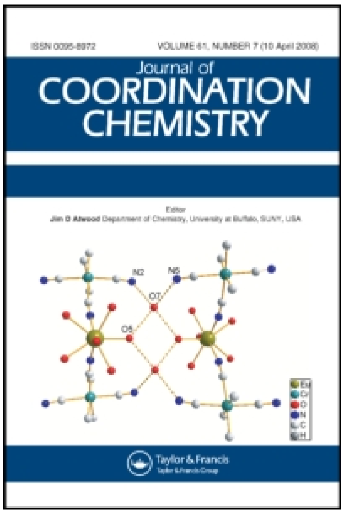

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Synthesis, structure and luminescence properties of two novel lanthanide complexes with 2-fluorobenzoic acid and 1,10-phenanthroline

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Synthesis, structure and luminescence properties of two novel lanthanide complexes with 2-fluorobenzoic acid and 1,10-phenanthroline

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Two lanthanide complexes with 2-fluorobenzoate (2-FBA) and 1,10-phenanthroline (phen) were synthesized and characterized by X-ray diffraction. The structure of each complex contains two non-equivalent binuclear molecules, $[Ln(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$ and $[Ln(2\text{-}FBA)_3 \cdot phen]_2$ (Ln = Eu (**1**) and Sm (**2**)). In $[Ln(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$, the Ln^{3+} is surrounded by eight atoms, five O atoms from five 2-FBA groups, one O atom from ethanol and two N atoms from phen ligand; 2-FBA groups coordinate Ln^{3+} with monodentate and bridging coordination modes. The polyhedron around Ln^{3+} is a distorted square-antiprism. In $[Ln(2\text{-}FBA)_3 \cdot phen]_2$, the Ln^{3+} is coordinated by nine atoms, seven O atoms from five 2-FBA groups and two N atoms of phen ligand; 2-FBA groups coordinate Ln^{3+} ion with chelating, bridging and chelating-bridging three coordination modes. The polyhedron around Ln^{3+} ion is a distorted, monocapped square-antiprism. The europium complex exhibits strong red fluorescence from $^5D_0 \rightarrow {}^7F_j$ ($j = 1$–4) transition emission of Eu^{3+}.

Keywords: Lanthanide complexes; 2-Fluorobenzoic acid; Synthesis; Structure; Luminescence property

1. Introduction

Lanthanide carboxylate complexes have a variety of structural types due to variations of the bonding forms of carboxyl groups. These complexes have potential applications in catalysis, magnetic materials, luminescent probes, etc. [1–4]. Therefore, such complexes have been extensively studied. Lanthanide mixed-ligand complexes with mono-organic acid and 2,2′-bipyridine or 1,10-phenanthroline have been reported [5–12], typically as binuclear molecules. The coordination number of the metal ion is eight or nine depending on the bridging of the metal ions by carboxyl groups. Compared to lanthanide mono-organic acid coordination polymers, the mixed-ligand complexes have more stable and intense luminescent properties and the europium complexes show an intense fluorescence. Very few lanthanide 2-fluorobenzoato complexes have been reported and complexes of lanthanides with either fluorobenzoates substituted in other positions or fluoride free benzoates with 1,10-phenanthroline have not been reported to date. The 2-fluorobenzoic acids and

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1,10-phenanthroline were used as ligands and some new lanthanide complexes were obtained using conventional solution reaction methods. The complexes have two non-equivalent binuclear molecules, $[Ln(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$ and $[Ln(2\text{-}FBA)_3 \cdot phen]_2$ (2-FBA = 2-fluorobenzoato; phen = 1,10-phenanthroline; Ln = Eu (**1**) and Sm (**2**)). The previously reported $Eu(4\text{-}CH_3C_6H_4COO)_3(phen)$ [5], has two independent molecules in the asymmetric unit from different coordination modes of carboxyl groups. However, this is rare in lanthanide carboxylate complexes. In the present article, the syntheses and structures of two complexes, and the luminescence of the europium complex are reported.

