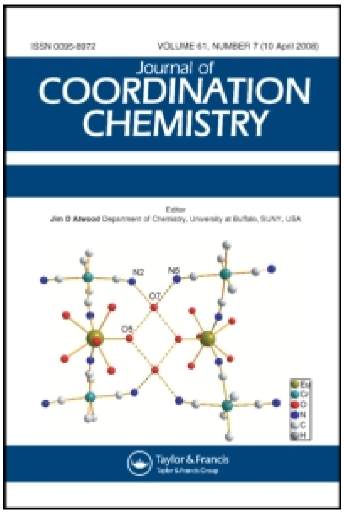

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Xia Li[a]; Yan-Ling Ju[a]; Ying-Quan Zou[b]
[a] Department of Chemistry, Capital Normal University, Beijing 100037, People's Republic of China [b] Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

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Synthesis, crystal structure and luminescence of three europium complexes with 2-iodobenzoic acid

XIA LI†, YAN-LING JU† and YING-QUAN ZOU*‡

†Department of Chemistry, Capital Normal University, Beijing 100037,
People's Republic of China
‡Department of Chemistry, Beijing Normal University, Beijing 100875,
People's Republic of China

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Three new complexes, $[Eu(2\text{-}IBA)_3 \cdot H_2O]_n$ (**1**), $[Eu(2\text{-}IBA)_3 \cdot 2,2'\text{-}bpy]_2$ (**2**), and $[Eu(2\text{-}IBA)_3 \cdot phen]_2$ (**3**) (2-IBA = 2-iodobenzoato; 2,2′-bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline) were synthesized, and their crystal structures determined by X-ray diffraction. In complex **1**, Eu^{3+} ions are linked through carboxylate groups via bridging – chelating – bridging coordination modes to form a one-dimensional polymeric chain. The carboxylate groups are tetradentate-bridged. Complex **2** is binuclear with an inversion center, in which europium is nine-coordinated with seven oxygen atoms from five 2-IBA ligands and two nitrogen atoms from one 2,2′-bpy molecule in a distorted monocapped square antiprism. The crystal structure of **3** is similar to that of **2**. These complexes emit red light luminescence. The $^5D_0 \rightarrow {}^7F_j$ ($j = 1$–4) transition emission of Eu^{3+} ion has been observed.

Keywords: Europium complexes; 2-Iodobenzoic acid; Synthesis; Structure; Luminescence

1. Introduction

Lanthanide carboxylate complexes have various structures and fascinating properties in optics, electronics, magnetism, etc. Many lanthanide carboxylate complexes have been reported, such as binary carboxylate complexes [1–7], ternary and quaternary carboxylate mixed-ligand complexes containing 4,4′-bipyridine(4,4′-bpy), 2,2′-bipyridine (2,2′-bpy), and 1,10-phenanthroline(phen) [4, 5, 8–14], exhibiting diverse structural types. A large number of lanthanide carboxylate complexes have been found to be polymeric or dimeric due to variation of the coordination modes of the carboxylate group. Carboxylate groups coordinate in four different coordination modes in lanthanide carboxylate complexes, monodentate, bidentate chelating, bidentate bridging, and tridentate bridging – chelating modes, which lead to polymeric or dimeric structures. Europium and terbium carboxylate complexes have attracted attention due to their luminescence; mixed-ligand complexes have shown higher thermal stability and strong luminescence [10–14]. Recently, we studied series of lanthanide complexes with benzoic acid and its derivatives. These complexes have different

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*Corresponding author. Fax: +86 10 58808204 (at work). Email: zouyq@263.net

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structures and their properties are related to the substitutent and its position on the benzene ring. We reported four terbium 2-fluorobenzoic acid complexes $[Tb(2\text{-}FBA)_3 \cdot (2\text{-}HFBA) \cdot H_2O]_2$, $\{[Tb(2\text{-}FBA)_3 \cdot (4,4'\text{-}bpy) \cdot H_2O]_3\}_n$, $[Tb(2\text{-}FBA)_3 \cdot (2,2'\text{-}bpy)]_2$, and $\{[Tb(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2 + [Tb(2\text{-}FBA)_3 \cdot phen]_2\}$ (2-HFBA: 2-fluorobenzoic acid, 4,4′-bpy: 4,4′-bipyridine, 2,2′-bpy: 2,2′-bipyridine, phen: 1,10-phenanthroline) [5]. As part of our investigation of lanthanide carboxylate complexes, we synthesized three new europium 2-iodobenzoic acid complexes, $[Eu(2\text{-}IBA)_3 \cdot H_2O]_n$ (**1**), $[Eu(2\text{-}IBA)_3 \cdot 2,2'\text{-}bpy]_2$ (**2**), and $[Eu(2\text{-}IBA)_3 \cdot phen]_2$ (**3**) (2-IBA = 2-iodobenzoate). The crystal structure **1** shows an infinite polymeric chain due to carboxylate groups in a bridging-chelating-bridging coordination mode. This is a rare example with tetradentate carboxylate groups linking different metals in a bridging-chelating-bridging mode. For example, in $La_2(C_2O_4)(SO_4)_2(H_2O)_2$, the oxalate group adopts the bridging-chelating-bridging coordination mode [15] and emits bright red luminescence. This article presents the synthesis, structures and luminescent properties of three Eu complexes.

2. Experimental section

2.1. *Materials and methods*

$EuCl_3 \cdot 6H_2O$ was prepared by dissolving its oxides in hydrochloric acid, and then drying the solution. Elemental analyses were performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Bruker EQUINOX-55 using KBr pellets. Thermogravimetric analysis was performed on a WCT-1A Thermal Analyzer at a heating rate $10^\circ C\,min^{-1}$ in air. The UV spectra were measured on a TU-1810 spectrophotometer. Fluorescence spectra were measured on a F-4500 FL Spectrophotometer in the solid state at room temperature.

