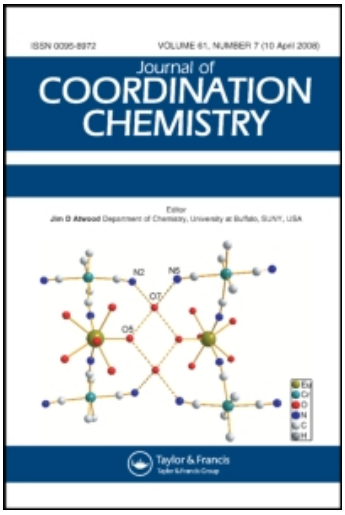

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Syntheses and crystal structures of two samarium(III) complexes with bio-relevant ligands

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Syntheses and crystal structures of two samarium(III) complexes with bio-relevant ligands

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Under hydrothermal conditions, Sm_2O_3 reacted with ciprofloxacin (Cip), oxalic acid (Ox) and KOH to give a 2D coordination polymer with the empirical formula of $[Sm(Cip)(Ox)_{1.5}]\cdot H_2O$ (**1**). $Sm(ClO_4)_3\cdot 6H_2O$ reacted with 3,5-dinitrobenzoic acid (dnb) and 1,10-phenanthroline(phen) to afford dimeric Sm(III) complex, $[Sm_2(Dnb)_6(phen)_2]$ (**2**). X-ray diffraction analyses show that **1** crystallizes in the monoclinic system, $C2/c$ space group, $a=28.279(3)$, $b=10.4514(8)$, $c=16.398(2)$ Å, $\beta=114.053°$, $V=4425.8(7)$ Å^3, $Z=8$, $D_c=1.896$ Mg m^{-3}, in which the network of SmO_8 and oxalate units form an extended two-dimensional layered structure through tetradentate oxalates, the chelated ciprofloxacin alternatively pointed up and down from the 2D plane, and a 3D lamellar structure is formed via strong intermolecular hydrogen bonds of N–H $\cdots$ O and O–H $\cdots$ O; **2** crystallizes in the triclinic system, $P\bar{1}$ space group, $a=12.063(3)$, $b=12.967(3)$, $c=13.260(3)$ Å, $\alpha=104.046(4)$, $\beta=113.750(4)$, $\gamma=100.391(5)°$, $V=1749.0(8)$ Å^3, $Z=2$, $D_c=1.830$ Mg m^{-3}, in which the molecular unit is a dimer with an inversion center and each Sm(III) adopts a nine-coordinate distorted tricapped trigonal-prism geometry defined by an N_2O_7 donor set from one phen and five 3,5-dinitrobenzoato ligands.

Keywords: Samarium(III); Coordination polymer; Crystal structure; Oxalate; Ciprofloxacin; 3,5-Dinitrobenzoic acid; 1,10-Phenanthroline

1. Introduction

Lanthanide complexes have received much attention due to their interesting photophysical properties which have potential applications as luminescent probes for chemical or biological macromolecules and as the active center for luminescent materials [1, 2]. Considerable research has focused on the design and assembly of lanthanide complexes with organic ligands such as aromatic carboxylic acids, β-diketone, cryptands, calixarenes, heterocyclic ligands, etc. Among the lanthanide

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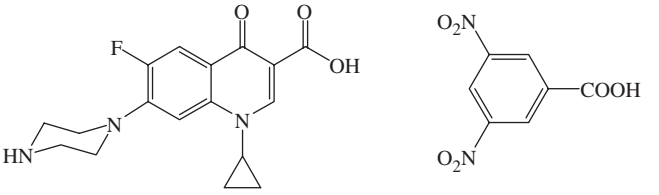

Ciprofloxacin 3,5-Dinitrobenzoic acid

Scheme 1. Two bio-relevant ligands.

complexes, aromatic carboxylic acids show higher thermal or luminescent stabilities for practical application than other lanthanide complex systems because they readily form the dimeric or infinite 1D, 2D and 3D polymeric structures [3, 4]. The oxalate ion can function as a bis-bidentate ligand, and its coordination to transition metal ions has been widely studied due to its remarkable ability to mediate strong magnetic interactions between the metal centers [5–7]. Currently, our work focuses on the coordination chemistry of organic drugs with the aim of investigating their coordination behavior. Amongst these ligands, quinolones are a group of synthetic antibacterial agents widely used in clinical practice; ciprofloxacin (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid, CIP, scheme 1) is used for the treatment of certain diseases caused by various Gram negative and some Gram positive microorganisms [8]. A breakthrough in the preparation of quinolone metal complexes by the solvothermal method [9] resulted in the isolation of several new compounds [10]. Some metals could form 2D square grid structures and apart from the normal chelate bonding of quinolone, a terminal piperazine nitrogen atom could also be involved in coordination if this atom is available in the molecule [11–13]. To the best of our knowledge, the combined use of oxalate, ciprofloxacin and lanthanide to assemble coordination polymers has not been accomplished.