2. Experimental

2.1. *Synthesis of complexes 1 and 2*

1.5 mmol 2-fluorobenzoic acid was dissolved in appropriate amounts of ethanol. The pH of the solution was controlled in a range of 6–7 with $2\,\mathrm{mol\,dm^{-3}}$ NaOH solution. Then an ethanolic solution of 1,10-phenanthroline (0.5 mmol) and ethanolic solution of $LnCl_3 \cdot 6H_2O$ (Ln = Eu (**1**) and Sm (**2**)) (0.5 mmol) were added, successively. The mixture was heated under reflux with stirring for two hours. Single crystals were obtained from the mother liquor after two weeks at room temperature. For complex **1**, Anal Calcd (%): C, 52.61; N, 3.98; H, 3.29. Found (%): C, 52.86; N, 3.62; H: 3.00. For complex **2**, Anal Calcd (%): C, 53.28; N, 3.96: H, 3.14. Found (%): C, 52.97; N, 3.63; H: 3.00.

2.2. *Single-crystal X-ray diffraction*

X-ray crystal data collection for the complexes was accomplished on a Bruker Smart 1000 CCD diffractometer with monochromated Mo-Kα radiation ($\lambda = 0.71073\,\text{Å}$) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer with SHELXS-97 and SHELXL-97 programs [13, 14]. The structures were solved by direct methods and refinement on $|F|^2$ used full-matrix least-squares methods. A summary of the crystallographic data and details of the structure refinements are listed in table 1.

2.3. *Fluorescence spectra*

Fluorescence spectra were measured on a F-4500 FL Spectrophotometer in the solid state at room temperature.

3. Results and discussion

3.1. *Structural description of* $\{[Eu(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2 \cdot [Eu(2\text{-}FBA)_3 \cdot phen]_2\}$ *(1)*

The crystal structure of complex **1** is shown in figure 1(a) and (b). The selected bond lengths and bond angles are listed in table 2. Obviously, two kinds of molecules exist

Table 1. Crystal data and structure refinement for complexes.

	1	**2**
Empirical formula	$C_{68}H_{46}Eu_2F_6N_4O_{13}$	$C_{68}H_{46}Sm_2F_6N_4O_{13}$
Formula weight	1545.01	1541.79
Color, habit	Colourless, block	Yellow, block
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.251(3)	11.251(3)
b (Å)	12.661(3)	12.675(4)
c (Å)	22.745(6)	22.711(6)
α (°)	81.170(4)	81.197(5)
β	78.381(4)	78.487(5)
γ (°)	80.841(4)	80.944(5)
V (Å^3)	3108.3(14)	3109.1(15)
Z	2	2
D_{calcd} (Mg m^{-3})	1.651	1.647
μ (mm^{-1})	2.086	1.957
$F(000)$	1532	1528
Crystal size (mm^3)	$0.22 \times 0.20 \times 0.16$	$0.34 \times 0.28 \times 0.20$
θ range for data collection (°)	0.92–26.41	0.92–25.01
Limiting indices	$-14 \le h \le 14$ $-6 \le k \le 15$ $-28 \le l \le 28$	$-12 \le h \le 13$ $-15 \le k \le 15$ $-22 \le l \le 27$
Reflections collected/unique	18,275/12,618 [R(int) = 0.0266]	16,409/10,938 [R(int) = 0.0264]
Data/restraints/parameters	12,618/0/859	10,938/0/859
Goodness-of-fit on F^2	1.022	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0376$ $wR_2 = 0.0694$	$R_1 = 0.0345$ $wR_2 = 0.0697$
R indices (all data)	$R_1 = 0.0685$ $wR_2 = 0.0801$	$R_1 = 0.0610$ $wR_2 = 0.0796$
Largest diff. peak and hole (e Å^{-3})	0.728 and −0.570	0.511 and −0.516

in the asymmetric unit (scheme 1), [Eu(2-FBA)$_3$ · phen · CH_3CH_2OH]$_2$ and [Eu(2-FBA)$_3$ · phen]$_2$, both of which are centrosymmetric. This is different from previously reported lanthanide complexes with mono-benzoic acid or its derivatives containing phen. The complexes [Eu(*m*-MBA)$_3$(phen)](H_2O)$_2$ (*m*-MBA = *m*-methylbenzoate) [6] and Eu(3,4-DMBA)$_3$(phen)(3,4-DMBA = 3,4-dimethylbenzoate) [7] have only a structure in which two central metal ions are bridged through four carboxylate groups by bidentate modes and each metal ion is eight-coordinate. Eu(phen)L$_3$ (L = benzoate) has two central metal ions linked through four carboxylate groups by bidentate and tridentate modes with each metal nine-coordinate [8]. The complex Eu(4-$CH_3C_6H_4COO$)$_3$(phen) has two independent molecules in the asymmetric unit [5]. In one, two central metal ions are bridged by four carboxylate groups; in the other, two central metal ions are bridged by two carboxylate groups. The crystal structure of **1** is completely different from the above-mentioned complexes, perhaps due to the different substituents on the benzene ring.

