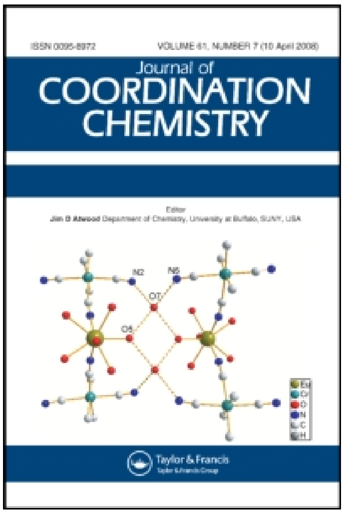

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A novel synthetic path to a luminescent, dimeric samarium complex induced by the hydrolysis of methyl pyridine-3-carboxylate

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A novel synthetic path to a luminescent, dimeric samarium complex induced by the hydrolysis of methyl pyridine-3-carboxylate

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A novel path to lanthanide complexes of aromatic carboxylates controlled by the hydrolysis of the corresponding aromatic carboxylate ester has been discovered. A dimeric samarium complex of pyridine-3-carboxylate (NIC) has been obtained using methyl pyridine-3-carboxylate (MNIC) as the starting ligand. With the hydrolysis of MNIC to NIC in the presence of sodium hydroxide, samarium ions coordinate to HNIC to form $[Sm(NIC)_3(H_2O)_2]_2$. X-ray analysis reveals the dimeric structure formed through bridging oxygen atoms of carboxylate groups. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.668(3)$, $b = 11.807(3)$, $c = 17.512(5)$ Å, $\beta = 92.361(3)^\circ$, $V = 1997.3(10)$ Å^3, $D_c = 1.838$ Mg m^{-3}, $Z = 2$, $R_1 = 0.0225$. The complex exhibits strong luminescence.

Keywords: Samarium complex; Dimer; Molecular structure; Luminescence; Hydrolysis; Methyl pyridine-3-carboxylate

1. Introduction

Lanthanide coordination compounds with organic ligands have great potential as luminescence probes for chemical or biological macromolecules and as active centres for luminescent, molecular-based materials because they possess special chelated structures and exhibit varied photophysical properties [1–6]. In particular, lanthanide complexes with aromatic carboxylic acids can readily form dimers or infinite chain polymeric structures, which show higher thermal stabilities than other lanthanide complex systems [7–10]. Pyridinecarboxylic acid lanthanide ions complexes have been discussed [11,12]. Complexes with pyridine-3(4)-carboxylic acids (L) show compositions which correspond to Ln:L:$H_2O = 1:3:1$ [13–17]. In this paper, by using methyl pyridine-3-carboxylate as a starting ligand, and by controlling the hydrolysis of methyl pyridine-3-carboxylate under basic conditions, a new dimeric samarium complex with pyridine-3-carboxylate (nicotinate) has been obtained. The complex exhibits the

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strong, characteristic luminescence of Sm^{3+}. Herein we report the crystal structure and spectroscopic properties.

2. Experimental

2.1. *Synthesis of [Sm(NIC)$_3$(H$_2$O)$_2$]$_2$ induced by the hydrolysis of HMNIC*

To an ethanol ($5\,cm^3$) solution of methyl pyridine-3-carboxylate (methyl nicotinate, as MNIC) (0.1846 g, 1.5 mmol), $Sm(NO_3)_3 \cdot 6H_2O$ (0.2231 g, 0.5 mmol), in a minimum amount of ethanol solution was slowly added with stirring. The pH of the mixed solution was adjusted to about 6.5 with sodium hydroxide and further stirred for 4 h, when a white precipitate appeared. The solution was filtered and the filtrate allowed to stand at room temperature. After one month, well-shaped, colourless single crystals suitable for analysis were obtained. Anal. Calcd. for $C_{36}H_{32}Sm_2N_6O_{16}$(%): C, 39.11; H, 2.92; N, 7.60; Sm, 27.21. Found: C, 39.28; H, 2.62; N, 7.43; Sm, 27.49. IR spectra exhibit a complicated pattern of bands in the range 4000–400 cm^{-1}; 1545 cm^{-1} (ν_{sCOO-}), 1412 cm^{-1} (ν_{asCOO-}).

