C(14)	10378(5)	9739(4)	7753(3)	26(1)
C(15)	9973(6)	8852(5)	7278(3)	36(1)
C(16)	10419(7)	8862(5)	6547(4)	47(2)
C(17)	11203(7)	9780(6)	6317(3)	52(2)
C(18)	11198(6)	10614(5)	7464(3)	38(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

bridged pyridine-3-carboxylates (O(3), O(5), O(4A), and O(6A) for Dy(1), O(4), O(6), O(3A), and O(5A) for Dy(1A)) and two chelated pyridine-3-carboxylates (O(1) and O(2) for Dy(1), O(1A) and O(2A) for Dy(1A)) per dimeric unit. The bridged pyridine-3-carboxylates are coordinated in such a manner that each oxygen atom is bound only to one dysprosium ion with Dy—O distances of 2.333(3) $\AA$ for Dy(1)—O(3), 2.335(4) $\AA$ for Dy(1)—O(5), 2.305(3) $\AA$ for Dy(1)—O(4A), and 2.303(4) $\AA$ for Dy(1)—O(6A), separately, while the chelated pyridine-3-carboxylate is coordinated with slightly longer Dy—O distances than bridged carboxylate oxygen atoms, 2.454(4) $\AA$ for Dy(1)—O(1) and 2.504(4) $\AA$ for Dy(1)—O(2), respectively. The distances between the oxygen atoms of the coordinated water molecules and dysprosium ions are 2.363(4) $\AA$ for Dy(1)—O(71), 2.385(4) $\AA$ for Dy(1)—O(8), respectively, interposing the bond distances between the two types of carboxylate oxygen atoms and dysprosium ions. The coordination polyhedron can be described as a highly distorted square antiprism with two square units (O(1), O(2), O(7), O(8) for one square and O(3), O(5), O(4A), O(6A) for another square). Selected bond distances and bond angles for the dinuclear dysprosium complex are listed in Table 2.

Fig. 2 shows the packing view of a unit cell for [Dy(NIC)$_3$(H$_2$O)$_2$]$_2$ dimer. The existence of water molecules causes the hydrogen bonding to all the nitrogen atoms of nicotinate. The hydrogen bonding interacts between the two different adjacent dimers so that this hydrogen bonding interaction joints the
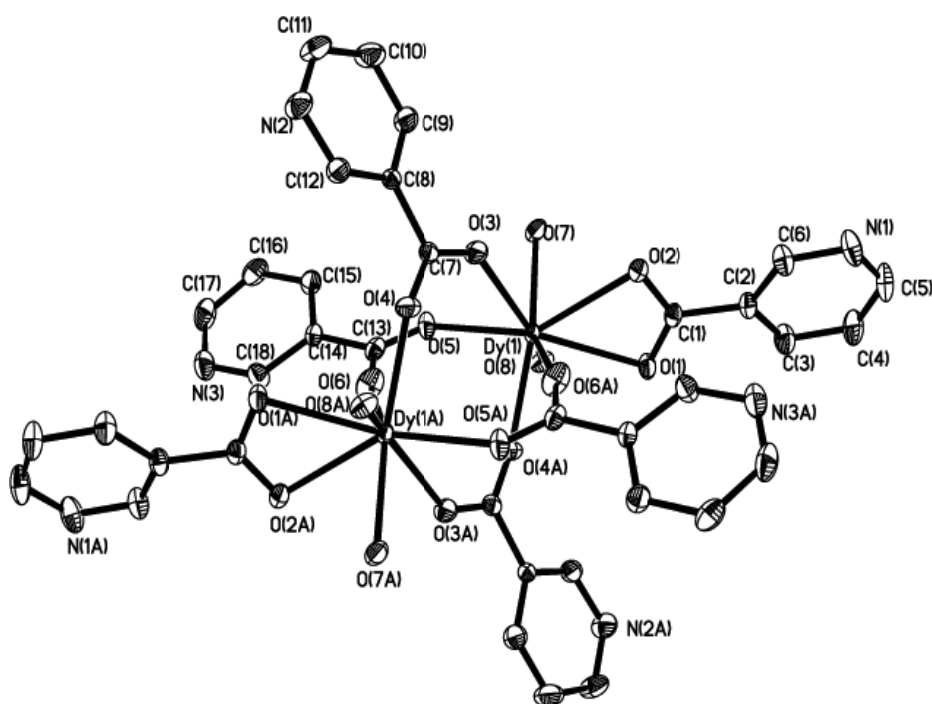
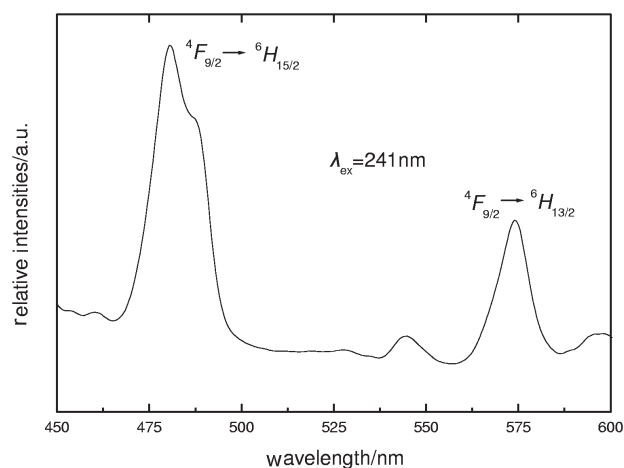**Fig. 1.** Molecular structure of the [Dy(NIC)$_3$(H$_2$O)$_2$]$_2$ complex.