2.2. *Synthesis of three complexes*

$Eu(2\text{-}IBA)_3 \cdot H_2O$ (**1**): 0.90 mmol 2-iodobenzoic acid was dissolved in 7 ml deionized water. The pH of the solution was adjusted to 5.0 with $2\,mol\,L^{-1}$ NaOH solution. Then 0.30 mmol $EuCl_3 \cdot 6H_2O$ was added to the solution. The mixture was placed in a 25 ml Teflon-lined reactor and heated at 180°C for 5 days, cooling slowly to room temperature to give colorless column crystals. Yield: 0.16 g, 57%. $C_{21}H_{14}EuI_3O_7$ (910.98). Calcd (%): C, 27.69; H, 1.55. Found (%): C, 27.77; H, 1.75. Selected IR (KBr pellet, ν/cm^{-1}): 3430 s, 1616 vs, 1582 s, 1541 m, 1474 m, 1405 vs, 1014 s, 749 m, 640 m, 426 w.

$[Eu(2\text{-}IBA)_3 \cdot 2,2'\text{-}bipy]_2$ (**2**): 0.90 mmol 2-iodobenzoic acid was dissolved in 7 ml deionized water. The pH of the solution was adjusted to 6 ~ 7 with $2\,mol\,L^{-1}$ NaOH solution. Then 0.45 mmol 2,2′-bipyridine and 0.30 mmol $EuCl_3 \cdot 6H_2O$ were added to the solution successively. The mixture was placed in a 25 ml Teflon-lined reactor and heated at 180°C for 5 days, cooling slowly to room temperature gave colorless column crystals. Yield: 0.20 g, 62%. $C_{31}H_{20}EuI_3O_6N_2$ (1049.18). Calcd (%): C, 35.49; H, 1.92; N, 2.67. Found (%): C, 35.64; H, 1.93. N, 2.68. Selected IR (KBr pellet, ν/cm^{-1}): 1615 vs, 1582 s, 1540 m, 1474 m, 1407 vs, 1014 s, 749 s, 640 m, 426 w.

$[Eu(2\text{-}IBA)_3 \cdot phen]_2$ (**3**): when 1,10-phenanthroline was used instead of 2,2′-bipyridine, (**3**) was obtained. Yield: 0.21 g, 65%. $C_{33}H_{20}EuI_3O_6N_2$ (1073.17). Calcd (%): C, 36.93; H, 1.88; N, 2.61. Found (%): C, 36.79; H, 2.03; N, 2.63. Selected IR (KBr pellet, ν/cm^{-1}): 1616 vs, 1584 m, 1542 m, 1517 m, 1399 vs, 1014 m, 850 m, 754 m, 728 m, 638 m, 416 w.

2.3. *X-ray crystallographic study*

X-ray crystal data collection for the complexes was on a Bruker Smart 1000 CCD diffratometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer with use of SHELXS-97 and SHELXL-97 programs [16, 17]. The structures were solved by direct methods and refinement on $|F|^2$ used the full-matrix least-squares methods. Summary of the crystallographic data and details of the structure refinements are listed in table 1. The selected bond lengths and bond angles of complexes **1**–**3** are listed in tables 2–4, respectively.

3. Results and discussion

3.1. *Structural description of* $[Eu(2\text{-}IBA)_3 \cdot H_2O]_n$

The crystal structure of **1** is shown in figure 1(a). O1–C1–O2 groups adopt a chelating mode, in which two O atoms coordinate to the same Eu^{3+} to form a four-membered ring. O3–C8–O4 groups coordinate Eu^{3+} in chelating mode as do O1–C1–O2 groups. O5–C15–O6 groups are linked to three different Eu^{3+} ions by bridging – chelating – bridging mode, in which O5 and O6 atoms chelate one Eu^{3+} and the two O atoms are also simultaneously linked to another two Eu^{3+} ions, respectively, in a tetradentate-bridged mode. Eu^{3+} ions are linked through carboxylate groups via the tetradentate-bridge to form a one-dimensional infinite chain. Carboxylate groups have four different coordination modes, monodentate (scheme 1a), chelating bidentate (scheme 1b), bridging bidentate (scheme 1c), bridging tridentate (scheme 1d). The tetradentate bridging coordination of carboxylate groups (scheme 1e) is relatively rare. Generally, in lanthanide mono-carboxylate complexes, lanthanide ions are linked through carboxylate groups via bidentate-bridging and tridentate bridging-chelating modes to form dimeric or polymeric structures. This article reports a rare example of carboxylate groups linked to different metals by bridging-chelating-bridging mode to form a polymeric structure. One Eu, three 2-IBA ligands, and one water molecule, $Eu(2\text{-}IBA)_3 \cdot H_2O$ is an independent crystallographic unit. $Eu(2\text{-}IBA)_3 \cdot H_2O$ may be viewed as the building blocks to form a zigzag chain along the *c*-axis (figure 1b). Viewed along *b*-axis the π–π stacking interactions of aromatic rings are observed in the one-dimensional chain (figure 1c). If viewed along *a*-axis the partial π–π stacking interactions of aromatic rings is observed between neighboring chains (figure 1d). In the chains Eu^{3+} ions are coplanar. The neighboring Eu ··· Eu distance is 4.242(10) Å. The Eu1A–Eu1–Eu1B angle is 110.8°. Each Eu^{3+} ion is also coordinated by two carboxylate groups in chelating coordination mode and one water molecule. Eu^{3+} ion is nine coordinate with eight carboxylate O atoms and one water molecule (figure 1a).

Table 1. Crystal data and structure refinement for **1**–**3**.