Another target bio-relevant ligand, 3,5-dinitrobenzoic acid (Dnb, scheme 1) acts as an antifungal agent and is used for the preparation of the drugs amoxycillin and flucloxacilin, [14, 15] but the anion can also serve as a ligand in metal complexes. The crystal engineering of 3,5-dinitrobenzoic acid has been well documented, [16] and a few of its metal complexes such as Li(I), Ca(II), Sr(II), Pb(II), Cd(II), Zn(II), Cu(II), Co(II), Ni(II), Mn(II), Ce(III), Pr(III) and Sm(III) in solid state have been crystallographically characterized [17], but it is still worthy investigating the structure diversity of such type of lanthanide complexes with 3,5-dinitrobenzoic acid.

Herein, we report the syntheses and crystal structures of two Sm(III) complexes with mixed-ligands: $[Sm(Cip)(Ox)_{1.5}] \cdot H_2O$ (**1**) and $[Sm_2(Dnb)_6(phen)_2]$ (**2**).

2. Experimental

2.1. *Materials and apparatus*

Ciprofloxacin and 3,5-dinitrobenzoic acid were provided by Fluka. All reagents used were of analytical grade. C, H, and N elemental analyses were carried out with a

Perkin-Elmer analyzer model 240II. IR spectra were recorded as KBr discs on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the range 400–4000 cm^{-1}.

2.2. *Synthesis of [Sm(Cip)(Ox)$_{1.5}$] · H$_2$O (1)*

An aqueous mixture (15 mL) containing Sm_2O_3 (0.5 mmol, 0.174 g), oxalic acid (1.5 mmol, 0.135 g), ciprofloxacin (1.0 mmol, 0.272 g) and KOH (0.5 mmol, 0.028 g) was placed in a Teflon-lined stainless steel vessel (25 mL). Then ethanol (5.0 mL) was added to the heterogeneous mixture, and the vessel was sealed and heated to 130°C for 96 h. Upon cooling to room temperature, brown block crystals of **1** were obtained. Yield 58%. $C_{20}H_{20}FN_3O_{10}Sm$: Anal. Calcd C, 38.02; H, 3.19; N, 6.65; Found: C, 38.10; H, 3.14; N, 6.73%. IR (KBr, cm^{-1}): 3547(m), 3257(s), 2962(w), 2912(w), 1645(s), 1593(s), 1560(s), 1471(m), 1406(m), 1353(s), 1332(w), 1254(w), 1244(w), 1116(w), 945(w), 931(w), 912(w), 760(s), 743(m), 644(w), 621(w), 568(w), 549(w), 516(w), 413(w).

2.3. *Synthesis of [Sm$_2$(dnb)$_6$(phen)$_2$] (2)*

An ethanolic solution (25 mL) of 3,5-dinitrobenzoic acid (3 mmol, 0.636 g) and phen (1 mmol, 0.176 g) was prepared and the pH was adjusted to 7–8 with dilute KOH solution. To the resulting solution, $Sm(ClO_4)_3 \cdot 6H_2O$ (1 mmol) in ethanol (10 mL) was added dropwise. Then the mixture was stirred at 70–80°C for 10 h. The precipitate was filtered off, and the filtered solution was allowed to stay at room temperature. After four weeks, yellowish block-shaped crystals of **2** suitable for structural analysis were isolated. Yield: 35%. Anal. Calcd for $C_{33}H_{17}N_8O_{18}Sm$: C, 41.12; H, 1.78; N, 11.63; Found: C, 41.21; H, 1.83; N, 11.55%. UV-vis (DMSO, nm): 285. IR(KBr, cm^{-1}): 3436(w), 3101(m), 2877(w), 1633(s), 1610(m), 1587(m), 1545(s), 1520(s), 1468(m), 1416(m), 1390(m), 1344(s), 1208(w), 1193(w), 1145(w), 1103(w), 1086(m), 1076(m), 935(w), 917(m), 864(w), 845(m), 794(m), 775(w), 724(s), 710(m), 640(w), 538(m), 521(w).

