

A Novel Synthesis Path to Dysprosium Coordination Polymer of Salicylic Acid Induced by the Hydrolysis of *O*-Acetylsalicylic Acid

^aY. S. SONG, ^aB. YAN*, and ^bZ. X. CHEN

^aDepartment of Chemistry, Tongji University, Shanghai 200092, P. R. China
e-mail: byan@tongji.edu.cn

^bDepartment of Chemistry, Fudan University, Shanghai 200433, P. R. China

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A one-dimensional dysprosium coordination polymer $\{[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2]_2 \cdot \text{H}_2\text{O}\}_n$ (Sal = 2-hydroxybenzoic acid) has been synthesized by a novel reaction from the hydrolysis process of *O*-acetylsalicylic acid. X-Ray analysis reveals that it forms one-dimensional chain-like structure through bridged oxygen atoms of carboxylate groups. The title coordination polymer crystallizes in the monoclinic system, space group $C2/c$, with lattice parameters $a = 16.217(5)\text{Å}$, $b = 14.896(5)\text{Å}$, $c = 9.835(3)\text{Å}$, $\beta = 101.453(4)^\circ$, $V = 2328.4(13)\text{Å}^3$, $D_c = 1.857\text{ Mg/m}^3$, $Z = 2$, $F(000) = 1280$, $\text{GOF} = 0.941$, $R_1 = 0.0281$. The photophysical properties have been studied with ultraviolet absorption, excitation, and emission spectra.

In the past decade there has been an increasing interest in the photophysical properties of strongly luminescent lanthanide complexes owing to their great applications in luminescence probes for chemical or biological macromolecules and the active centre for luminescent molecular-based materials [1–6]. Particularly lanthanide complexes with aromatic carboxylic acids readily form dimeric or infinite chain polymeric structures so that they show higher thermal or luminescent stability for practical applications than other lanthanide complex systems [7–10]. Different methods have been used for the synthesis of luminescent lanthanide complexes including hydrothermal and chemical coprecipitation, *etc.* [11–15]. Previously, lanthanide complexes with 2-hydroxybenzoic acid (HSal) have been synthesized with HSal as the starting ligand, and the detailed crystal structures of cerium and terbium complexes have been reported [16]. Cerium complex is a dimer, in which both carboxyl group and hydroxyl group participate in the coordination to Ce^{3+} , while terbium complex shows a one-dimensional chain-like polymeric structure, with only carboxyl group coordinated to Tb^{3+} [16].

In this paper, we found a novel path to synthesize lanthanide complex of aromatic carboxylate controlled by the hydrolysis of the corresponding ester of aromatic carboxylic acid. Generally speaking, there exists H^+ or OH^- , thus the ester can be easily hydrolyzed to the corresponding aromatic carboxylate. So the lanthanide aromatic carboxylate complexes can be expected to form under this kind of conditions. In

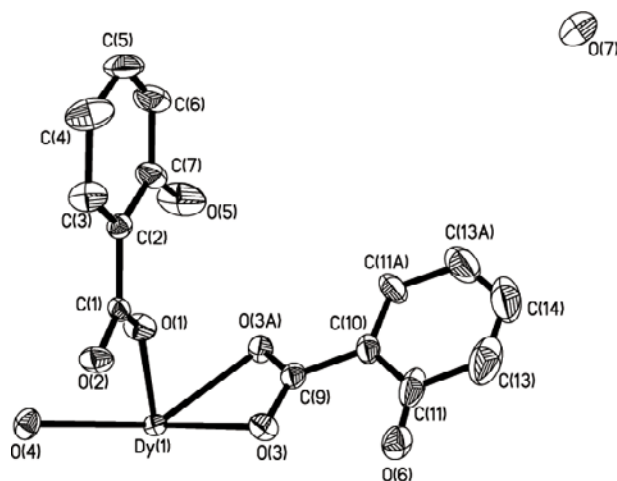


Fig. 1. Molecular structure of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

terms of this idea, we achieved a dysprosium coordination polymer of Hsal using *O*-acetylsalicylic acid (OASal) as the starting ligand. With the hydrolysis of OASal under sodium hydroxide, the dysprosium coordination polymer $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ was synthesized. Especially, the one-dimensional coordination polymer exhibits strong luminescence of Dy^{3+} .

