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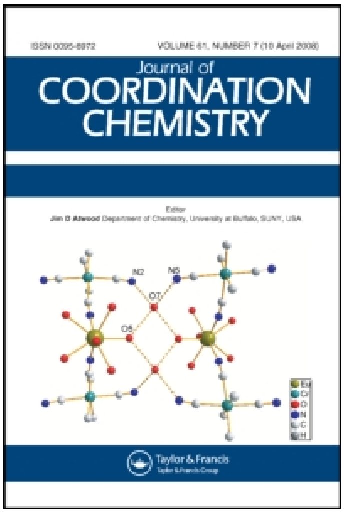

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A novel dimeric complex of dysprosium with pyridine-3-carboxylic acid: structure and photophysical properties

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A NOVEL DIMERIC COMPLEX OF DYSPROSIUM WITH PYRIDINE-3-CARBOXYLIC ACID: STRUCTURE AND PHOTOPHYSICAL PROPERTIES

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A dimeric complex $[Dy(NIC)_3(H_2O)_2]_2$ (HNIC = pyridine-3-carboxylic acid) 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 space group $P2_1/c$, with $a = 9.560(3)$, $b = 11.601(4)$, $c = 17.731(5)$ Å, $\beta = 91.572(4)°$, $V = 1965.7(10)$ Å^3, $D_c = 1.909$ Mg/m^3, $Z = 2$, $F(000) = 1100$, GOF = 0.956, $R_1 = 0.0248$. Photophysical properties have been studied with ultraviolet absorption, excitation and emission spectra. The complex exhibits strong blue emission.

Keywords: Dysprosium complex; Dimer; Molecular structure; Photophysical properties

INTRODUCTION

Much research has been carried out on lanthanide complexes of organic ligands which exhibit photophysical properties suitable for application as luminescence probes for chemical or biological macromolecules and active centres for molecular-based luminescent materials [1–6]. Lanthanide complexes of aromatic carboxylic acids show higher thermal or luminescent stability for practical applications than other lanthanide complex systems because they readily form the dimeric or infinite chain polymeric structures [7–10]. Pyridine-carboxylic acids, as ligands, have received some attention [11,12]. Basic compositions for these lanthanide complexes with pyridine-3(4)-carboxylic acids (L) correspond to $Ln : L : H_2O = 1 : 3 : 1$ [13,14]. In this article, we report a new dimeric dysprosium complex of pyridine-3-carboxylic acid (nicotinic acid) with a similar composition, but with a novel dimmer structure, $[Dy(PIC)_3(H_2O)_2]_2$. In particular, the dinuclear complex exhibits strong luminescence and the blue emission is much stronger than the yellow one. We report detailed crystal structure and photophysical properties.

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EXPERIMENTAL

Synthesis of $[Dy(PIC)_3(H_2O)_2]_2$

To a dimethylformide (5 cm^3) solution of $Dy(NO_3)_3 \cdot 6H_2O$ (0.2281 g, 0.5 mmol), pyridine-3-carboxylic acid (nicotinic acid, HNIC) (0.1846 g, 1.5 mmol) in a minimum amount of DMF was slowly added with stirring. The pH of the mixed solution was adjusted to be about 6.5 and further stirred for 4 h, when a little white precipitate appeared. The resulting solution was filtered and the filtrate allowed to standing at room temperature. After two weeks, well-shaped, colourless, single crystals suitable for analysis were obtained. Anal. Calcd. for $C_{36}H_{32}Dy_2N_6O_{16}$: C, 38.28; H, 2.86; N, 7.44; Dy, 28.77%. Found: C, 38.61; H, 2.55; N, 7.69; Dy, 28.48%. IR spectra exhibit a complicated pattern of bands in the range 4000–400 cm^{-1}: 1544.6 cm^{-1} (v_{sCOO-}), 1411 cm^{-1} (v_{asCOO-}).

X-ray Crystallography

Diffraction data for a crystal with dimensions 0.20 × 0.20 × 0.10 mm were collected using graphite-monochromated MoKα radiation on an Enraf-Nonius CAD4 four-circle diffractometer, using the ω–2θ scan technique. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS–97 and SHELXL–97 [15,16]. A summary of crystallographic data and refinement parameters is given in Table I. Additional material available from the Cambridge Crystallographic Data Center comprise complete lists of atomic coordinates, thermal parameters, and bond lengths and angles (No. CCDC-212331).