2.4. *X-ray crystallography*

Measurements of **1** and **2** were made on a Rigaku Mercury CCD X-ray diffractometer and a Bruker CCD area detector diffractometer, respectively. The structures were solved by the direct methods and refined by full-matrix least-squares on F^2. The empirical absorption corrections were applied. All non-hydrogen atoms were located from the trial structure and then refined anisotropically. Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms, but the hydrogen atoms attached to solvent ethanol molecules of compound **1** are not fixed. All calculations were performed using the SHELXTL 5.1 program package [18]. The crystallographic data of complexes **1** and **2** are summarized in table 1.

Table 1. Crystal data and structure refinement for complexes **1** and **2**.

Empirical formula	$C_{20}H_{20}FN_3O_{10}Sm$	$C_{33}H_{17}N_8O_{18}Sm$
Formula weight	631.79	963.9
Temperature (K)	193(2)	293(2)
Crystal size (mm^3)	$0.10 \times 0.20 \times 0.15$	$0.34 \times 0.20 \times 0.06$
θ range for data collection	3.07–27.48	2.56–28.43
Wavelength (Å)	0.7107	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	28.279(3)	12.063(3)
b (Å)	10.4514(8)	12.967(3)
c (Å)	16.398(2)	13.260(3)
α (°)	90	104.046(4)
β (°)	114.053	113.750(4)
γ (°)	90	100.391(5)
V ($Å^3$)	4425.8(7)	1749.0(8)
Z	8	2
D_c ($Mg\,m^{-3}$)	1.896	1.83
μ (mm^{-1})	2.725	1.776
$F(000)$	2496	954
Limiting indices	$-36 \le h \le 28$, $-13 \le k \le 13$, $-21 \le l \le 21$	$-15 \le h \le 7$, $-16 \le k \le 17$, $-14 \le l \le 17$
Reflections collected	17 332	11 125
Independent reflection	5045	8240
Max. and min. transmission	0.7722 and 0.6117	0.9009 and 0.5835
Goodness-of-fit on F^2	1.045	1.122
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0228$, $wR_2 = 0.0564$	$R_1 = 0.0529$, $wR_2 = 0.0942$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.878 and −0.517	1.078 and −2.606

3. Results and discussion

3.1. *Description of the crystal structure of 1*

As illustrated in figure 1, the asymmetric unit of **1** consists of $[Sm(Cip)(Ox)_{1.5}]$ and one co-crystallized water. The samarium in **1** is linked with three oxalates and one ciprofloxacin molecule. The samarium possesses distorted square antiprism coordination environment and is surrounded by six oxalate O and two O atoms from ciprofloxacin. The Sm–O distances are in the range 2.333(3)–2.464(3) Å [$(Sm–O)_{av} = 2.408$ Å] and the O–Sm–O bond angles are in the range 64.59(11)–159.05(11)° [$(O–Sm–O)_{av} = 100.2036°$]. The C–O bond distance and O–C–O bond angle of oxalate, and the geometrical parameters of ciprofloxacin are as expected. Selected bond distances and angles are presented in table 2.

In the structure of **1**, the network of SmO_8 and oxalate units form an extended two-dimensional layered structure, with one ciprofloxacin molecule directly chelated to Sm through one carboxylate O and one quinoline carboxyl O. Similar to $[Cd(C_2O_4)_2(C_3N_2H_4)_3(H_2O)]_\infty$ [19], the connectivity between the Sm atoms and the oxalate units forms a unique layered architecture, along the *bc* plane, with twelve-membered rectangle-shaped apertures (six Sm and six oxalate units) within the layers as shown in figure 2(a). Sm(1) is connected to three oxalates in a typical tetradentate fashion (chelate bis-bidentate) [7]. The chelated ciprofloxacin alternatively pointed up and down from the plane due to the steric hindrance of ciprofloxacin (figure 2b), with the terminal N of the piperazyl ring of ciprofloxacin protonated without

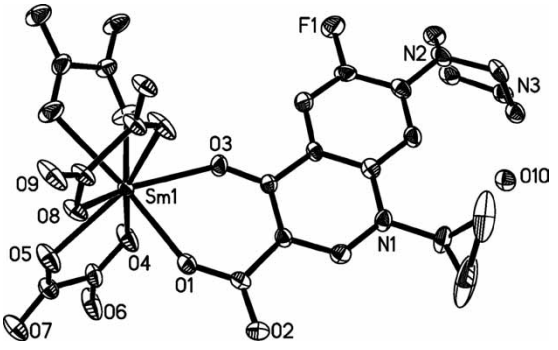

Figure 1. The coordination environment of complex **1**. The related coordination atoms are labeled. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected bond distances (Å) and bond angles (°) for **1**.