In [Eu(2-FBA)$_3$ · phen · CH_3CH_2OH]$_2$ (figure 1a), the two central europium ions are held together by four bridging 2-FBA groups with distance Eu1···Eu1A of 4.4366(10) Å. Each europium ion (Eu1^{3+}) is further bonded to one 2-FBA group, one ethanol molecule and one phen molecule, making a coordination number of eight, with a distorted square-antiprism, in which the top square face is defined by atoms O5, O7,

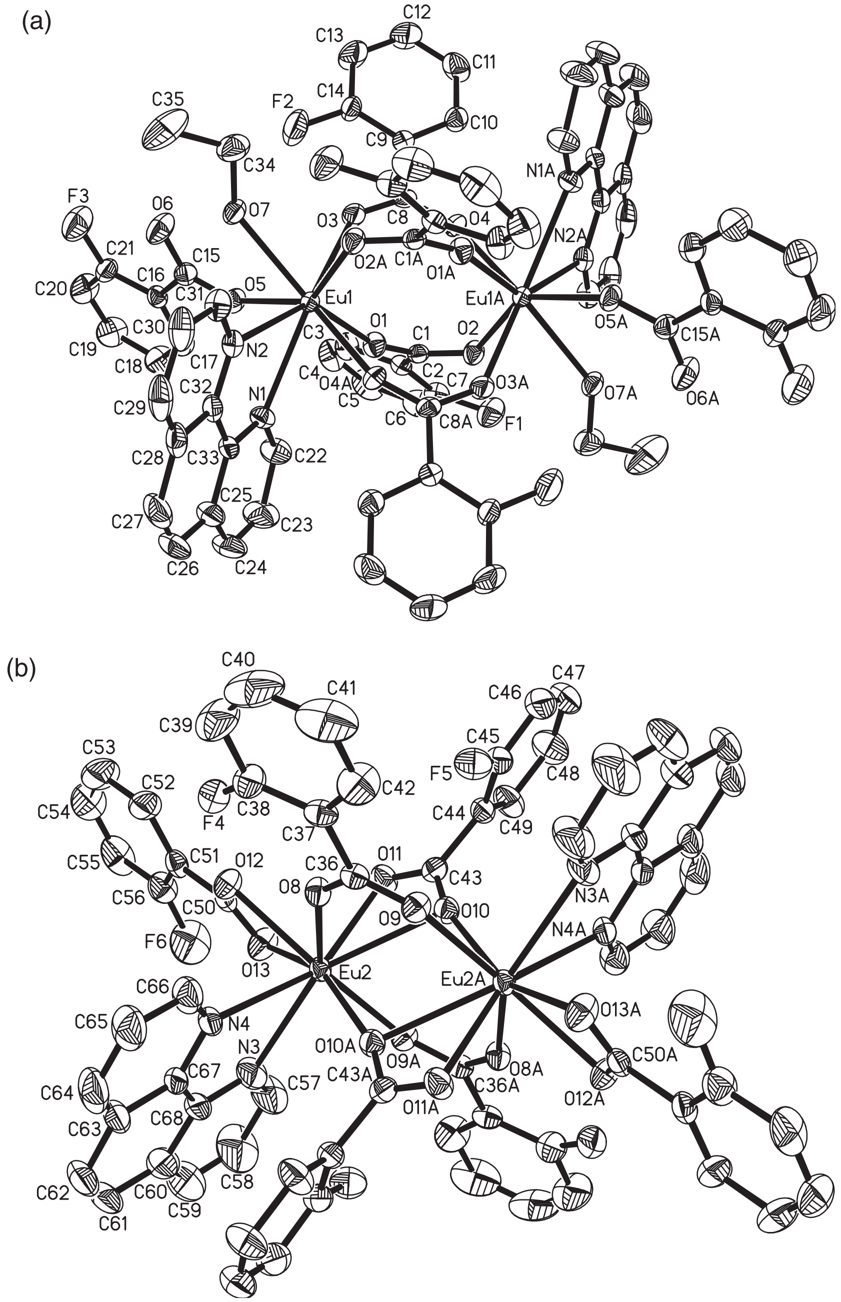


Figure 1. Molecular structure of complex **1**; (a) and (b) show two different structures. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