Compound	**1**	**2**	**3**
Chemical formula	$C_{21}H_{14}EuI_3O_7$	$C_{33}H_{20}EuI_3N_2O_6$	$C_{31}H_{20}EuI_3N_2O_6$
Formula weight	910.98	1073.17	1049.15
Temperature (K)	294(2)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)	$P\bar{1}$	$P\bar{1}$
a (Å)	12.945(4)	11.756(3)	11.495(2)
b (Å)	6.984(2)	13.118(4)	12.505(2)
c (Å)	26.428(9)	13.423(4)	13.065(2)
α (°)	90	115.427(4)	103.573(3)
β (°)	101.372(6)	114.148(4)	96.601(3)
γ (°)	90	91.275(4)	112.933(3)
Volume (Å^3)	2342.3(14)	1655.9(8)	1636.0(5)
Z	4	2	2
D_c (mg m^{-3})	2.583	2.152	2.130
Absorption coefficient (mm^{-1})	6.672	4.736	4.791
F(000)	1672	1004	980
Crystal size (mm)	0.40 × 0.08 × 0.06	0.22 × 0.20 × 0.16	0.38 × 0.14 × 0.10
θ range for data (°)	1.92–25.01	1.87–25.01	1.65–26.44
Limiting indices	$14 \le h \le 15$, $-8 \le k \le 8$, $-27 \le l \le 31$	$-13 \le h \le 13$, $-15 \le k \le 15$, $-15 \le l \le 13$	$-14 \le h \le 12$, $-7 \le k \le 15$, $-16 \le l \le 16$
Reflections collected/unique	10926/4078 [*R*(int) = 0.0729]	8391/5781 [*R*(int) = 0.0254]	9336/6632 [*R*(int) = 0.0277]
Data/restraints/parameters	4078/6/289	5781/0/406	6632/221/485
Goodness-of-fit on F^2	1.057	1.060	1.024
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0707$; $wR_2 = 0.1699$	$R_1 = 0.0478$; $wR_2 = 0.1304$	$R_1 = 0.0519$; $wR_2 = 0.1211$
R indices (all data)	$R_1 = 0.0950$; $wR_2 = 0.1865$	$R_1 = 0.0626$; $wR_2 = 0.1437$	$R_1 = 0.0743$; $wR_2 = 0.1358$
Largest diff. peak and hole (e Å^{-3})	3.794 and −2.464	2.374 and −2.051	1.406 and −2.299

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

Eu(1)–O(4)	2.386(9)	Eu(1)–O(3)	2.390(11)
Eu(1)–O(6)#1	2.430(8)	Eu(1)–O(5)#2	2.430(9)
Eu(1)–O(7)	2.441(9)	Eu(1)–O(1)	2.454(9)
Eu(1)–O(2)	2.500(10)	Eu(1)–O(5)	2.608(8)
Eu(1)–O(6)	2.634(9)		
O(4)–Eu(1)–O(3)	54.3(4)	O(4)–Eu(1)–O(6)#1	82.2(3)
O(3)–Eu(1)–O(6)#1	93.4(4)	O(4)–Eu(1)–O(5)#2	87.0(3)
O(3)–Eu(1)–O(5)#2	95.1(4)	O(6)#1–Eu(1)–O(5)#2	158.7(3)
O(4)–Eu(1)–O(7)	78.8(3)	O(3)–Eu(1)–O(7)	133.1(3)
O(6)#1–Eu(1)–O(7)	80.4(3)	O(5)#2–Eu(1)–O(7)	79.5(3)
O(4)–Eu(1)–O(1)	122.8(4)	O(3)–Eu(1)–O(1)	75.6(4)
O(6)#1–Eu(1)–O(1)	74.6(3)	O(5)#2–Eu(1)–O(1)	126.5(3)
O(7)–Eu(1)–O(1)	143.3(3)	O(4)–Eu(1)–O(2)	124.4(3)
O(3)–Eu(1)–O(2)	75.7(4)	O(6)#1–Eu(1)–O(2)	127.2(3)
O(5)#2–Eu(1)–O(2)	73.9(3)	O(7)–Eu(1)–O(2)	142.8(3)
O(1)–Eu(1)–O(2)	52.6(3)	O(4)–Eu(1)–O(5)	140.8(3)
O(3)–Eu(1)–O(5)	144.7(4)	O(6)#1–Eu(1)–O(5)	66.0(3)
O(5)#2–Eu(1)–O(5)	114.5(2)	O(7)–Eu(1)–O(5)	73.9(3)
O(1)–Eu(1)–O(5)	71.5(3)	O(2)–Eu(1)–O(5)	93.9(3)
O(4)–Eu(1)–O(6)	143.7(3)	O(4)–Eu(1)–O(6)	143.7(3)
O(6)#1–Eu(1)–O(6)	114.9(2)	O(5)#2–Eu(1)–O(6)	65.6(3)
O(7)–Eu(1)–O(6)	73.3(3)	O(1)–Eu(1)–O(6)	93.2(3)
O(2)–Eu(1)–O(6)	72.1(3)	O(5)–Eu(1)–O(6)	49.8(3)

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

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

Eu(1)–O(6)#1	2.329(8)	Eu(1)–O(2)#1	2.367(7)
Eu(1)–O(5)	2.388(7)	Eu(1)–O(1)	2.424(8)
Eu(1)–O(4)	2.439(8)	Eu(1)–O(3)	2.462(9)
Eu(1)–O(2)	2.780(8)	Eu(1)–N(1)	2.595(9)
Eu(1)–N(2)	2.617(10)		
O(6)#1–Eu(1)–O(2)#1	75.4(3)	O(6)#1–Eu(1)–O(5)	133.5(3)
O(2)#1–Eu(1)–O(5)	75.7(3)	O(6)#1–Eu(1)–O(1)	82.8(3)
O(2)#1–Eu(1)–O(1)	125.9(3)	O(5)–Eu(1)–O(1)	85.7(3)
O(6)#1–Eu(1)–O(4)	77.8(3)	O(2)#1–Eu(1)–O(4)	78.7(3)
O(5)–Eu(1)–O(4)	129.9(3)	O(1)–Eu(1)–O(4)	143.2(3)
O(6)#1–Eu(1)–O(3)	130.0(3)	O(2)#1–Eu(1)–O(3)	85.7(3)
O(5)–Eu(1)–O(3)	82.6(3)	O(1)–Eu(1)–O(3)	142.1(3)
O(4)–Eu(1)–O(3)	53.0(3)	O(6)#1–Eu(1)–O(2)	66.2(3)
O(2)#1–Eu(1)–O(2)	76.8(3)	O(5)–Eu(1)–O(2)	72.3(3)
O(1)–Eu(1)–O(2)	49.1(2)	O(4)–Eu(1)–O(2)	140.5(3)
O(3)–Eu(1)–O(2)	152.2(3)	N(1)–Eu(1)–N(2)	62.0(3)