Physical Measurements

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

RESULTS AND DISCUSSION

Description of the Crystal Structure

Final atomic coordinates for non-hydrogen atoms are listed in Table II. Figure 1 shows the coordination geometry and atom labelling in the crystal structure of $[Dy(NIC)_3(H_2O)_2]_2$. X-ray diffraction reveals that the dimeric formulation $[Dy(NIC)_3(H_2O)_2]_2$ has two equivalent structural units related by a crystallographic inversion centre. This is similar to the structures of other lanthanide pyridine-3-carboxylates [13,14]. 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

TABLE I Crystal data and structure refinement details for the title complex

Complex	$[Dy(NIC)_6(H_2O)_2]_2$
Formula	$C_{36}H_{32}Dy_2N_6O_{16}$
Relative molecular weight M	1129.68
Colour	Colourless
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	MoKα
Crystal system	$P2_1/c$
Space group	Monoclinic
Unit dimensions	$a = 9.560(3)$ Å $b = 11.601(4)$ Å $c = 17.731(5)$ Å $\beta = 91.572(4)$ Å
Volume	1965.7(10)
Z	2
Calculated density	1.909 Mg/m^3
Absorption coefficient	3.853 nm^{-1}
$F(000)$	1100
Crystal size	0.20 mm × 0.20 mm × 0.10 mm
Θ range for data collection	2.10° to 26.99°
Reflections/collected/unique	9556/4248 [$R(\mathrm{int}) = 0.0275$]
Completeness to $2\Theta = 26.99$	99.1%
Absorption correction	Psi-scan
Max. and min. transmission	0.6993 and 0.5129
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4248/0/287
Goodness-of-fit on F^2	0.956
Final R indices [$1 > 2\sigma(I)$]	$R_1 = 0.0248$, $wR_2 = 0.0470$
Extinction coefficient	0.0003 (3)
Largest diff. peak and hole	$4.644\,e \cdot Å^{-3}$ and $-0.737\,e \cdot Å^{-3}$

to give coordination number for dysprosium of 8. The pyridine-3-carboxylate groups are coordinated to the two dysprosium ions solely by carboxylate oxygen atoms from four bridged pyridine-3-carboxylates (O(1), O(2), O(3) and O(4) for Dy(1), O(1A), O(2A), O(3A) and O(4A) for Dy(1A)) and two chelated pyridine-3-carboxylates (O(5) and O(6) for Dy(1), O(5A) and O(6A) for Dy(1A)). The bridged pyridine-3-carboxylates are coordinated in such a manner that each oxygen atom is bound to one dysprosium ion with Dy–O distances of 2.293(3) Å for Dy(1)–O(1), 2.335(3) Å for Dy(1)–O(2), 2.306(2) Å for Dy(1)–O(3) and 2.322(2) Å for Dy(1)-O(4), while the chelated pyridine-3-carboxylate is coordinated with slightly longer Dy–O distances, 2.452(2) Å for Dy(1)–O(1) and 2.499(2) Å for Dy(1)–O(2). Distances between the oxygen atoms of the coordinated water molecules and dysprosium ions are 2.372(2) Å for Dy(1)–O(1)O and 2.363(2) Å for Dy(1)–O(2). The coordination polyhedron can be described as a highly distorted square antiprism with O(5), O(6), O(7), O(8) forming one square face and O(5A), O(6A), O(7A), O(8A) the other. Selected bond distances and bond angles for the dysprosium complex are listed in Table III. Water molecules are involved in hydrogen bonding to all nitrogen atoms of pyridine-3-carboxylic acid. Hydrogen bonds link adjacent dimers to form a three-dimensional network. The oxygen atoms of the coordinated H_2O molecules in dimeric (O(7) and O(8) or O(7A) and O(8A)) with N(1), N(2) and N(3) or N(1A), N(2A) and N(3A), respectively, with angles in the range 155(5)–174(5)°. Other hydrogen bonds exist between the oxygen atoms of H_2O molecules and the oxygen atoms of chelated carboxylates. Data for hydrogen bonding are given in Table IV.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (10^3 Å) for the complex

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Dy(1)	1894(1)	−1047(1)	10051(1)	22(1)
O(1)	707(3)	−359(3)	9004(2)	49(1)
O(2)	−1054(3)	817(2)	8734(1)	44(1)
O(3)	2070(2)	934(2)	10107(2)	38(1)
O(4)	194(2)	2070(2)	9952(1)	36(1)
O(5)	3931(2)	−929(2)	9244(7)	36(1)
O(6)	2523(3)	−2381(2)	9007(1)	39(1)
O(7)	3925(3)	−672(3)	10810(2)	34(1)
O(8)	2561(3)	−2804(3)	10632(2)	38(1)
N(1)	4710(3)	3515(3)	9466(2)	43(1)
N(2)	1585(4)	−639(3)	6744(2)	52(1)
N(3)	4830(4)	−3425(3)	7186(2)	50(1)
C(1)	−16(4)	233(3)	8562(2)	32(1)
C(2)	384(3)	262(3)	7750(2)	26(1)
C(3)	−29(4)	1142(3)	7281(2)	35(1)
C(4)	411(4)	1142(4)	6550(2)	47(1)
C(5)	1202(5)	231(4)	6316(2)	53(1)
C(6)	1190(4)	−610(3)	7459(2)	39(1)
C(7)	1471(4)	1867(3)	9933(2)	27(1)
C(8)	2406(3)	2830(3)	9682(2)	25(1)
C(9)	1852(4)	3849(3)	9399(2)	38(1)
C(10)	2747(4)	4696(3)	9166(2)	50(1)
C(11)	4156(4)	4485(4)	9199(2)	50(1)
C(12)	3838(4)	2712(3)	9704(2)	34(1)
C(13)	3606(4)	−1826(3)	8875(2)	30(1)
C(14)	4554(4)	−2246(3)	8273(2)	31(1)
C(15)	5921(4)	−1875(4)	8229(2)	44(1)
C(16)	6729(4)	−2305(4)	7664(2)	53(1)
C(17)	6151(5)	−3076(4)	7168(2)	53(1)
C(18)	4063(4)	−3011(3)	7737(2)	41(1)