2.2. *X-ray crystallography*

Diffraction data for a crystal with dimensions $0.30 \times 0.15 \times 0.10$ mm are collected with graphite-monochromated Mo Kα 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 techniques. Hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS97 and SHELXL97 [18,19]. A summary of crystallographic data and refinement parameters is given in table 1.

2.3. *Physical measurements*

Elemental analyses (C, H, N) were determined on an Elementar Cario instrument. Infrared spectroscopy (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.

3. Results and discussion

3.1. *Hydrolysis of MNIC and the coordination reaction*

The typical hydrolysis process can be described as:

$$C_5NH_4COOCH_3(MNIC) + NaOH \rightarrow C_5NH_4COONa(NaNIC) + CH_3OH \qquad (1)$$

In the presence of NaOH in the mixed reaction solution, methyl nicotinate hydrolyzes to yield sodium nicotinate and methanol and coordination between nicotinate and

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

Complex	$[Sm(NIC)_3(H_2O)_2]_2$
Formula	$C_{36}H_{32}Sm_2N_6O_{16}$
Relative molecular weight M	1105.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Radiation	Mo Kα
Space group	$P2_1/c$
Unit cell dimensions (Aring;)	$a=9.668(3)$ $b=11.807(3)$ $\beta=92.361(3)^\circ$ $c=17.512(5)$
V (Å^3)	1997.3(10)
Z	2
Calculated density (Mg m^{-3})	1.838
Absorption coefficient (mm^{-1})	2.991
$F(000)$	1084
Crystal size (mm)	$0.30 \times 0.15 \times 0.10$
θ range for data collection (°)	2.08 to 26.01
Reflections collected unique	8814/3906 [R(int) = 0.0271]
Completeness to $2\theta = 26.01$ (%)	99.8
Absorption correction	None
Max. and min. transmission	0.7541 and 0.4673
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3906/4/336
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0225$, $wR_2 = 0.0586$
Largest diff. peak and hole (e Å^{-3})	0.611 and −0.920

Sm^{3+} takes place. The slow formation of the dimeric Sm complex is controlled by both the hydrolysis process and the coordination reaction.

3.2. *Crystal structure*

Final atomic coordinates for non-hydrogen atoms are listed in table 2. Figure 1 shows coordination geometry and atom labelling in the structure of $[Sm(NIC)_3(H_2O)_2]_2$. Two equivalent structural units (one half of the dimer) are related by a crystallographic inversion centre, similar to the case with other lanthanide pyridine-3-carboxylates [13–17]. The two symmetry-related samarium 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 samarium ion to give a coordination number of 8. Pyridine-3-carboxylate groups are coordinated to the two samarium ions by carboxylate oxygen atoms from four bridging pyridine-3-carboxylates [O(1), O(2A), O(3) and O(4A) for Sm(1), O(1A), O(2), O(3A) and O(4) for Sm(1A)] and two chelated pyridine-3-carboxylates [O(5) and O(6) for Sm(1), O(5A) and O(6A) for Sm(1A)]. The bridging ligands are coordinated in such a manner that each oxygen atom is only bound to one samarium ion [Sm–O distances are 2.963(19) Å for Sm(1)–O(1), 2.3699(19) Å for Sm(1)–O(2A), 2.417(2) Å for Sm(1)–O(3) and 2.371(2) Å for Sm(1)–O(4A)]. Chlelated pyridine-3-carboxylate is coordinated with slightly longer Sm–O distances: 2.569(2) Å for Sm(1)–O(5) and 2.496(2) Å for Sm(1)–O(6). Distances to the oxygen atoms of coordinated water

Table 2. Atomic coordinates (10^4) and equivalent isotropic displacement parameters (10^3 Å^2) for the complex.