N1, N2, and the bottom one is formed by O1, O3, O2A, O4A (figure 2a). The dihedral angle between them is 3.3°. The bond distances Eu1–O(carboxyl) range from 2.330(3) to 2.390(3) Å, with an average distance of 2.370 Å. The bond angles O–Eu1–O vary considerably, 73.10(11)–144.48(11)°. The bond length between coordinated ethanol

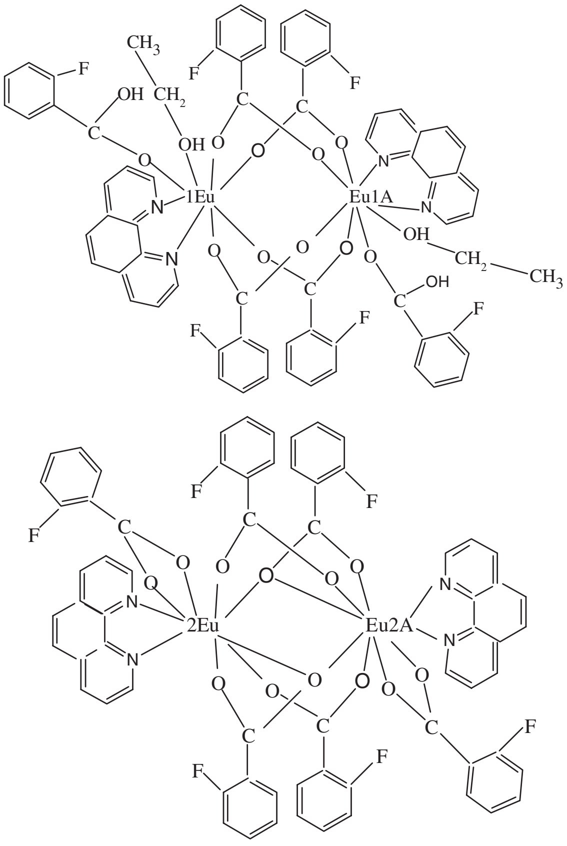
Table 2. Bond lengths (Å) and angles (°) for complex **1**.

Eu(1)–O(1)	2.330(3)	Eu(1)–O(3)	2.366(3)
Eu(1)–O(2)#1	2.377(3)	Eu(1)–O(5)	2.388(3)
Eu(1)–O(4)#1	2.390(3)	Eu(1)–O(7)	2.457(3)
Eu(1)–N(2)	2.579(4)	Eu(1)–N(1)	2.613(4)
Eu(2)–O(10)#2	2.339(3)	Eu(2)–O(8)	2.362(3)
Eu(2)–O(9)#2	2.379(3)	Eu(2)–O(12)	2.448(3)
Eu(2)–O(11)	2.474(3)	Eu(2)–O(13)	2.508(3)
Eu(2)–N(3)	2.586(4)	Eu(2)–N(4)	2.675(4)
Eu(2)–O(10)	2.678(3)		
O(1)–Eu(1)–O(3)	74.89(11)	O(1)–Eu(1)–O(2)#1	121.75(11)
O(3)–Eu(1)–O(2)#1	80.14(12)	O(1)–Eu(1)–O(5)	84.16(11)
O(3)–Eu(1)–O(5)	84.70(12)	O(2)#1–Eu(1)–O(5)	144.48(11)
O(1)–Eu(1)–O(4)#1	78.25(11)	O(3)–Eu(1)–O(4)#1	123.13(11)
O(2)#1–Eu(1)–O(4)#1)	73.10(11	O(5)–Eu(1)–O(4)#1	140.60(11)
O(1)–Eu(1)–O(7)	143.85(11)	O(3)–Eu(1)–O(7)	75.55(11)
O(2)#1–Eu(1)–O(7)	72.35(11)	O(5)–Eu(1)–O(7)	72.82(11)
O(4)#1–Eu(1)–O(7)	136.35(10)	N(2)–Eu(1)–N(1)	63.02(13)
O(10)#2–Eu(2)–O(8)	77.29(11)	O(10)#2–Eu(2)–O(9)#2	73.87(11)
O(8)–Eu(2)–O(9)#2	135.51(10)	O(10)#2–Eu(2)–O(12)	143.38(11)
O(8)–Eu(2)–O(12)	74.40(11)	O(9)#2–Eu(2)–O(12)	142.48(10)
O(10)#2–Eu(2)–O(11)	123.40(11)	O(8)–Eu(2)–O(11)	88.78(11)
O(9)#2–Eu(2)–O(11)	79.89(12)	O(12)–Eu(2)–O(11)	78.87(12)
O(10)#2–Eu(2)–O(13)	156.12(12)	O(8)–Eu(2)–O(13)	124.84(12)
O(9)#2–Eu(2)–O(13)	91.67(12)	O(12)–Eu(2)–O(13)	52.06(11)
O(11)–Eu(2)–O(13)	70.62(12)	O(10)#2–Eu(2)–O(10)	74.68(11)
O(8)–Eu(2)–O(10)	66.78(10)	O(9)#2–Eu(2)–O(10)	73.33(10)
O(12)–Eu(2)–O(10)	113.61(11)	O(11)–Eu(2)–O(10)	49.81(10)
O(13)–Eu(2)–O(10)	119.97(11)	N(3)–Eu(2)–N(4)	61.88(16)