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

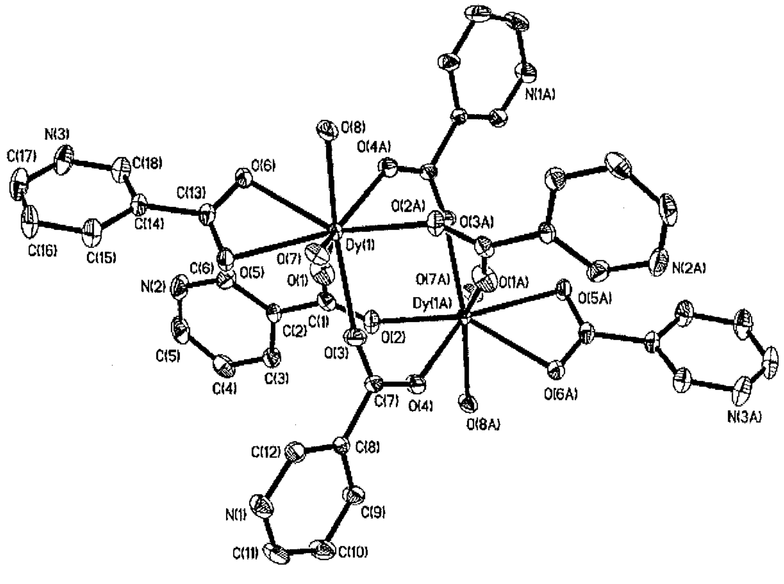

FIGURE 1 Molecular structure of the $[Dy(PIC)_3(H_2O)_2]_2$ complex.