Table 2. Selected Bond Distances/$\mathring{A}$ and Bond Angles/$^\circ$ for the Title Complex

Dy(1)—O(6)[a]	2.303(4)	Dy(1)—O(7)	2.363(4)
Dy(1)—O(4)[a]	2.305(3)	Dy(1)—O(8)	2.385(4)
Dy(1)—O(3)	2.333(3)	Dy(1)—O(1)	2.454(4)
Dy(1)—O(5)	2.335(4)	Dy(1)—O(2)	2.504(4)
O(6)[a]—Dy(1)—O(4)[a]	74.02(16)	O(5)—Dy(1)—O(2)	148.23(13)
O(6)[a]—Dy(1)—O(3)	76.64(15)	O(7)—Dy(1)—O(2)	73.89(14)
O(4)[a]—Dy(1)—O(3)	124.72(13)	O(8)—Dy(1)—O(2)	109.03(13)
O(6)[a]—Dy(1)—O(5)	122.23(16)	O(1)—Dy(1)—O(2)	52.55(12)
O(4)[a]—Dy(1)—O(5)	82.49(14)	O(7)—Dy(1)—O(8)	72.96(13)
O(3)—Dy(1)—O(5)	75.17(15)	O(6)[a]—Dy(1)—O(1)	83.83(15)
O(6)[a]—Dy(1)—O(7)	140.76(16)	O(4)[a]—Dy(1)—O(1)	85.05(12)
O(4)[a]—Dy(1)—O(7)	145.17(14)	O(3)—Dy(1)—O(1)	136.43(13)
O(3)—Dy(1)—O(7)	77.36(13)	O(5)—Dy(1)—O(1)	146.05(15)
O(5)—Dy(1)—O(7)	77.88(14)	O(7)—Dy(1)—O(1)	95.44(13)
O(6)[a]—Dy(1)—O(8)	140.72(14)	O(8)—Dy(1)—O(1)	70.69(13)
O(4)[a]—Dy(1)—O(8)	74.43(14)	O(6)[a]—Dy(1)—O(2)	74.87(15)
O(3)—Dy(1)—O(8)	141.83(13)	O(4)[a]—Dy(1)—O(2)	129.28(13)
O(5)—Dy(1)—O(8)	75.57(14)	O(3)—Dy(1)—O(2)	84.62(12)