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

The coordination sphere of the Eu^{3+} is a distorted monocapped square-antiprism, in which the top square face is defined by O3, O5A, O6A, and O7, and the bottom one is formed by O1, O2, O5, and O6. The dihedral angle between the square faces is 0.3°. Atom O4 occupies the cap position (figure 1e). The bond distances of Eu1–O(carboxyl) are in the range 2.386(9)–2.634(9) Å. Eu1–O5 (2.608(8) Å) and Eu1–O6 (2.634(9) Å), the longest due to O5 and O6 atoms in the tetradentate bridge form unstable four – membered chelating ring with Eu1 and C15. The average Eu1–O(carboxyl) distance is 2.479 Å. The bond distance of water to Eu1 is 2.441(9) Å.

Table 4. Bond lengths (Å) and angles (°) for complex **3**.

Eu(1)–O(3)	2.359(6)	Eu(1)–O(4)#1	2.365(5)
Eu(1)–O(5)#1	2.381(5)	Eu(1)–O(2)	2.469(5)
Eu(1)–O(1)	2.490(5)	Eu(1)–O(6)	2.499(6)
Eu(1)–O(5)	2.692(5)	Eu(1)–N(1)	2.660(6)
Eu(1)–N(2)	2.634(7)		
O(3)–Eu(1)–O(4)#1	133.42(18)	O(3)–Eu(1)–O(5)#1	76.20(19)
O(4)#1–Eu(1)–O(5)#1	74.40(19)	O(3)–Eu(1)–O(2)	87.54(19)
O(4)#1–Eu(1)–O(2)	132.74(19)	O(5)#1–Eu(1)–O(2)	149.85(19)
O(3)–Eu(1)–O(1)	136.86(19)	O(4)#1–Eu(1)–O(1)	80.47(19)
O(5)#1–Eu(1)–O(1)	146.7(2)	O(2)–Eu(1)–O(1)	52.63(19)
O(3)–Eu(1)–O(6)	84.7(2)	O(4)#1–Eu(1)–O(6)	82.7(2)
O(5)#1–Eu(1)–O(6)	123.93(18)	O(2)–Eu(1)–O(6)	78.5(2)
O(1)–Eu(1)–O(6)	72.9(2)	O(3)–Eu(1)–O(5)	67.88(17)
O(4)#1–Eu(1)–O(5)	69.84(18)	O(5)#1–Eu(1)–O(5)	74.31(19)
O(2)–Eu(1)–O(5)	122.91(19)	O(1)–Eu(1)–O(5)	116.92(18)
O(6)–Eu(1)–O(5)	49.71(17)	N(2)–Eu(1)–N(1)	62.4(2)

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

The polymer chain structure of **1** is similar to numerous binary lanthanide carboxylate complexes, such as $Ln(HCl_2CCOO)_3$ [1], $Nd(2\text{-}CH_3OC_6H_4COO)_3 \cdot 4H_2O$ [2], $[Eu(2,3\text{-}DMOBA)_3]_n$ (2,3-DMOBA = 2,3-dimethoxybenzoate) [3], and $[\{Eu_3(MeCH{=}CHCO_2)_9 \cdot (H_2O)_4\} \cdot H_2O \cdot EtOH]_n$ [4]. However, the latter four complexes display a one-dimensional polymer chain with carboxylate groups in bidentate bridging or bridging – chelating modes. Complex $[Tb(2\text{-}FBA)_3 \cdot (2\text{-}HFBA) \cdot H_2O]_2$ [5] is a dimeric unit, rarely found in binary lanthanide complexes containing mono-carboxylate, such as dimeric $[Tb_2(CH_3COO)_6(H_2O)_4] \cdot 4H_2O$, $[Tb_2(CF_3COO)_6(H_2O)_6]$ [6], and $[Eu(AClBA)_3(H_2O)_2] \cdot H_2O]_2$ (ACIBA = 5-amino-2-chlorobenzoic acid) [7].

3.2. *Structural description of [Eu(2-IBA)$_3$ • 2,2′-bpy]$_2$*

The molecular structure of **2** is shown in figure 2. The crystal structure consists of two Eu^{3+} ions with a center of inversion between the metal ions. Two bidentate-bridging and two tridentate-bridging carboxyl groups exist between the two Eu^{3+} ions. The separation of Eu1–Eu1A is 4.041(12) Å. The 2-IBA groups adopt the common chelating, bridging, and chelating-bridging coordination modes with Eu^{3+}; O3–C8–O4 groups are in a chelating mode, O5–C15–O6 groups are in a bidentate-bridging mode, and O1–C1–O2 groups are in a chelating-bridging mode. The 2,2′-bpy chelates Eu^{3+}. Therefore, seven O atoms of carboxylate groups and two N atoms of 2,2′-bpy complete nine-coordination at Eu^{3+}. The coordination geometry around Eu^{3+} is described as a distorted monocapped square antiprism with O2 as the capping atom. Atoms O1, O2A, O5, O6A and O3, O4, N1, N2 occupy the top and bottom square faces, respectively, with the dihedral angles between them of 5.3°. The bond distances of Eu1–O(carboxyl) are in the range 2.329(8)–2.780(8) Å with an average distance of 2.456 Å. The bond distances of Eu1–N are in the range 2.595(9)–2.617(10) Å with an average distance of 2.606 Å.