	x/a	y/b	z/c	U/eq
O(1)	10254(2)	2922(2)	9910(1)	38(1)
O(1)	10254(2)	2922(2)	9910(1)	38(1)
O(2)	12129(2)	4020(2)	10067(1)	42(1)
O(3)	8808(3)	4122(2)	8633(1)	52(1)
O(4)	10473(3)	5292(2)	9015(1)	57(1)
O(5)	7561(2)	2658(2)	11049(1)	41(1)
O(6)	6121(2)	4051(2)	10783(1)	43(1)
O(7)	6028(2)	4385(2)	9187(1)	38(1)
O(8)	7410(2)	2214(2)	9361(1)	41(1)
N(1)	14722(3)	1469(2)	9437(2)	47(1)
N(2)	5151(3)	1532(3)	12811(2)	54(1)
N(3)	11598(3)	5697(3)	6757(2)	51(1)
C(1)	11524(3)	3108(2)	9893(2)	30(1)
C(2)	12432(3)	2149(2)	9646(2)	29(1)
C(3)	13855(3)	2270(3)	9668(2)	38(1)
C(4)	14157(4)	507(3)	9181(2)	52(1)
C(5)	12756(4)	301(3)	9145(2)	53(1)
C(6)	11877(3)	1140(3)	9375(2)	43(1)
C(7)	9834(3)	4722(3)	8512(2)	36(1)
C(8)	10337(3)	4748(2)	7715(2)	30(1)
C(9)	11146(3)	5632(3)	7462(2)	41(1)
C(10)	11286(4)	4847(3)	6289(2)	52(1)
C(11)	10496(4)	3937(3)	6477(2)	49(1)
C(12)	9993(3)	3890(3)	7206(2)	37(1)
C(13)	6449(3)	3171(2)	11155(2)	32(1)
C(14)	5489(3)	2733(3)	11739(2)	34(1)
C(15)	5949(3)	1964(3)	12279(2)	44(1)
C(16)	3831(4)	1862(4)	12804(2)	56(1)
C(17)	3284(4)	2636(4)	12294(2)	56(1)
C(18)	4125(3)	3079(3)	11752(2)	48(1)

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

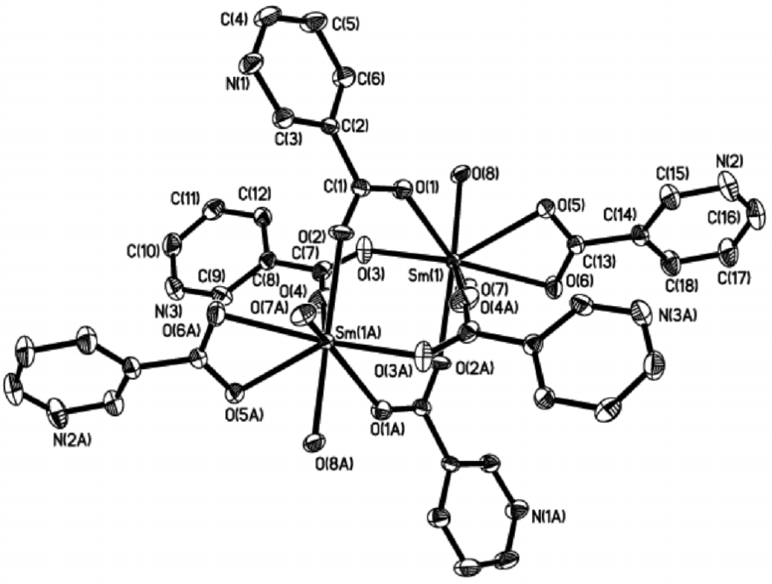

Figure 1. Molecular structure of the $[Sm(NIC)_3(H_2O)_2]_2$ complex.