Final atomic coordinates for nonhydrogen atoms are listed in Tab. 1. Fig. 1 shows the coordination geometry and atom labeling in the crystal structure of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$. X-Ray diffraction crys-

*The author to whom the correspondence should be addressed.

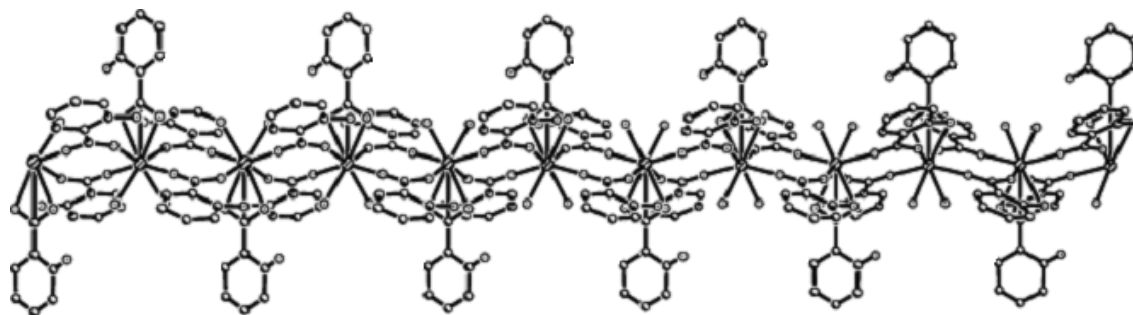


Fig. 2. Chain structure of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

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

Atom $U(\text{eq})$	x	y	z
Dy(1)	10000	-19(1)	7500
28(1)			
O(1)	8844(2)	502(2)	8366(4)
47(1)			
O(2)	8995(2)	356(2)	10630(4)
44(1)			
O(3)	10395(2)	1459(2)	8537(3)
40(1)			
O(4)	9440(4)	-1301(3)	8516(6)
47(1)			
O(5)	7621(3)	1369(4)	6965(4)
91(2)			
O(6)	11006(6)	3028(6)	9404(9)
53(3)			
O(7)	7201(3)	6598(3)	1020(5)
83(2)			
C(1)	8576(3)	595(3)	9489(5)
30(1)			
C(2)	7733(3)	986(3)	9387(5)
32(1)			
C(3)	7371(4)	1022(4)	10540(6)
52(2)			
C(4)	6592(4)	1410(5)	10484(8)
76(2)			
C(5)	6173(4)	1763(5)	9251(9)
74(3)			
C(6)	6511(4)	1721(4)	8088(8)
68(2)			
C(7)	7294(4)	1348(4)	8140(7)
51(2)			
C(9)	10000	1886(5)	7500
40(2)			
C(10)	10000	2894(5)	7500
49(2)			
C(11)	10536(5)	3349(5)	8590(9)
73(3)			
C(13)	10523(6)	4283(6)	8549(12)
121(4)			
C(14)	10000	4701(9)	7500
151(10)			

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

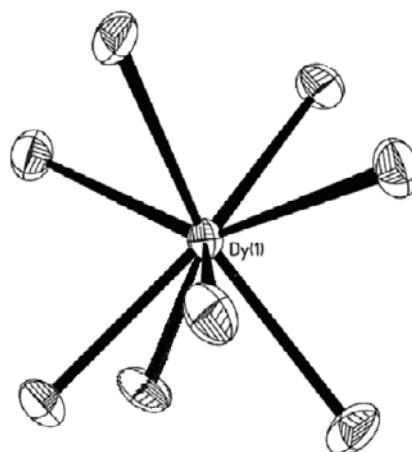


Fig. 3. The coordination polyhedron of Dy^{3+} ion in $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