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

oxygen atom (O7) and $Eu1^{3+}$ is 2.457(3) Å. O1–C1–O2 and O3–C8–O4 groups adopt a bidentate bridging coordination mode, in which two oxygen atoms coordinate two different europium ions ($Eu1^{3+}$ and $Eu1A^{3+}$). The O6–C15–O5 group is monodentate with one oxygen atom (O5) bound to europium. The uncoordinated carboxyl oxygen atom forms a hydrogen bond with a coordinated ethanol, O7–H7···O6 with d(O7···O6) = 2.576 Å and ∠O7H7O6 = 137.51°. The phen ligand chelates the europium ion to form a five-membered ring. The bond distances of Eu1–N are 2.613(4) and 2.579(4) Å, respectively, with average distance of 2.596(4) Å. The bond angle of N–Eu1–N is 63.02(13)°.

In $[Eu(2\text{-}FBA)_3 \cdot phen]_2$ (figure 1b), the two central europium ions are held together by four 2-FBA groups, two bidentate bridging and another two chelating-bridging, with Eu2···Eu2A distance of 3.9946(9) Å. Each europium ion is further chelated to one 2-FBA group and one phen molecule, making a coordination number of nine. The coordination geometry around $Eu2^{3+}$ may be described as a distorted monocapped square-antiprism; atoms O8, O11, O9A, O10A and O12, O13, N3, N4 form upper and lower square planes with a dihedral angle between them of 8.7°; atom O10 caps the upper plane (figure 2b). All 2-FBA ligands are coordinated to Eu^{3+} and can be classified into three different coordination modes in the complex. Carboxyl groups O12–C50–O13 adopt a bidentate chelating mode, in which two oxygen atoms coordinate the same europium ion ($Eu2^{3+}$). The O8–C36–O9 group is bidentate bridging with two oxygen atoms coordinating different europium ions ($Eu2^{3+}$ and $Eu2A^{3+}$) to form a bidentate bridge. The O10–C43–O11 groups are bridging-chelating,



Scheme 1. Schematic representation of the coordination geometry of Eu(III) in **1**.