Symmetry transformations used to generate equivalent atoms: *a*) $-x + 2$, $-y + 2$, $-z + 2$.
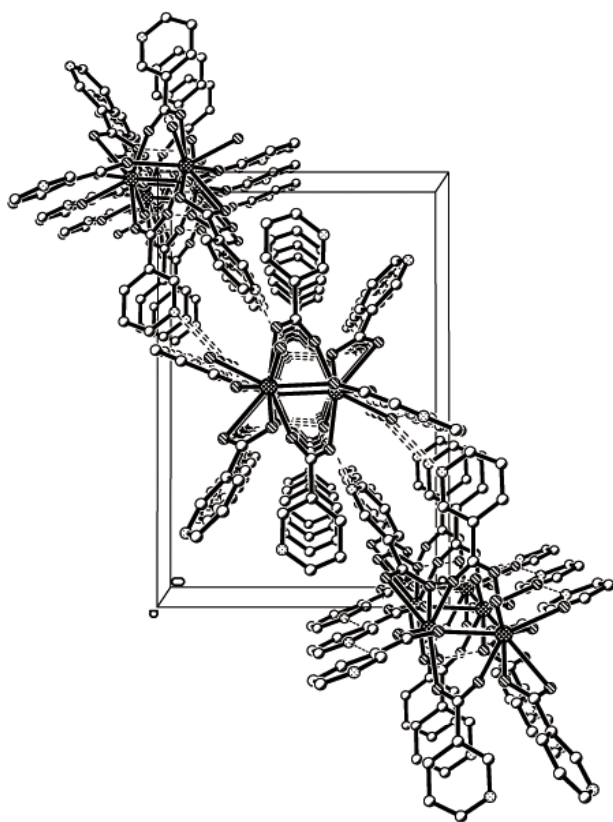
Fig. 2. Packing view of the unit cell for the [Dy(NIC)$_3$-(H$_2$O)$_2$]$_2$ complex.

Fig. 3. Emission spectrum of the [Dy(NIC)$_3$(H$_2$O)$_2$]$_2$ complex.

dimeric unit together to form the supramolecular three-dimensional hydrogen bonding network. The oxygen atoms of the coordinated H$_2$O molecules in a dimeric unit (O(7) and O(8) or O(7A) and O(8A)) form the hydrogen bonding with the three nitrogen atoms of pyridine-3-carboxylates (N(1), N(2), and N(3) or N(1A), N(2A), and N(3A)) with angles in the range 155(5)—174(5)$^\circ$. Besides this O—H$\cdots$N hydrogen bonding, there also exists another type of hydrogen bonding O—H$\cdots$O between the oxygen atoms of H$_2$O molecules and the oxygen atoms of chelated carboxylates, the angle of which is 172(4)$^\circ$. The detailed data of hydrogen bonding are shown in Table 3.

The ultraviolet absorption spectrum of [Dy(NIC)$_3$-(H$_2$O)$_2$]$_2$ (10^{-4} mol dm^{-3} ethanol solution) shows a domain absorption band at $\lambda = 255$ nm in ultraviolet region, which is attributed to the characteristic absorption of nicotinate. This indicates that NIC is the energy donor and luminescence sensitizer of Dy^{3+} ion. The excitation spectra of these complex systems show that they have no effective absorption in long wavelength ultraviolet region of the range 300—400 nm. The effective energy absorption mainly takes place in the narrow ultraviolet region of 210—275 nm and the

Table 3. Hydrogen Bonds for the Title Complex

D—H$\cdots$A	d(D—H)$/\text{Å}$	d(H$\cdots$A)$/\text{Å}$	d(D$\cdots$A)$/\text{Å}$	ω(DHA)$/°$
O(8)—H(8A)$\cdots$O(1)[a]	0.879(10)	1.91(3)	2.762(5)	163(10)
O(7)—H(7A)$\cdots$N(2)[b]	0.878(10)	1.89(2)	2.751(6)	167(8)
O(7)—H(7B)$\cdots$N(3)[c]	0.878(10)	2.04(3)	2.849(6)	153(5)
O(8)—H(8B)$\cdots$N(1)[d]	0.881(10)	1.92(2)	2.770(6)	162(6)

Symmetry transformations used to generate equivalent atoms: a) $-x+1$, $-y+2$, $-z+2$; b) $x-1$, y, z; c) $-x+2$, $y-1/2$, $-z+3/2$; d) x, $-y+3/2$, $z-1/2$.