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

Sm(1)–O(2)#1	2.3699(19)	O(3)–C(7)	1.244(4)
Sm(1)–O(4)#1	2.371(2)	O(4)–C(7)	1.250(4)
Sm(1)–O(1)	2.3963(19)	O(4)–Sm(1)#1	2.371(2)
Sm(1)–O(3)	2.417(2)	O(5)–C(13)	1.255(3)
Sm(1)–O(8)	2.422(2)	O(6)–C(13)	1.260(3)
Sm(1)–O(7)	2.441(2)	N(1)–C(4)	1.330(5)
Sm(1)–O(6)	2.496(2)	N(1)–C(3)	1.337(4)
Sm(1)–O(5)	2.569(2)	N(2)–C(16)	1.334(5)
Sm(1)–C(13)	2.896(3)	N(2)–C(15)	1.336(4)
O(1)–C(1)	1.249(3)	N(3)–C(10)	1.322(5)
O(2)–C(1)	1.257(3)	N(3)–C(9)	1.329(4)
O(2)–Sm(1)#1	2.3699(19)		
O(2)#1–Sm(1)–O(4)#1	73.11(9)	O(8)–Sm(1)–O(5)	73.80(8)
O(2)#1–Sm(1)–O(1)	128.02(8)	O(7)–Sm(1)–O(5)	108.76(8)
		O(6)–Sm(1)–O(5)	51.30(7)
O(4)#1–Sm(1)–O(1)	75.90(8)	O(2)#1–Sm(1)–C(13)	105.66(8)
O(2)#1–Sm(1)–O(3)	87.63(9)	O(4)#1–Sm(1)-C(13)	82.87(9)
O(4)#1–Sm(1)–O(3)	122.94(9)	O(1)–Sm(1)–C(13)	110.67(8)
O(1)–Sm(1)–O(3)	75.62(8)	O(3)–Sm(1)–C(13)	153.87(8)
O(2)#1–Sm(1)–O(8)	145.36(8)	O(8)–Sm(1)–C(13)	81.78(8)
O(4)#1–Sm(1)–O(8)	141.38(9)	O(7)–Sm(1)–C(13)	88.53(8)
O(1)–Sm(1)–O(8)	76.82(7)	O(6)–Sm(1)–C(13)	25.67(7)
O(3)–Sm(1)–O(8)	74.95(8)	O(5)–Sm(1)–C(13)	25.66(7)
O(2)#1–Sm(1)–O(7)	73.21(8)	C(1)–O(1)–Sm(1)	138.23(19)
O(4)#1–Sm(1)–O(7)	141.39(8)	C(1)–O(2)–Sm(1)#1	142.9(2)
O(1)–Sm(1)–O(7)	141.47(7)	C(7)–O(3)–Sm(1)	116.3(2)
O(3)–Sm(1)–O(7)	73.63(8)	C(7)–O(4)–Sm(1)#1	168.5(2)
O(8)–Sm(1)–O(7)	73.23(8)	C(13)–O(5)–Sm(1)	91.88(17)
O(2)#1–Sm(1)–O(6)	83.35(8)	C(13)–O(6)–Sm(1)	95.21(17)
O(4)#1–Sm(1)–O(6)	88.19(9)	Sm(1)–O(7)–H(7A)	132(3)
O(1)–Sm(1)–O(6)	136.07(7)	Sm(1)–O(7)–H(7B)	124(3)
O(3)–Sm(1)–O(6)	143.27(8)	Sm(1)–O(8)–H(8A)	121(3)
O(8)–Sm(1)–O(6)	92.91(7)	Sm(1)–O(8)–H(8B)	125(2)
O(7)–Sm(1)–O(6)	69.67(8)	O(5)–C(13)–Sm(1)	62.45(14)
O(2)#1–Sm(1)–O(5)	125.83(8)	O(6)–C(13)–Sm(1)	59.11(14)
O(4)#1–Sm(1)–O(5)	77.09(9)	C(14)–C(13)–Sm(1)	175.9(2)
O(1)–Sm(1)–-O(5)	85.04(7)		
O(3)–Sm(1)–O(5)	146.21(8)		

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

are 2.441(2) Å for Sm(1)–O(7) and 2.422(2) Å for Sm(1)–O(8). The coordination polyhedron can be described as a highly distorted square antiprism with O(5), O(6), O(7) and O(8) forming one square and O(5A), (O(6A), O(7A) and O(8A) the other. Selected bond distances and angles for the complex are listed in table 3.

Figure 2 shows a packing view for a unit cell. The existence of water molecules gives rise to hydrogen bonding to all the nitrogen atoms of pyridine-3-carboxylic acid. There are hydrogen bonding interactions between two adjacent dimers and this H-bonding joins dimeric units to form a supramolecular, three-dimensional network. Oxygen atoms of coordinated H_2O molecules, [O(7) and O(8)] form hydrogen bonds with nitrogen atoms [N(1), N(2) and N(3)] with angles in the range 159(3) to 178(4)°. Besides O–H···N interaction, O–H···O bonding between H_2O molecules and chelated carboxylates, [angle 168(4)°] is observed. Detailed data for hydrogen bonding are given in table 4.