Sm(1)–O(1)	2.333(3)	Sm(1)–O(5)	2.422(3)
Sm(1)–O(3)	2.345(3)	Sm(1)–O(8)	2.464(3)
Sm(1)–O(4)	2.446(4)		
O(1)–Sm(1)–O(3)	72.43(10)	O(3)–Sm(1)–O(7)#2	69.54(11)
O(1)–Sm(1)–O(5)	88.95(12)	O(5)–Sm(1)–O(7)#2	114.78(13)
O(3)–Sm(1)–O(5)	145.19(12)	O(1)–Sm(1)–O(4)	84.59(13)
O(1)–Sm(1)–O(9)#1	88.89(13)	O(3)–Sm(1)–O(4)	82.68(11)
O(3)–Sm(1)–O(9)#1	76.37(11)	O(5)–Sm(1)–O(4)	66.13(11)
O(5)–Sm(1)–O(9)#1	133.77(11)	O(9)#1–Sm(1)–O(4)	159.05(11)
O(1)–Sm(1)–O(7)#2	139.23(11)	O(7)#2–Sm(1)–O(4)	76.63(12)
O(1)–Sm(1)–O(8)	80.73(11)	O(3)–Sm(1)–O(8)	133.57(11)
O(7)#2–Sm(1)–O(6)#2	64.59(11)	O(8)–Sm(1)–O(6)#2	73.53(11)

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

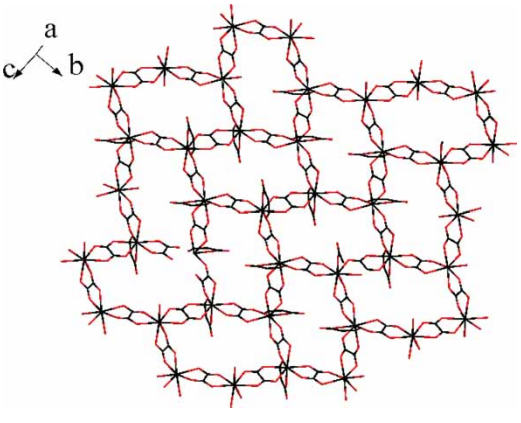

Figure 2. (a) 2D network of **1** constructed by oxalate viewed along the *a*-axis. Parts of ciprofloxacin ligands are omitted for clarity.

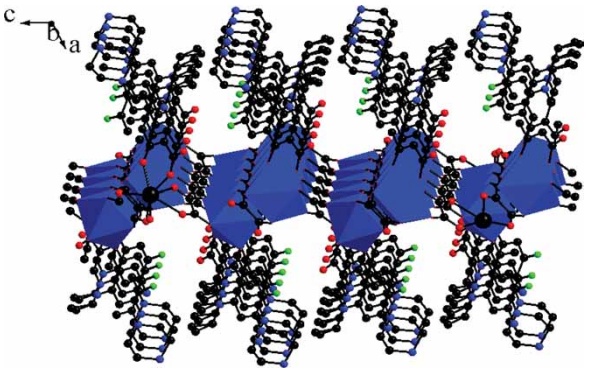

Figure 2. (b) 2D network of **1** constructed by oxalate and the ciprofloxacin ligands pointed up and down viewed along the *b*-axis.