3.3. *Structural description of [Eu(2-IBA)$_3$ • phen]$_2$*

The molecular structure of **3** is dimeric with an inversion center as shown in figure 3. The molecular structure of **3** is similar to that of **2**. Each Eu^{3+} ion is coordinated to

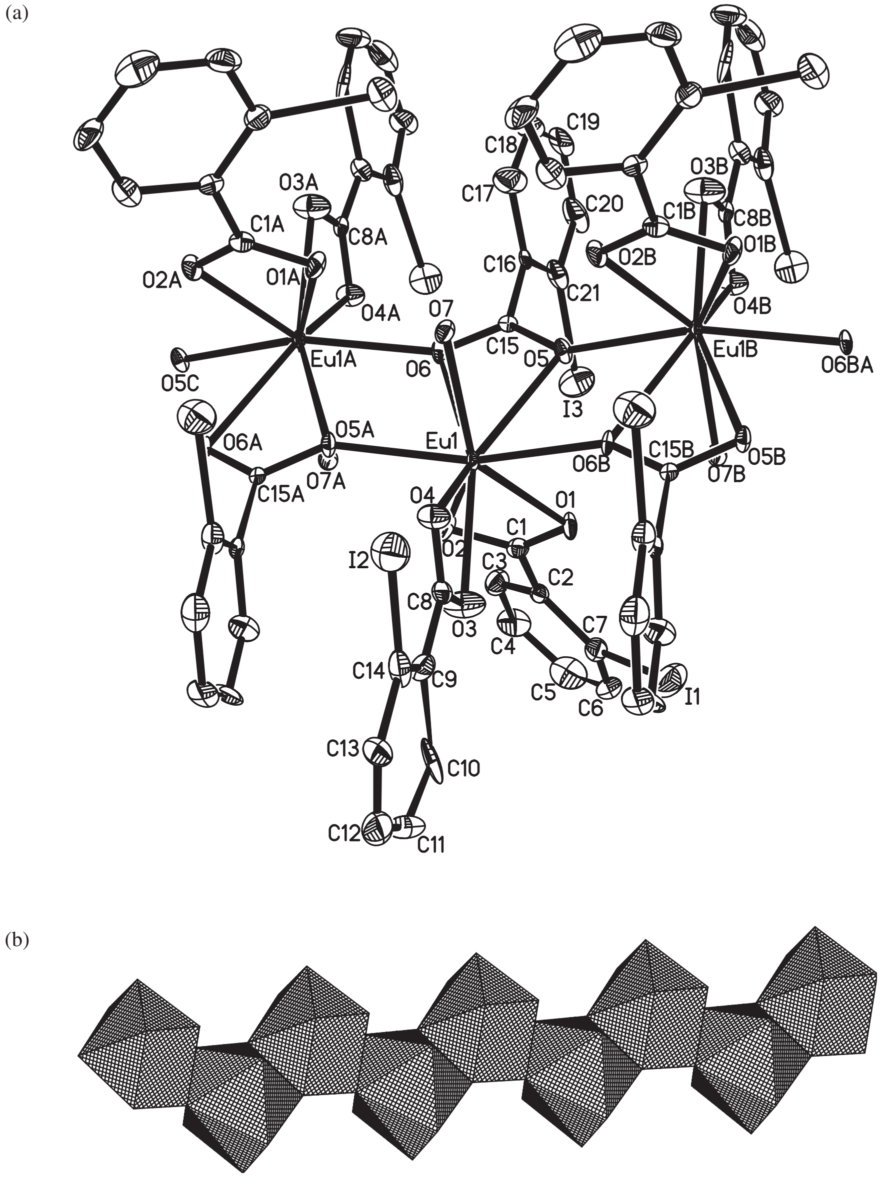


Figure 1. (a) Molecular structure of complex **1**; (b) Chain built by coordination polyhedra showing zigzag structure along *c*-axis; (c) Packing diagram showing the π–π stacking interactions of aromatic rings in a one-dimensional chain along *b*-axis; (d) Packing diagram showing partial π–π stacking interactions of aromatic ring between neighboring chains along *a*-axis; (e) Coordination polyhedron of the Eu(III) ion. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

seven O atoms of 2-IBA groups and two N atoms of phen giving a nine-coordinate, monocapped square antiprism. Atoms O3, O4A, O5A, O6 and O1, O2, N1, N2 form upper and lower square planes, respectively, with the dihedral angle between them of 1.9°. O5 caps the upper plane. The bond lengths of Eu1–O(carboxyl) are in the range 2.359(6)–2.692(5) Å with an average distance of 2.465 Å, which is comparable with

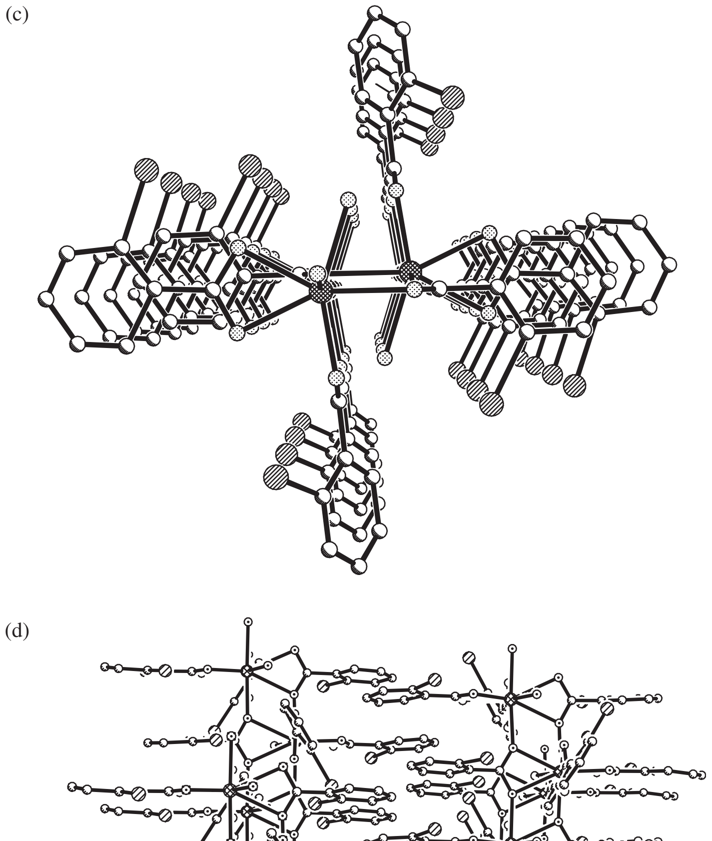


Figure 1. Continued.