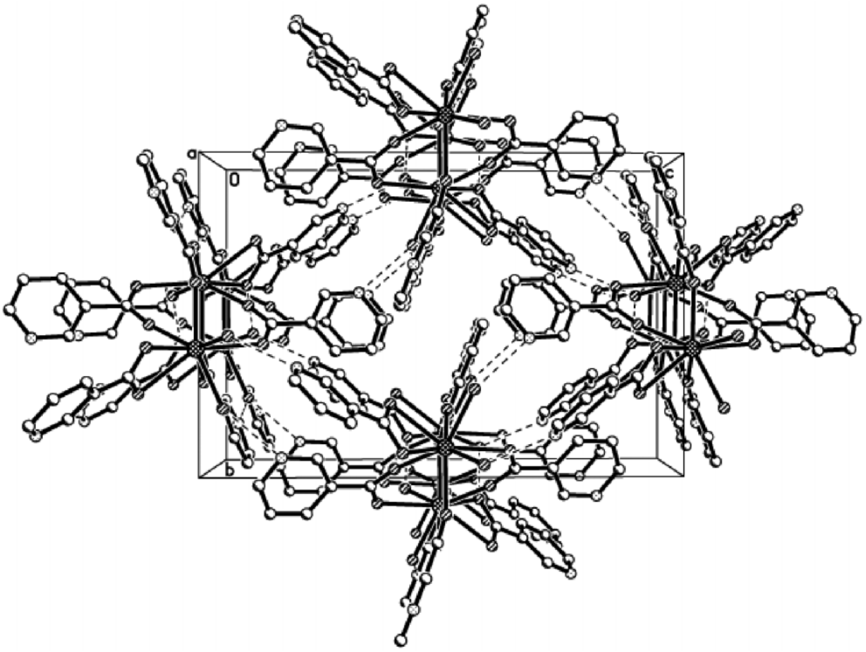

Figure 2. Packing view in a unit cell of $[Sm(NIC)_3(H_2O)_2]_2$.

Table 4. Hydrogen bonds (Å) in the complex.

D–H···A	d(D–H)	D(H···A)	d(D···A)	<(DHA)
O(8)–H(8A)···N(1)#2	0.876(10)	1.876(11)	2.752(3)	178(4)
O(7)–H(7A)···O(6)#3	0.873(10)	1.922(13)	2.781(3)	168(4)
O(7)–H(7B)···N(2)#4	0.876(10)	1.894(16)	2.744(4)	163(4)
O(8)–H(8B)···N(3)#5	0.869(10)	2.021(16)	2.850(3)	159(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z+2$; #2 $x-1$, y, z; #3 $-x+1$, $-y+1$, $-z+2$; #4 x, $-y+1/2$, $z-1/2$; #5 $-x+2$, $y-1/2$, $-z+3/2$.

3.3. *Photophysical properties*

The ultraviolet absorption spectrum of $[Sm(NIC)_3(H_2O)_2]_2$ (10^{-4} M ethanol solution) shows a band at 263 nm attributed to pyridine-3-carboxylate. This indicates that HNIC is the energy donor and luminescence sensitizer of the Sm^{3+} ion. Excitation spectrum of these complex systems show that they have no effective absorption in the long-wavelength ultraviolet region in the range 300–400 nm. Effective energy absorption mainly takes place in the narrow ultraviolet range of 210–275 nm and the excitation band consists of four main peaks at 221, 241, 257 and 271 nm. We further measured corresponding emission spectra by selective excitation at the four different excitation wavelengths; they show similar emission positions but different luminescent intensities. Four apparent emission bands can be observed with maximum emission wavelengths at 561, 596, 643 and 722 nm. These correspond to the characteristic emission $^4F_{5/2} \rightarrow {}^6H_j$ ($j = 5/2$, 7/2, 9/2, 11/2) transitions of the Sm^{3+} ion.

Supplementary data

Complete lists of atomic coordinates, thermal parameter and bond lengths and angles are available from the Cambridge Crystallographic Data Centre (No. CCDC-230253).

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