TABLE III Selected bond distances (Å) and bond angles (°) for the title complex

Dy(1)–O(1)	2.293(3)	O(3)–C(7)	1.259(4)
Dy(1)–O(3)	2.306(2)	O(4)–C(7)	1.245(4)
Dy(1)–O(4)#1	2.322(2)	O(4)–Dy(1)#1	2.322(2)
Dy(1)–O(2)#1	2.335(3)	O(5)–C(13)	1.264(4)
Dy(1)–O(8)	2.363(3)	O(6)–C(13)	1.247(4)
Dy(1)–O(7)	2.372(3)	N(1)–C(11)	1.325(5)
Dy(1)–O(5)	2.452(2)	N(1)–C(12)	1.326(4)
Dy(1)–O(6)	2.499(2)	N(2)–C(5)	1.308(5)
Dy(I)–C(13)	2.834(3)	N(2)–C(6)	1.334(5)
O(1)–C(1)	1.239(4)	N(3)–C(17)	1.327(5)
O(2)–C(1)	1.246(4)	N(3)–C(18)	1.327(4)
O(2)–Dy(1)#1	2.335(3)		
O(1)–Dy(1)–O(3)	73.86(10)	O(2)#1–Dy(1)–C(13)	159.31(10)
O(1)–Dy(1)–O(4)#1	76.69(9)	O(8)–Dy(1)–C(13)	83.72(11)
O(3)–Dy(1)–O(4)#1	124.85(8)	O(7)–Dy(1)–C(13)	89.74(10)
O(1)–Dy(1)–O(2)#1	122.15(10)	O(5)–Dy(1)–C(13)	26.41(9)
O(3)–Dy(1)–O(2)#1	82.69(9)	O(6)–Dy(1)–C(13)	26.09(9)
O(4)#1–Dy(1)–O(2)#1	75.12(9)	C(1)–O(1)–Dy(1)	163.9(3)
O(1)–Dy(1)–O(8)	140.77(11)	C(1)–O(2)–Dy(1)#1	125.8(2)
O(3)–Dy(1)–O(8)	145.30(10)	C(7)–O(3)–Dy(1)	144.4(2)
O(4)#1–Dy(1)–O(8)	77.39(10)	C(7)–O(4)–Dy(1)#1	138.3(2)
O(2)#1–Dy(1)–O(8)	78.03(11)	C(13)–O(5)–Dy(1)	93.9(2)
O(1)–Dy(1)–O(7)	140.79(11)	C(13)–O(6)–Dy(1)	92.2(2)
O(3)–Dy(1)–O(7)	74.64(10)	C(11)–N(1)–C(12)	117.4(3)
O(4)#1–Dy(1)–O(7)	141.74(10)	C(5)–N(2)–C(6)	116.7(4)
O(2)#1–Dy(1)–O(7)	75.68(10)	C(17)–N(3)–C(18)	116.9(4)
O(8)–Dy(1)–O(7)	72.79(11)	O(1)–C(1)–O(2)	125.4(3)
O(1)–Dy(1)–O(5)	83.78(9)	O(1)–C(1)–C(2)	117.9(3)
O(3)–Dy(1)–O(5)	84.92(8)	O(2)–C(1)–C(2)	116.7(3)
O(4)#1–Dy(1)–O(5)	136.34(8)	N(2)–C(5)–C(4)	124.6(4)
O(2)#1–Dy(1)–O(5)	146.18(9)	N(2)–C(6)–C(2)	123.4(4)
O(8)–Dy(1)–O(5)	95.32(10)	O(4)–C(7)–O(3)	126.6(3)
O(7)–Dy(1)–O(5)	70.72(9)	O(4)–C(7)–C(8)	117.3(3)
O(1)–Dy(1)–O(6)	74.91(10)	N(1)–C(11)–C(10)	123.4(4)
O(3)–Dy(1)–O(6)	129.09(8)	N(1)–C(12)–C(8)	123.8(3)
O(4)#1–Dy(1)–O(6)	84.59(8)	O(6)–C(13)–O(5)	121.4(3)
O(2)#1–Dy(1)–O(6)	148.21(9)	O(6)–C(13)–C(14)	119.2(3)
O(8)–Dy(1)–O(6)	73.77(10)	O(5)–C(13)–C(14)	119.4(3)
O(7)–Dy(1)–O(6)	108.90(9)	O(6)–C(13)–Dy(1)	61.75(17)
O(5)–Dy(1)–O(6)	52.50(8)	O(5)–C(13)–Dy(1)	59.66(17)
O(1)–Dy(1)–C(13)	78.37(10)	C(14)–C(13)–Dy(1)	178.0(2)
O(3)–Dy(1)–C(13)	107.86(10)	N(3)–C(17)–C(16)	123.7(4)
O(4)#1–Dy(1)–C(13)	110.41(10)	N(3)–C(18)–C(14)	123.9(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z+2$.

Photophysical Properties

The electronic absorption spectrum of $[Dy(NIC)_3(H_2O_2)]_2$ (10^{-4} mol cm^{-3} ethanol solution) shows an absorption band at 263 nm, attributed to the characteristic absorption of pyridine-3-carboxylate. This indicates that HNIC is the energy donor and luminescence sensitizer of Dy^{3+} ion. Excitation spectra show that the complex has no effective absorption in long wavelength ultraviolet region in the range 300–400 nm, and effective energy absorption mainly takes place in the narrow range from 210 to 275 nm. Excitation bands consist of four main peaks at 221, 241, 257 and 271 nm. Corresponding emission spectra were measured by selectively excitating the four different excitation wavelengths; this results in similar emission frequencies but with different luminescent

TABLE IV Hydrogen bonds details (Å) for the complex

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*d(DHA)*
O(8)–H(8B)···N(2)#2	0.66(4)	2.24(4)	2.850(4)	155(5)
O(8)–H(8A)···N(1)#3	0.94(6)	1.81(6)	2.746(4)	174(5)
O(7)–H(7B)···N(3)#2	0.78(4)	2.01(4)	2.772(4)	165(4)
O(7)–H(7A)···O(5)#3	0.77(3)	2.00(4)	2.770(4)	172(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z+2$; #2 $x, -y-1/2, z+1/2$; #3 $-x+1, -y, -2+2$.

intensities. Thus these four bands are taken to be the effective absorbers for luminescence of Dy ions in the complex.

Under excitation of 241 nm, two emission bands are observed with maximum emission wavelengths at 483.9 nm and 574.2 nm, respectively, corresponding to the characteristic emission $^4F_{9/2} \rightarrow {}^6H_j (j = 15/2, 13/2)$ transitions of the Dy^{3+} ion. It is worth pointing out that the blue emission intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is much stronger than the yellow one, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, suggesting that pyridine-3-carboxylate is suitable for the sensitization of blue luminescence of Dy^{3+} in a narrow ultraviolet region.

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