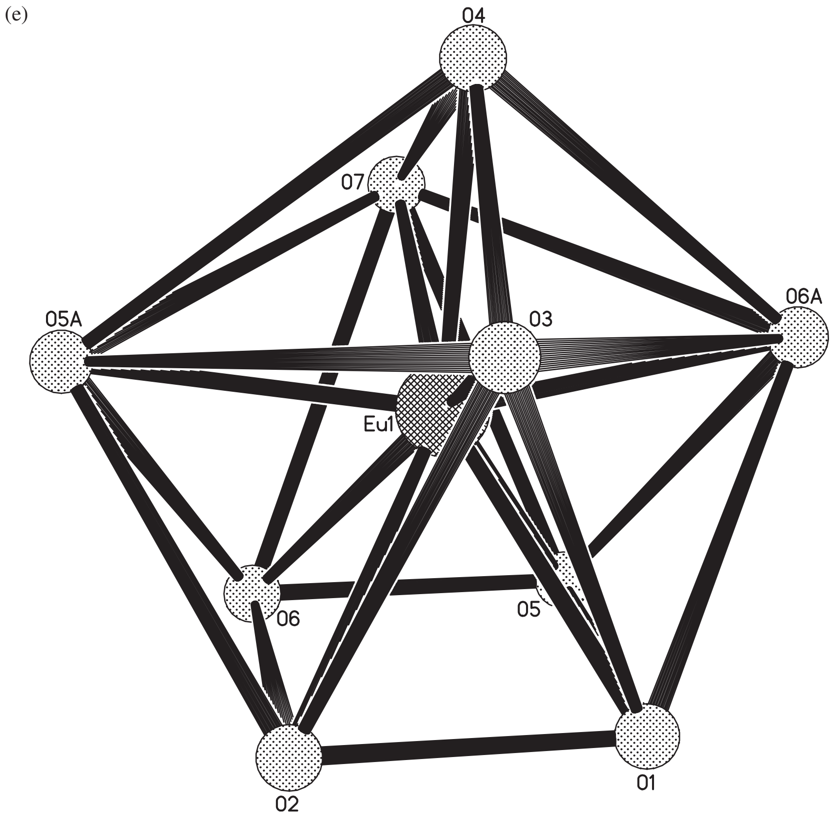
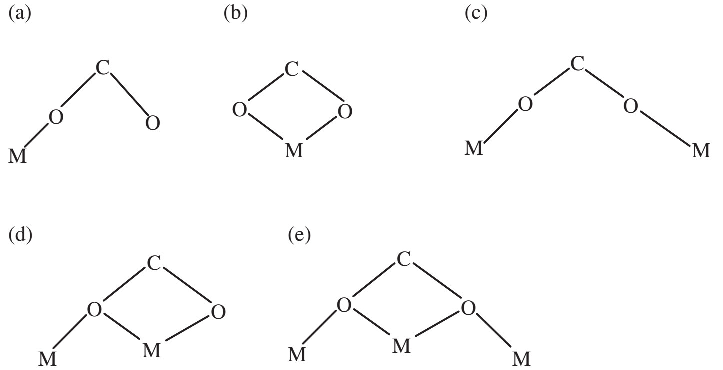


Figure 1. Continued.



Scheme 1. Coordination modes of carboxylate groups.

the corresponding values in **2**. The bond distances of Eu1–N are in the range 2.634(7)–2.660(6) Å with an average distance of 2.647 Å.

The two europium 2-iodobenzoic acid complexes containing 2,2′-bpy or phen are different from the terbium 2-fluorobenzoic acid complexes. For example, $[Tb(2\text{-}FBA)_3 \cdot (2,2'\text{-}bpy)]_2$ contains three independent binuclear molecules [5], and