tal structure analysis reveals that it leads to a formulation $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ with two bridged Sal anions connecting two neighbouring dysprosium ions. Fig. 2 shows the one-dimensional chain-like structure diagram of the coordination polymer. All Dy ions are equivalent in the same coordination environment and so there is only one type of metal configuration. Each central Dy ion belongs to eight-coordinated by eight oxygen atoms, the coordination geometry of which can be described as a distorted square antiprism geometry (Fig. 3). Oxygen atoms are from four bridged Sal anions (O(1), O(1#), O(2), and O(2#) for Dy(1)) with the bond distances 2.258(3) \AA (O(2)—Dy(1)) and 2.340(3) \AA (O(1)—Dy(1)), respectively. In addition, two oxygen atoms are from chelated Sal anion (O(3) and O(3#) for Dy(1)), the bond distance of which is longer, 2.459(3) \AA . Besides this, there exist another two-coordinated oxygen atoms from the three water molecules (O(4) and O(4#) for Dy(1)) with the bond distances 2.414(5) \AA between the Dy ion and oxygen atoms. The average bond distance of Dy(1)—O is 2.368 \AA . The bond angle consisting of Dy ions and the oxygen atoms of chelated Sal anions is 52.72(16) $^\circ$ (O(3)—Dy(1)—O(3#)). Selected bond distances and bond angles for the chain-like dysprosium coordination polymer are listed in Table 2.

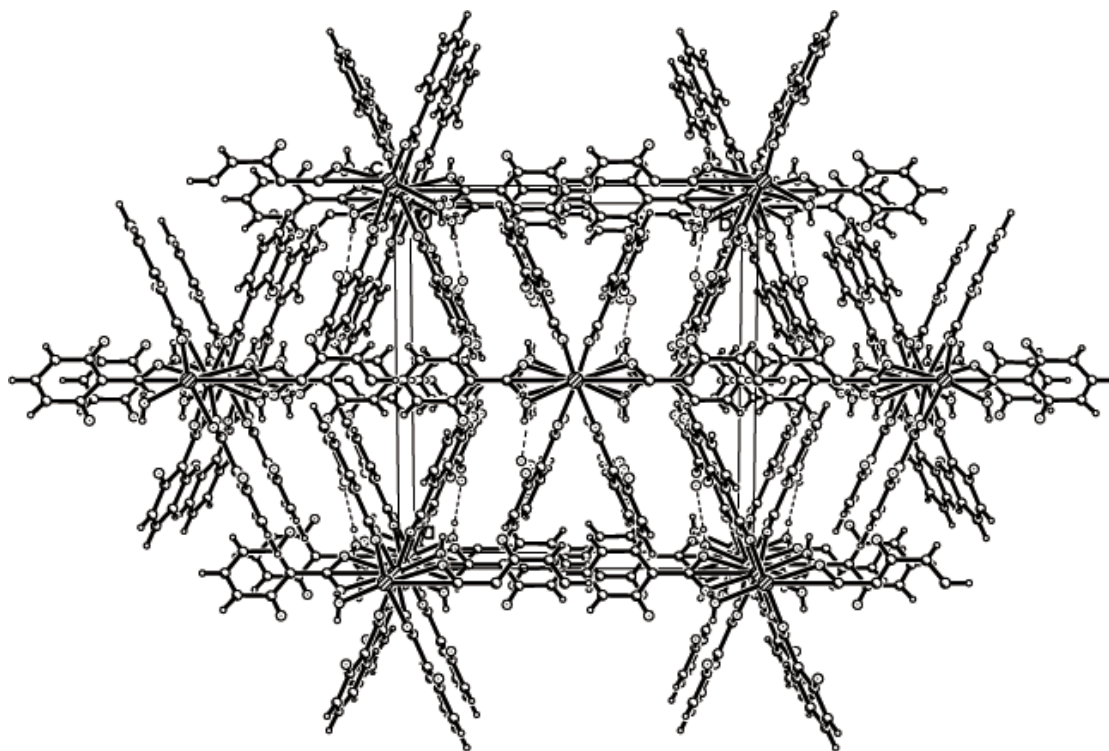


Fig. 4. Packing view of the unit cell for $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