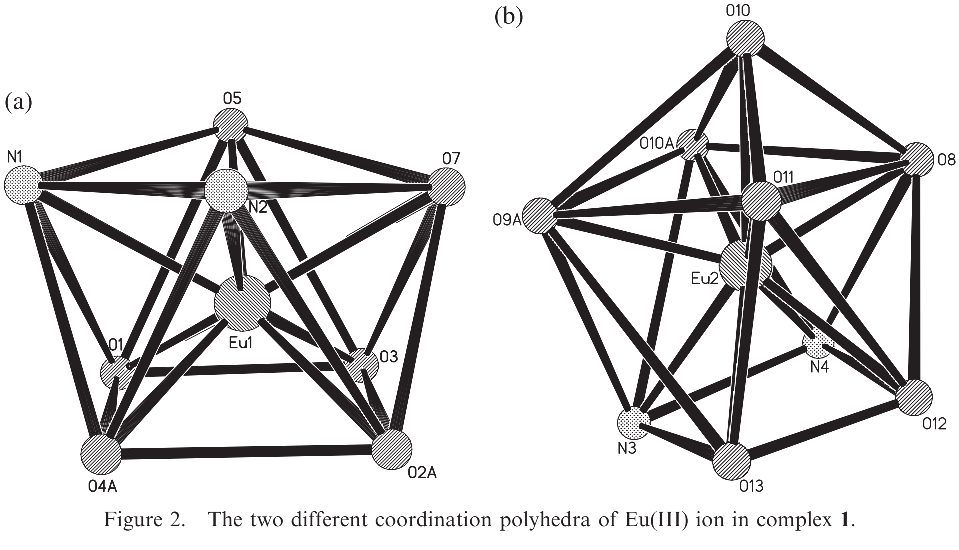


Figure 2. The two different coordination polyhedra of Eu(III) ion in complex **1**.

in which two O atoms chelate one europium ion (Eu2^{3+}) and one also simultaneously links another europium ion (Eu2A^{3+}) to form a tridentate bridge. The structure is typical of lanthanide carboxylate complexes. A similar coordination environment has been observed in other nine-coordinated lanthanide carboxylates containing phen or 2,2′-bpy, [Eu(α-FURA)$_3$ · phen]H$_2$O (α-FURA = α-furoic acid) [9], La$_2$(CH$_3$CO$_2$)$_6$ · (phen)$_2$ (Ln = Ce, Gd) [10], and La$_2$(propiorato)$_6$ · (2,2′-bpy)$_2$ [11]. The average Eu2–O distance for the chelating carboxyl, 2.478 Å, is longer than that for the bidentate bridging carboxyl, 2.3705 Å, and is shorter than that for the chelating-bridging carboxyl, 2.497 Å, as is common for lanthanide carboxylate complexes. The average Eu2–O(carboxyl) distance is 2.455 Å. Bond angles O–Eu2–O vary considerably from 52.06(11) to 156.12(12)°. The phen molecule coordinates the europium ion with two N atoms, forming a five-membered ring. The average Eu2–N distance and bond angle of N–Eu2–N are 2.6305 Å and 61.88(16)°, respectively. By comparing figure 1(b) with figure 1(a), their composition, coordination environment of metal ion, coordination mode of carboxylate groups and coordination number of metal ion are different and result in different distances of Eu–O, Eu–N and Eu···Eu. The mean distances of Eu2–O(carboxyl) are longer than for Eu1–O(carboxyl), and the Eu2···Eu2A distance is shorter than that of Eu1···Eu1A. Similar features were observed in complex **2**. The fact that Ln^{3+} ions are bridged by chelating-bridging carboxylate groups results in a larger Ln–O distance and a smaller Ln–Ln distance.

Table 3. Bond lengths (Å) and angles (°) for complex **2**.