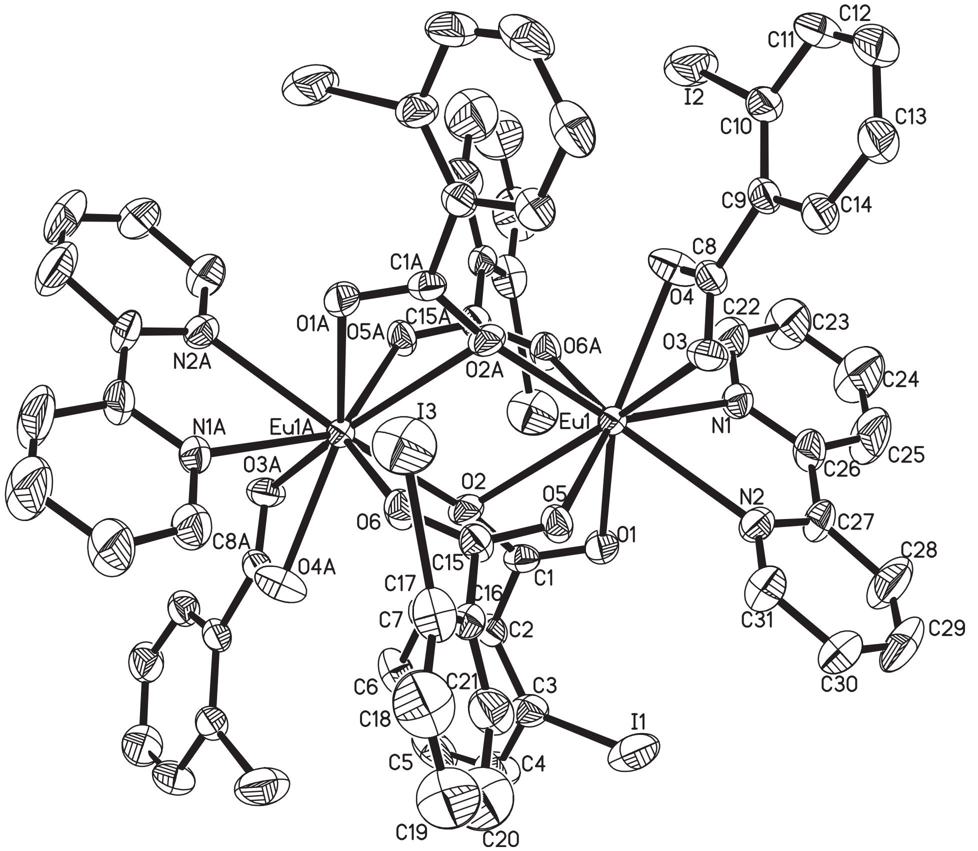


Figure 2. Molecular structure of complex (**2**). All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

the terbium 2-fluorobenzoic acid complex with phen containing two non-equivalent binuclear molecules, $[Tb(2\text{-}FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$ and $[Tb(2\text{-}FBA)_3 \cdot phen]_2$ [5]. The crystal structures of complexes **2** and **3** are common in lanthanide carboxylate complexes containing 2,2′-bpy or phen, $[Ln_2(MeCH{=}CHCO_2)_6 \cdot (phen)_2] \cdot 2H_2O$, (Ln = Eu, Tb) [4], $[Ln_2(CH_3CO_2)_6 \cdot (phen)_2]$, (Ln = Ce, Gd) [8], $[Gd_2(ClH_2CCOO)_6(bipy)_2]$ (bipy = 2,2′-bipyridine) [9], and $[Eu(2,3\text{-}DMOBA)_3(bpy)]_2$ (2,3-DMOBA = 2,3-dimethoxybenzoate; bpy = 2,2′-bipyridine) [10]. In these complexes, two central metal ions are linked through four carboxylate groups, two in bidentate-bridging and the other two in tridentate-bridging mode, as well as each metal ion also chelated by one carboxylate group and one 2,2′-bpy or phen molecule leading to a dimer with coordination number of nine. This is a common feature of lanthanide carboxylate complexes containing 2,2′-bpy or phen.

3.4. *Thermogravimetric analysis*

The thermal behavior of the complexes was studied in the temperature range from 25 to 1000°C. The DTA–TG diagram of **1** shows an endothermic peak at 243.0°C and

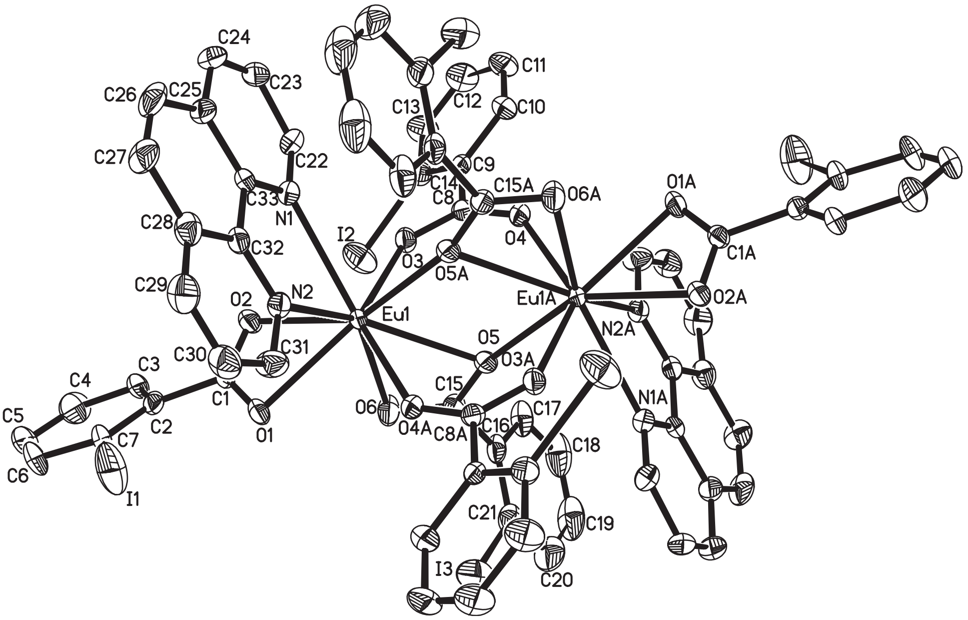


Figure 3. Molecular structure of complex **3**. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

an exothermic peak at 479.0°C, correspond to total mass loss of 81.06%, indicating the complex is completely degraded into Eu_2O_3 (theoretical mass loss 80.68%). For complex **2**, an endothermic peak at 244°C and an exothermic peak at 455.0°C on the DTA curve correspond to the two decomposition steps on the TG curve. The mass loss of 14.93% in the first step, corresponds to loss of 2,2′-bpy (theoretical mass loss is 14.89%). The total mass loss is 82.43%, indicates residual Eu_2O_3, Calcd 83.23%. For **3**, an endothermic peak at 332°C and an exothermic peak at 490.0°C on the DTA curve correspond to two decomposition steps on the TG curve, indicating loss of phen ligand (observed, 17.49%; Calcd, 16.79%) and final decomposition product of Eu_2O_3 (total mass: observed, 83.06%; Calcd, 83.60%).

Comparing thermal decomposition temperature of **3** with those **1** and **2**, complex **3** is most stable due to the large conjugate system of the phen ligand.