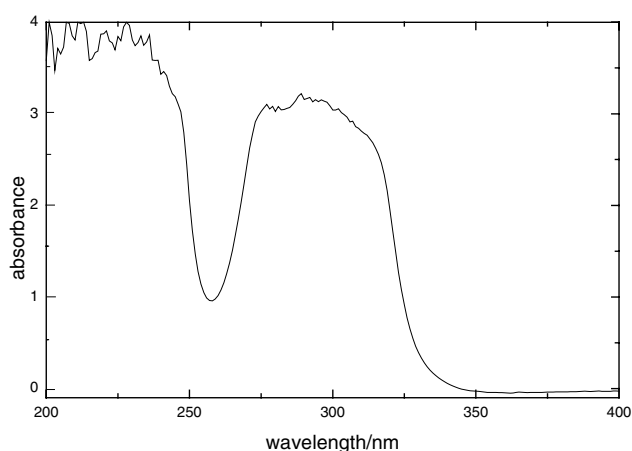


Fig. 5. Ultraviolet absorption spectrum of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

All Sal anions are deprotonated and all the oxygen atoms of the carboxylic groups take part in the coordination to the two central metal ions. There are two types of coordination modes of Sal anions existing in the molecular structure: 1. bidentates bridging, Dy ions are connected into chain-like structure by this coordination mode, 2. bidentates chelation, both oxygen atoms of one carboxyl are coordinated with one central Dy ion.

Fig. 4 shows the packing view of a unit cell for $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer. There exist three types of O—H...O intermolecu-

lar hydrogen bonds in the unit cell of the title complex: one is the O—H...O intermolecular hydrogen bonding between the oxygen atoms of coordinated water molecules and the oxygen atoms of the crystal water molecules, the angle of which is $158(7)^\circ$ (O(4)—H(4A)...O(7)#4); the other is the O—H...O intermolecular hydrogen bonding between the oxygen atoms of the coordinated water molecules and the oxygen atoms of chelated Sal anions, with bond angle of $151(7)^\circ$ (O(4)—H(4B)...O(3)#2); the last is the O—H...O intermolecular hydrogen bonding between the oxygen atoms of the coordinated water molecules and the oxygen atoms of bridged Sal anions, the bond angle of which is $98(6)^\circ$ (O(4)—H(4B)...O(2)#2). In addition, there exists one type of O—H...O intramolecular hydrogen bonds between the oxygen atoms of the coordinated water molecules and the oxygen atoms of bridged Sal anions, the bond angle of which is $88(6)^\circ$ (O(4)—H(4A)...O(1)). All these hydrogen bondings link up the complex units, resulting in a 3-D network and making the whole network structure system stable. The detailed data of hydrogen bonding are shown in Table 3.

The ultraviolet absorption spectrum of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (10^{-4} mol dm^{-3} ethanol solution) (Fig. 5) shows a domain absorption band at $\lambda = 270$ nm, which is attributed to the characteristic absorption of Sal. This indicates that Sal is the energy donor for the luminescence of Dy^{3+} ion.

The excitation spectrum exhibits that the effective energy absorption mainly takes place in the narrow

Table 2. Selected Bond Distances/ \AA and Bond Angles/ $^\circ$ for the Title Complex