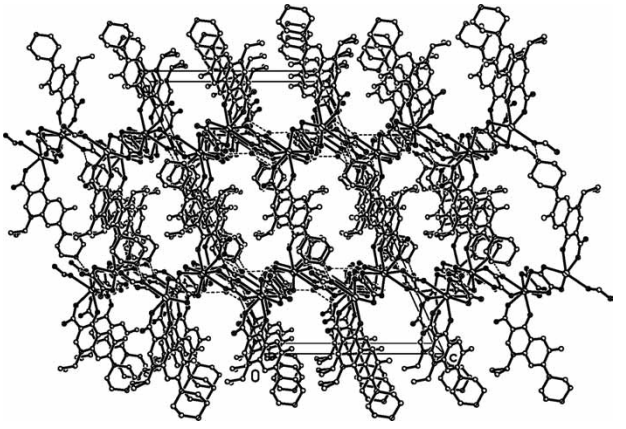

Figure 3. Packing drawing of **1** viewing along *b*-axis.

coordination ability.The layer arrangement, viewed along the *bc* plane, consists of samarium oxalate layers separated by the ciprofloxacin as shown in figure 3. 3D supramolecular structure is generated through π–π stacking interactions of quinoline rings with a centroid–centroid distance of 3.945 Å between the planes and strong intermolecular hydrogen bonds involving piperazyl terminal N–H, carboxylate group and co-crystallized water molecules (table 3).

3.2. *Description of the crystal structure of 2*

As shown in figure 4, complex **2** is a dimeric structure with an inversion center, each samarium adopting a nine-coordinate distorted tricapped trigonal-prism geometry (figure 5) defined by N_2O_7 donor set from one phen and five 3,5-dinitrobenzoates, respectively. Similar to, $[Eu_2(Dnb)_6(phen)_2]$ [20] and $[Tb_2(Dnb)_6(phen)_2]$ [21], the two Sm(III) ions are bridged by four-fold 3,5-dinitrobenzoato, in which two Dnb^- are in the *syn–syn* bidentate bridging mode with an O–C–O angle of 126.8(5)°, and two

Table 3. Hydrogen bond distances (Å) and bond angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(3)–H(3A)–O(8)#4	0.92	1.88	2.791(5)	169.3
N(3)–H(3B)–O(10)	0.92	1.91	2.811(6)	164.5
O(10)–H(10B)–O(1)#5	0.89(2)	2.00(3)	2.860(5)	162(5)
O(10)–H(10B)–O(2)#5	0.89(2)	2.60(5)	3.244(5)	129(5)
O(10)–H(10C)–O(7)#4	0.89(2)	2.17(5)	2.875(5)	135(6)

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

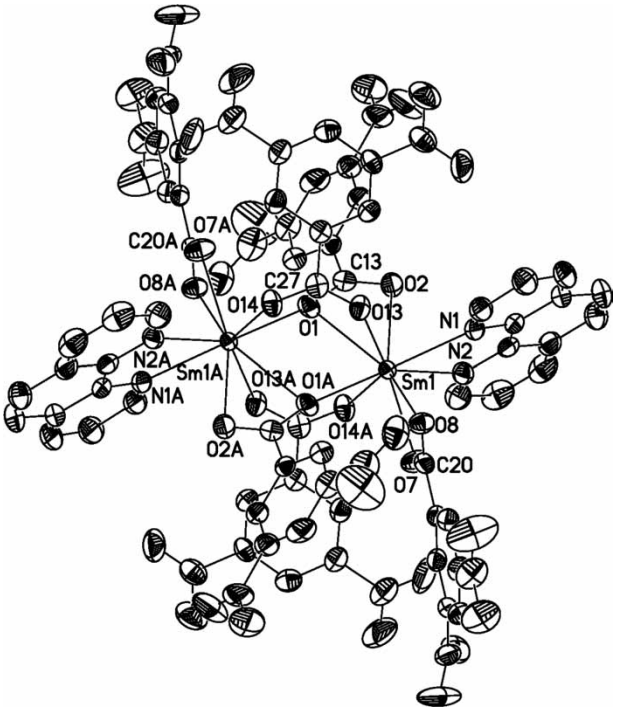

Figure 4. ORTEP drawing of $[Sm_2(Dnb)_6(phen)_2]$ (**2**). The related coordination atoms are labeled. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Dnb^- tridentate bridging. One terminal chelating phen and one chelating bidentate Dnb^- complete the nine-coordination for each Sm(III) ion. Therefore, three coordination modes exist for 3,5-dinitrobenzoato in **2**. Whilst, in $[Sm_2(Dnb)_6(H_2O)_4]_n$ [17(k)], a one-dimensional chain polymeric structure, whose irregular square-antiprism coordination environment of the Sm ion is completed by six O atoms from six Dnb^- ligands and two aqua O atoms, and the Sm ions are bridged alternatively by four Dnb^- in the bidenate bridging coordination mode. The distances of Sm–O range from 2.382(3) to 2.755(3) Å, Sm–N from 2.547(4) to 2.612(4) Å and the Sm···Sm separation is 4.017 Å, but the bond distances in the aromatic ring of the 3,5-dinitrobenzoato and phen are comparable to the literature's values. [20, 21] Selected bond distances and angles are presented in table 4.