3.5. *UV spectra*

The UV absorption spectra of the three complexes were measured in DMF solution with $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ in the range 200 to 400 nm. Results show that UV spectral peak shapes and peak positions of the three complexes are very similar. The broad absorption bands at 282 nm ($\varepsilon = 3.26 \times 10^4$), 281 nm ($\varepsilon = 4.08 \times 10^4$), and 281 nm ($\varepsilon = 5.18 \times 10^4$), are attributed to the electronic transition of the π–π^* of ligands, respectively. The absorption wavelengths are consistent, and molar absorption coefficients increase in the order of **1**, **2**, and **3** perhaps from steric effects. This order is in accord with increasing conjugation of the complexes.

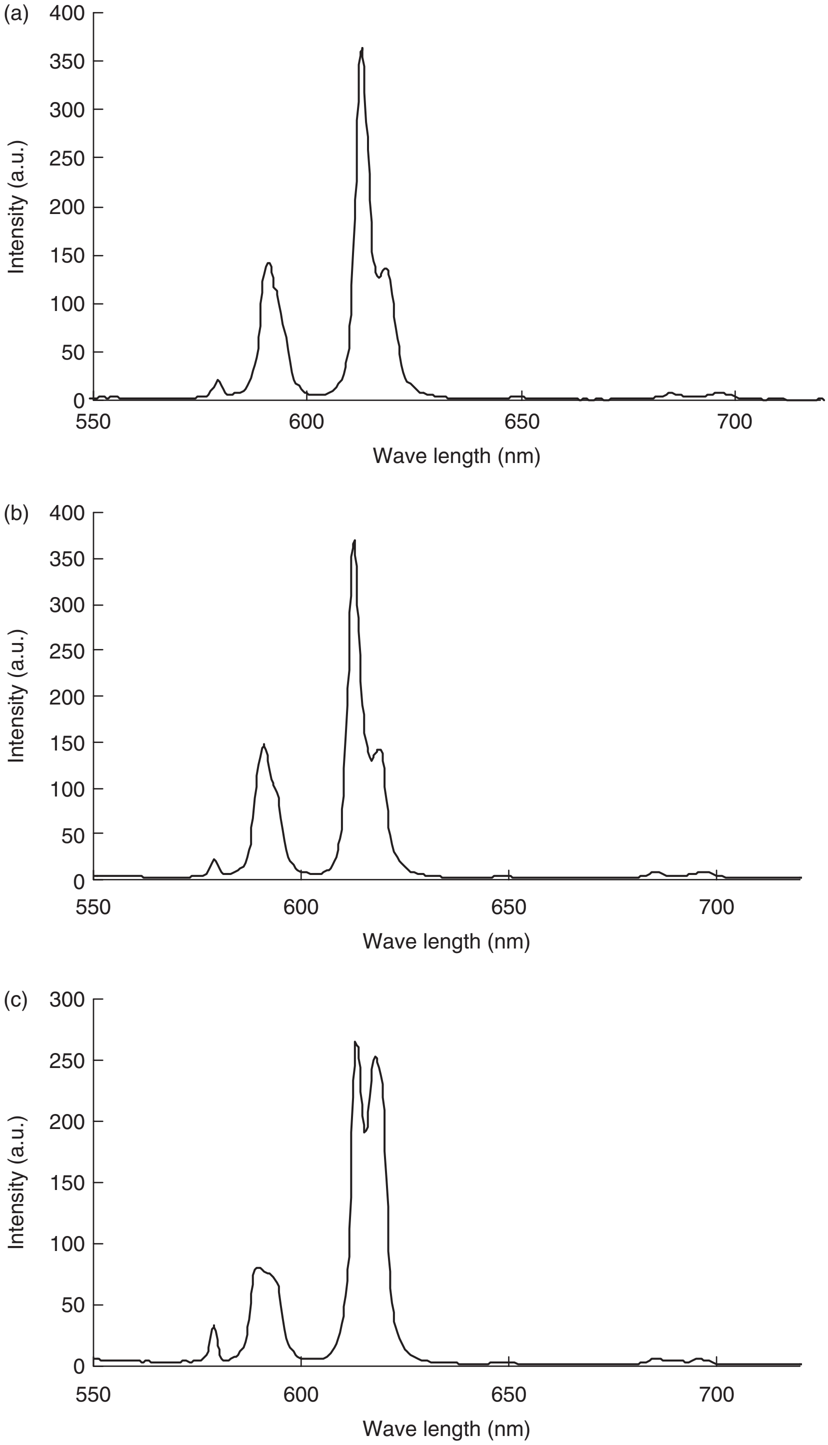


Figure 4. The fluorescence spectra of complexes (a) **1** ($\lambda_{exc} = 395\,nm$); (b) **2** ($\lambda_{exc} = 395\,nm$); and (c) **3** ($\lambda_{exc} = 395\,nm$).

3.6. *Luminescence properties*

The three complexes emit red light when excited by UV in the solid state. The solid-state excitation and luminescence spectra of Eu^{3+} power complexes were recorded at room temperature. The excitation spectra were measured under emission wavelength 613 nm in the range from 300 to 450 nm. The fluorescence spectra of the three complexes generated in the range from 500 to 750 nm under selective excitation wavelength of 395 nm, are shown in figure 4 (a, b and c), respectively. Their fluorescence spectra are essentially identically, exhibiting characteristic $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) emission of Eu^{3+}. The bands at 579, 591, and 649 nm are attributed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_3$ transition emission of Eu^{3+} ion, respectively. The double peaks at 613 and 619 nm are due to $^5D_0 \rightarrow {}^7F_2$ ion. For **1** and **2** the band at 619 nm is a weak shoulder, whereas for (**3**) the peaks at 613 and 619 nm are clearly split. The weak double peaks at 685 and 696 nm are due to the $^5D_0 \rightarrow {}^7F_4$ emission of Eu^{3+}. The strongest intensity of emission luminescence is due to the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm. The large intensity ratios of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ indicate the low symmetry of Eu^{3+} sites in the three complexes, in agreement with the crystal structures determined by X-ray diffraction.

Supplementary data

CCDC-298028, 298029, and 298030 for **1**, **2** and **3**, respectively, contains the supplementary crystallographic data. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; (Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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