Dy(1)—O(1)	Dy(1)—O(3)
2.340(3) \AA	2.459(3) \AA
Dy(1)—O(1#)	Dy(1)—O(3#)
2.340(3) \AA	2.459(3) \AA
Dy(1)—O(2)	Dy(1)—O(4)
2.258(3) \AA	2.414(5) \AA
Dy(1)—O(2#)	Dy(1)—O(4#)
2.258(3) \AA	2.414(5) \AA
O(2)—Dy(1)—O(2#)	O(4#)—Dy(1)—O(4)
154.35(18) $^\circ$	75.5(2) $^\circ$
O(2)—Dy(1)—O(1#)	O(2)—Dy(1)—O(3)
106.16(12) $^\circ$	128.56(12) $^\circ$
O(2#)—Dy(1)—O(1#)	O(2#)—Dy(1)—O(3)
82.48(13) $^\circ$	76.97(12) $^\circ$
O(2)—Dy(1)—O(1)	O(1#)—Dy(1)—O(3)
82.48(13) $^\circ$	72.05(12) $^\circ$
O(2#)—Dy(1)—O(1)	O(1)—Dy(1)—O(3)
106.16(12) $^\circ$	73.33(13) $^\circ$
O(1#)—Dy(1)—O(1)	O(4#)—Dy(1)—O(3)
141.22(18) $^\circ$	142.35(17) $^\circ$
O(2)—Dy(1)—O(4#)	O(4)—Dy(1)—O(3)
75.96(18) $^\circ$	128.69(15) $^\circ$
O(2#)—Dy(1)—O(4#)	O(2)—Dy(1)—O(3#)
83.77(18) $^\circ$	76.97(12) $^\circ$
O(1#)—Dy(1)—O(4#)	O(2#)—Dy(1)—O(3#)
73.59(16) $^\circ$	128.56(12) $^\circ$
O(1)—Dy(1)—O(4#)	O(1#)—Dy(1)—O(3#)
143.86(17) $^\circ$	73.33(13) $^\circ$
O(2)—Dy(1)—O(4)	O(1)—Dy(1)—O(3#)
83.77(18) $^\circ$	72.05(12) $^\circ$
O(2#)—Dy(1)—O(4)	O(4#)—Dy(1)—O(3#)
75.96(18) $^\circ$	128.69(15) $^\circ$
O(1#)—Dy(1)—O(4)	O(4)—Dy(1)—O(3#)
143.86(17) $^\circ$	142.35(17) $^\circ$
O(1)—Dy(1)—O(4)	O(3)—Dy(1)—O(3#)
73.59(16) $^\circ$	52.72(16) $^\circ$

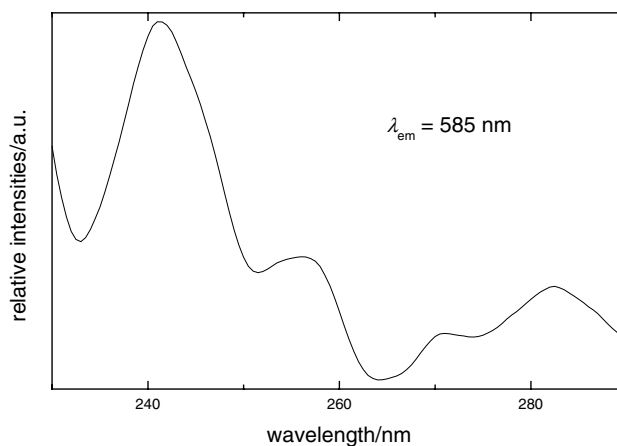
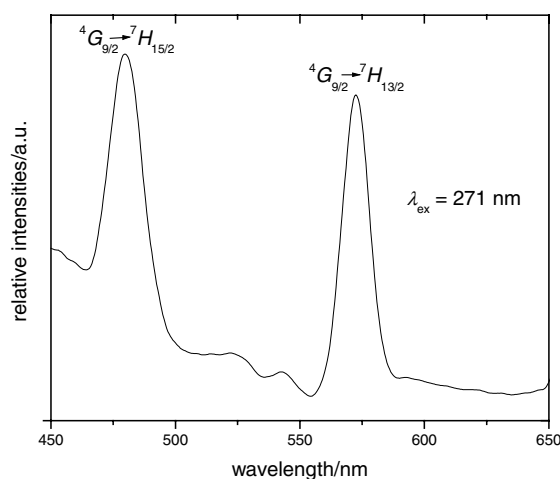
Symmetry transformations used to generate equivalent atoms:
 #1 $-x + 2, y, -z + 3/2$.

Table 3. Hydrogen Bonds Distance/ \AA , Angle/ $^\circ$ for the Title Complex

D—H...A	$d(\text{D—H})$	$d(\text{H...A})$	$d(\text{D...A})$
O(4)—H(4A)...O(7)#4	0.70(5) \AA	2.16(6) \AA	2.822(7) \AA
O(4)—H(4B)...O(3)#2	0.70(6) \AA	2.23(6) \AA	2.866(7) \AA
O(4)—H(4B)...O(2)#2	0.70(6) \AA	2.70(6) \AA	2.878(7) \AA
O(4)—H(4A)...O(1)	0.70(5) \AA	2.78(7) \AA	2.848(7) \AA

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

ultraviolet region of 230–290 nm, and the excitation bands consist of four main peaks at 241 nm, 257 nm,

**Fig. 6.** Excitation spectrum of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.**Fig. 7.** Emission spectrum of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ coordination polymer.