excitation bands consist of four main peaks at 223 nm, 241 nm, 258 nm, and 274 nm, respectively. Fig. 3 shows the emission spectra of $[Dy(NIC)_3(H_2O)_2]_2$. Under the excitation of 241 nm, two apparent emission bands can be observed and the maximum emission wavelengths are at 484 nm and 575 nm, respectively, which corresponds with the characteristic emission $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2, 13/2$) transitions of Dy^{3+} ion. Especially, it needs to be referred that the blue emission intensity of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is much stronger than that of the yellow one of $^4F_{9/2} \rightarrow {}^6H_{13/2}$, suggesting that the pyridine-3-carboxylate is suitable for the sensitization of blue luminescent of Dy^{3+} in the narrow ultraviolet region.

EXPERIMENTAL

Diffraction data for a crystal with dimensions 0.25 mm $\times$ 0.15 mm $\times$ 0.10 mm were obtained with graphite-monochromated Mo$K\alpha$ radiation on an Enraf-Nonius CAD4 four-circle diffractometer and were collected by the ω-2θ scan technique. The structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and were not refined. All calculations were performed using SHELXS-97 and SHELXL-97 [16, 17]. A summary of crystallographic data and refinement parameters is given in Table 4. Additional materials available from the Cambridge Crystallographic Data Centre comprise complete lists of atomic coordinates, thermal parameters, and bond lengths and angles (No. CCDC-230254).

Elemental analyses (C, H, N) were determined on a Cario elemental analyzer. Infrared spectroscopy on KBr pellets was performed on a Nexus 912 AO446 FT-IR spectrophotometer in the 400—4000 cm^{-1} region. Ultraviolet absorption spectra were taken with an Aligent 8453 spectrophotometer. Excitation and emission spectra were measured with a Perkin—Elmer LS-55 model spectrophotometer.

Complex

To an ethanol (5 cm^3) solution of methyl pyridine-3-carboxylate (MNIC) (0.1846 g; 1.5 mmol), Dy(NO$_3$)$_3$ $\cdot$6H$_2$O (0.2281 g; 0.5 mmol) in a minimum amount

Table 4. Crystal Data and Structure Refinement for the Title Complex

Complex	$[Dy(NIC)_3(H_2O)_2]_2$
Formula	$C_{36}H_{32}Dy_2N_6O_{16}$
Relative molecular mass M_r	1129.68
Colour	Colourless
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	Mo$K\alpha$
Crystal system	$P2_1/c$
Space group	Monoclinic
Unit dimensions	$a = 9.575(2)$ Å
	$b = 11.600(2)$ Å
	$c = 17.758(5)$ Å
	$\beta = 91.565(4)°$
Volume	1971.6(7) Å^3
Z	2
Calculated density	1.903 Mg/m^3
Absorption coefficient	3.842 mm^{-1}
$F(000)$	1100
Crystal size	0.25 mm $\times$ 0.15 mm $\times$ 0.10 mm
Θ range for data collection	2.10° to 25.01°
Reflections/collected/unique	7989/3466 [R(int) = 0.0373]
Completeness to $2\Theta = 25.01$	99.7 %
Absorption correction	None
Max. and min. transmission	0.6999 and 0.4468
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3466/4/287
Goodness-of-fit on F^2	1.144
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0337$, $wR_2 = 0.0897$
Largest diff. peak and hole	0.720 $e \cdot \text{Å}^{-3}$ and -2.679 $e \cdot \text{Å}^{-3}$

of solution was slowly added under stirring. The pH value of the mixed solution was adjusted with sodium hydroxide to be about 6.5 and the solution was further stirred for 4 h, then a little white precipitate appeared. The resulting solution was filtered and the filtrate was allowed to stand at room temperature. After one month, well-shaped light colourless single crystals suitable for analysis were obtained. For $C_{36}H_{32}Dy_2N_6O_{16}$ w_i(calc.): 38.28 % C, 2.86 % H, 7.44 % N, 28.77 % Dy; w_i(found): 38.44 % C, 2.53 % H, 7.31 % N, 28.55 % Dy. IR spectrum exhibits a complicated pattern of bands in the range 400—4000 cm^{-1}: 1544.6 ν_{as}(COO$^-$), 1411 ν_{as}(COO$^-$).

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