Sm(1)–O(1)	2.340(3)	Sm(1)–O(3)	2.378(4)
Sm(1)–O(2)#1	2.393(3)	Sm(1)–O(4)#1	2.403(3)
Sm(1)–O(5)	2.404(3)	Sm(1)–O(7)	2.468(3)
Sm(1)–N(2)	2.593(4)	Sm(1)–N(1)	2.636(4)
Sm(2)–O(10)#2	2.351(3)	Sm(2)–O(8)	2.376(3)
Sm(2)–O(9)#2	2.394(3)	Sm(2)–O(12)	2.456(3)
Sm(2)–O(11)	2.489(3)	Sm(2)–O(13)	2.515(4)
Sm(2)–N(3)	2.598(5)	Sm(2)–O(10)	2.677(3)
Sm(2)–N(4)	2.682(4)		
O(1)–Sm(1)–O(3)	74.82(12)	O(1)–Sm(1)–O(2)#1	121.99(11)
O(3)–Sm(1)–O(2)#1	80.49(13)	O(1)–Sm(1)–O(4)#1	78.34(12)
O(3)–Sm(1)–O(4)#1	123.10(12)	O(2)#1–Sm(1)–O(4)#1	72.90(12)
O(1)–Sm(1)–O(5)	84.39(12)	O(3)–Sm(1)–O(5)	84.69(12)
O(2)#1–Sm(1)–O(5)	144.27(12)	O(4)#1–Sm(1)–O(5)	140.85(12)
O(1)–Sm(1)–O(7)	144.03(12)	O(3)–Sm(1)–O(7)	75.83(12)
O(2)#1–Sm(1)–O(7)	72.31(11)	O(4)#1–Sm(1)–O(7)	136.12(11)
O(5)–Sm(1)–O(7)	72.60(11)	N(2)–Sm(1)–N(1)	62.56(14)
O(10)#2–Sm(2)–O(8)	77.12(12)	O(10)#2–Sm(2)–O(9)#2	73.52(11)
O(8)–Sm(2)–O(9)#2	135.57(11)	O(10)#2–Sm(2)–O(12)	143.56(11)
O(8)–Sm(2)–O(12)	74.62(12)	O(9)#2–Sm(2)–O(12)	142.62(11)
O(10)#2–Sm(2)–O(11)	123.19(11)	O(8)–Sm(2)–O(11)	89.39(12)
O(9)#2–Sm(2)–O(11)	79.87(12)	O(12)–Sm(2)–O(11)	79.16(12)
O(10)#2–Sm(2)–O(13)	156.02(13)	O(8)–Sm(2)–O(13)	125.12(12)
O(9)#2–Sm(2)–O(13)	91.72(12)	O(12)–Sm(2)–O(13)	52.07(12)
O(11)–Sm(2)–O(13)	70.59(13)	O(10)#2–Sm(2)–O(10)	74.58(12)
O(8)–Sm(2)–O(10)	66.83(11)	O(9)#2–Sm(2)–O(10)	73.63(11)
O(12)–Sm(2)–O(10)	113.62(11)	O(11)–Sm(2)–O(10)	49.83(10)
O(13)–Sm(2)–O(10)	120.02(12)	N(3)–Sm(2)–N(4)	61.61(17)

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

3.2. *Structural description of the samarium complex, $\{[\mathrm{Sm(2\text{-}FBA)_3\cdot phen\cdot CH_3CH_2OH}]_2\cdot[\mathrm{Sm(2\text{-}FBA)_3\cdot phen}]_2\}$ (2)*

The selected bond lengths and bond angles are listed in table 3. The crystal structure of complex **2** is shown in figure 3(a) and (b). Obviously, the samarium 2-fluorobenzoato complex containing phen is similar to the europium complex.