271 nm, and 282 nm, respectively (Fig. 6).

From the corresponding emission spectra of $[\text{Dy}(\text{Sal})_3(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ under the excitation of 241 nm, two apparent emission bands can be observed and the maximum emission wavelengths are at 480 nm and 572 nm, respectively, corresponding to the characteristic emission $^4F_{9/2} \rightarrow ^6H_J$ ($J = 15/2, 13/2$) transitions of Dy^{3+} ion (as shown in Fig. 7).

EXPERIMENTAL

$\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving its respective oxides in concentrated nitric acid followed by drying. *O*-Acetylsalicylic acid was purchased from Aldrich and used without further purification. All the other reagents were commercially available and used as received.

Elemental analyses (C, H, N) were determined on a Carlo elemental analyzer. Infrared spectroscopy (KBr

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

Complex	[Dy(Sal) ₃ (H ₂ O) ₂ · 2H ₂ O] _n
Formula	C ₂₁ H ₂₃ DyO ₁₃
Relative molecular mass <i>M_r</i>	645.89
Colour	Colourless
Temperature	298(2) K
Wavelength	0.71073 Å
Radiation	MoKα
Crystal system	C2/c
Space group	Monoclinic
Unit dimensions	<i>a</i> = 16.217(5) Å <i>b</i> = 14.896(5) Å <i>c</i> = 9.835(3) Å <i>β</i> = 101.453(4)°
Volume	2328.4(13) Å ³
<i>Z</i>	4
Calculated density	1.843 Mg/m ³
Absorption coefficient	3.278 mm ⁻¹
<i>F</i> (000)	1276
Crystal size	0.10 mm × 0.08 mm × 0.05 mm
Θ range for data collection	1.87° to 26.01°
Reflections/collected/unique	5287/2285 [<i>R</i> (int) = 0.0344]
Completeness to 2Θ = 26.00	99.7 %
Absorption correction	Psi-scan
Max. and min. transmission	0.8533 and 0.7352
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2285/0/173
Goodness-of-fit on <i>F</i> ²	0.941
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0281, <i>wR</i> ₂ = 0.0522
Largest diff. peak and hole	0.775 <i>e</i> · Å ⁻³ and -0.567 <i>e</i> · Å ⁻³

pellets) was performed on a Nexus 912 AO446 FT-IR spectrophotometer in the range 400–4000 cm⁻¹. Ultraviolet absorption spectra were taken with an Ali-gent 8453 spectrophotometer. Excitation and emission spectra were measured with a Perkin–Elmer LS-55 model spectrophotometer.

Diffraction data for a crystal with dimensions 0.10 mm × 0.08 mm × 0.05 mm were obtained with graphite-monochromated MoKα 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 [17, 18]. A summary of crystallographic data and refinement parameters is given in Table 4. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-230255. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Complex

To ethanol solution 5 cm³ of *O*-acetylsalicylic acid (0.2700 g; 1.5 mmol) and Dy(NO₃)₃ · 6H₂O (0.2281 g; 0.5 mmol) in a minimum amount of ethanol was slowly added under stirring. The pH value of the mixed solution was adjusted to about 6.5 with sodium hydroxide and further the solution was stirred for 4 h. The resulting solution was filtered and the filtrate allowed to stand at room temperature. After three weeks, well-shaped light colourless single crystals suitable for analysis were obtained. For C₂₁H₂₃DyO₁₃ (*M_r* = 1301.74) *w_i*(calc.): 39.02 % C, 3.56 % H; *w_i*(found): 40.05 % C, 3.44 % H. IR spectrum exhibits a complicated pattern of bands in the range 400–4000 cm⁻¹: 1544.6 (*ν*_{as}(COO⁻)), 1411 (*ν*_s(COO⁻)).

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