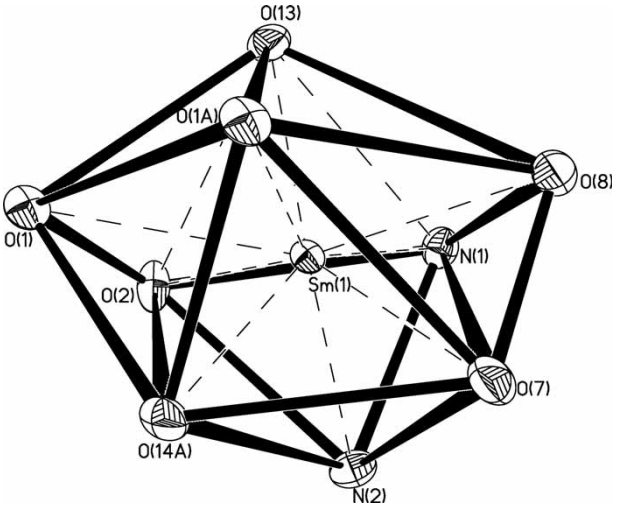

Figure 5. coordination polyhedron of Sm(III) in **2**: distorted tricapped trigonal-prism.

Table 4. Selected bond distances (Å) and bond angles (°) for **2**.

Sm(1)–O(1)	2.755(4)	Sm(1)–O(8)	2.507(3)
Sm(1)–O(2)	2.497(3)	Sm(1)–O(13)	2.396(3)
Sm(1)–O(7)	2.445(4)	Sm(1)–O(1A)	2.391(3)
Sm(1)–O(14A)	2.382(3)	Sm(1)–N(1)	2.547(4)
Sm(1)–N(2)	2.612(4)		
O(1)–Sm(1)–O(2)	49.23(10)	O(2)–Sm(1)–O(7)	143.57(13)
O(1)–Sm(1)–O(8)	147.87(11)	O(2)–Sm(1)–O(8)	146.65(12)°
O(1)–Sm(1)–O(13)	70.01(12)	O(7)–Sm(1)–O(13)	136.53(13)
O(1)–Sm(1)–N(1)	119.88(11)	O(1)–Sm(1)–N(2)	108.05(12)
N(1)–Sm(1)–N(2)	63.68(15)	O(2)–Sm(1)–N(2)	70.12(13)

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

3.3. *IR spectra*

Compound **1** exhibits a broad split band between 3600 and 2900 cm^{-1}, which can be assigned to the O–H stretching vibration of water and also includes the N–H stretching vibration of the protonated piperazinyl moiety [22]. Furthermore, the carboxylate stretching mode for **1** is observed at 1704 cm^{-1} while the pyridone carbonyl stretch is at 1645 cm^{-1}. Upon samarium conjugation the former band disappears as noted by Chen *et al*. [9] while the latter is found to be shifted to lower energy side which is indicative of these two as the donor atom set involved in metal coordination [10]. The oxalate stretching vibrations appear at 1593 cm^{-1} [$\nu_{as}(COO^-)$, 1353cm^{-1} [$\nu_a(COO^-)$] [23].

Compound **2** exhibits the characteristic features of Dnb^- and phen, but with obvious shifts in comparison with the corresponding free ligands. The bands of free phen at 1559 ($\gamma_{C=N}$) and 851, 736 cm^{-1}(δ_{C-H}) are shifted to 1545, 845, 724 cm^{-1}, respectively, suggesting that phen is coordinated to Sm [24]. The characteristic stretching vibrations of free carboxylic acid at 1730cm^{-1} disappeared and split into two peaks: 1633

($\nu_{as}(COO^-)$) and 1468 cm^{-1}($\nu_s(COO^-)$) for **2** with $\Delta\nu = 165\,cm^{-1}$, which indicates that carboxylate groups are not in single coordination mode [25], and consistent with the crystal structural analysis results of **2**.

Supplementary material

Crystallographic data for compounds **1** and **2** are deposited to the Cambridge Crystallographic Data Center, the deposition numbers are CCDC 262521 and 217208, respectively. These material can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: C44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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