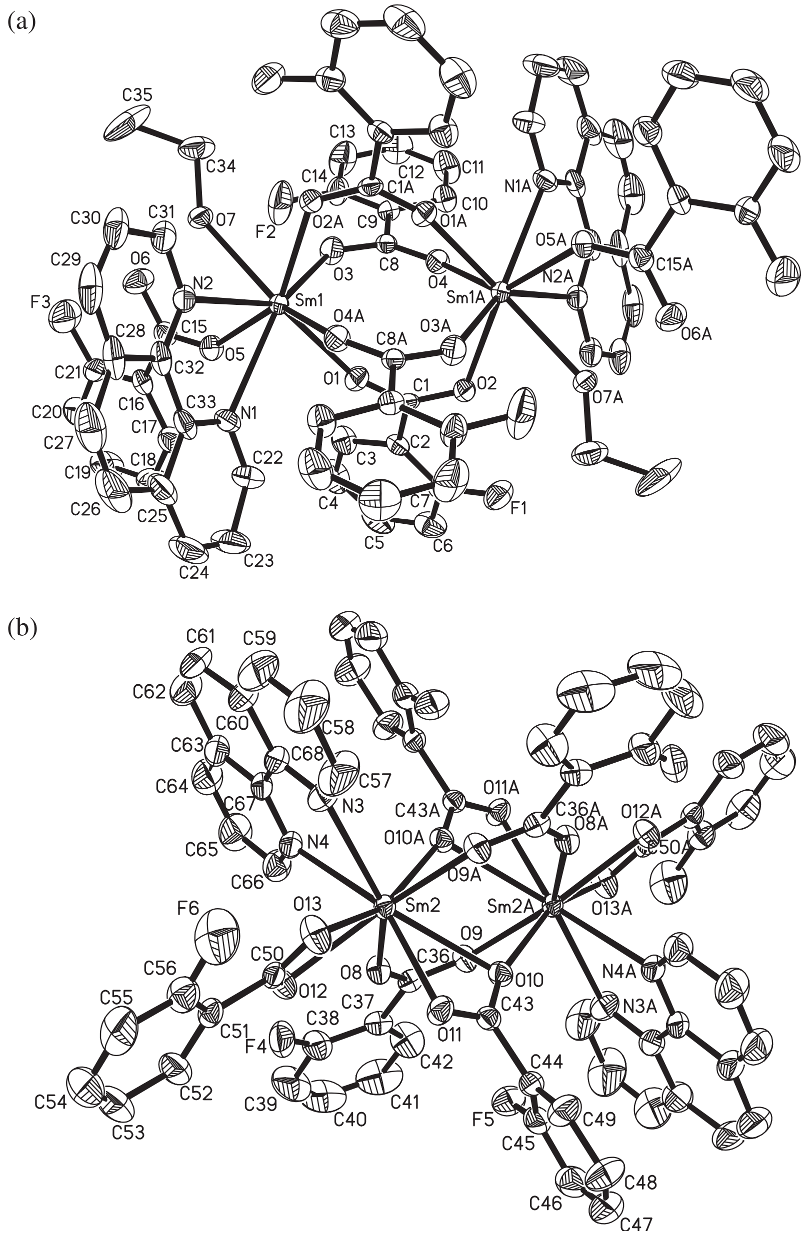


Figure 3. Molecular structure of complex **2**, with (a) and (b) showing two different structures. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

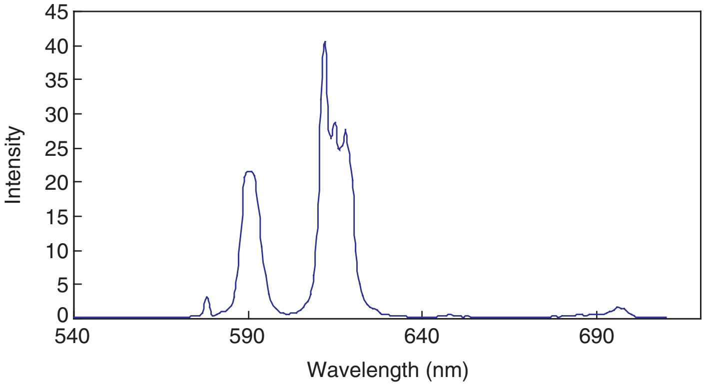


Figure 4. Fluorescence spectra of **1** ($\lambda_{ex} = 394$ nm).

For $[Sm(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$ (figure 3a), the bond distances of Sm1–O(carboxyl) (on average), Sm1–N (on average) and Sm1–O(ethanol) are 2.3836, 2.6145 and 2.468(3) Å, respectively. The Sm1···Sm1A distance is 4.437 Å. For $[Sm(2\text{-}FBA)_3 \cdot phen]_2$ (figure 3b), the average distances of Sm2–O and Sm2–N are 2.465 and 2.64 Å, respectively. The Sm2···Sm2A distance is 4.005 Å.

The two complexes are isomorphous. Because of the different ionic radius of Ln^{3+}, the corresponding distances decrease successively, according to Sm and Eu, for example, d(Sm–O(carboxyl)) > d(Eu–O(carboxyl)), and d(Sm···Sm) > d(Eu···Eu) >. These separations show a lanthanide contraction over the series. However, complexes containing two molecules with different compositions and structures are uncommon.

3.3. *Luminescence properties of europium complex 1*

The europium complex **1** produces a bright red color when irradiated by UV light in the solid state. The photoluminescence spectra of **1** obtained using 394 nm excitation at room temperature (figure 4) shows emission lines of $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transition in the range 540–720 nm. The emissions at 579, 592, and 697 nm are attributed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_4$ of Eu^{3+}, respectively. A weak line centered at 649 nm was observed in the region of the $^5D_0 \rightarrow {}^7F_3$ transitions. Triple peaks observed at 612, 615, 618 nm are assigned to $^5D_0 \rightarrow {}^7F_2$ transitions. The emissions at 615, 618 nm are weak shoulders on the stronger, 612 nm. The strongest $^5D_0 \rightarrow {}^7F_2$ indicates the hypersensitive transition, which is dependent on the environment of Eu^{3+}. The ratio between the intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ emission bands is 1.8, indicating that the Eu^{3+} is not situated at site symmetry.

Supplementary data

Supplementary data for the two structures are deposited with the Cambridge Crystallographic Data Center, CCDC-257185 and 258195 for complexes **1** and **2**, respectively. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: + 4(0)1223-336033; Email: deposit@ccdc.cam.ac.uk.

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