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# Synthesis, crystal structure and properties of three new holmium 2-fluorobenzoato complexes

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#### Abstract

This paper reports three new holmium 2-fluorobenzoato (2-FBA) complexes with 1,10-phenanthroline (phen), 2,2'-bipydine (2,2'-bpy) and 4,4'-bipyridine, respectively. A rare and interesting structural feature of holmium 2-FBA complex containing phen is two non-equivalent binuclear molecules existed in an asymmetric unit, namely,  $[Ho(2-FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$  and  $[Ho(2-FBA)_3 \cdot phen]_2$ . The dimeric complex  $[Ho(2-FBA)_3 \cdot 2,2'-bpy]_2$  is a type of eight-coordinated lanthanide carboxylate complexes containing 2,2'-bpy. The  $\{[Ho(2-FBA)_3 \cdot 2H_2O] \cdot (4,4'-bpy)\}_n$  is in one-dimensional polymeric structure, and the 3D supramolecular network structure is formed by the hydrogen bonds and  $\pi$ - $\pi$  stacking interactions.

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# 1. Introduction

Lanthanide carboxylate complexes have variety of crystal structures because of high coordination number of the lanthanide ions and the various coordination modes of carboxylate groups. This kind of complexes has potential applications in calatysts, magnetic materials and luminescent probes and many others. Dimeric and polymeric forms are most frequently observed for these compounds [1-10]. We have reported some mixed-ligands lanthanide carboxylate complexes with aromatic diamines such as 1,10-phenanthroline, 2,2'-bipydine, and 4,4'bipyridine [3,4,10]. In the present work, 2-fluorobenzoic acid (2-HFBA), phen, 2,2'-bpy, and 4,4'-bpy, respectively, were used as ligands to holmium ion and three new complexes with different crystal structure, [Ho(2- $FBA_{3}$ ·phen·CH<sub>3</sub>CH<sub>2</sub>OH]<sub>2</sub> and  $[Ho(2-FBA)_{3}$ ·phen]<sub>2</sub>,  $[Ho(2-FBA)_3 \cdot 2, 2'-bpy]_2$ , and  $\{[Ho(2-FBA)_3 \cdot 2H_2O] \cdot (4, 4'$  $bpy)_n$  were obtained.

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# 2. Experimental

## 2.1. Materials and methods

 $HoCl_3 \cdot 6H_2O$  was prepared by dissolving its oxide in hydrochloric acid, and then drying the solution. Elemental analysis was performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Bruker EQUINOX-55 using the KBr pellet technique. Thermogravimetric analysis was performed on a WCT-1A Thermal Analyzer at a heating rate 10 °C/min in air. The UV–VIS spectra were measured on a TU-1810 spectrophotometer in DMF.

## 2.2. Synthesis of complexes

About 1.5 mmol of 2-fluorobenzoic acid were dissolved in appropriate amounts of ethanol. The pH of the solution was controlled in a range of 5–6 with 2 mol dm<sup>-3</sup> NaOH solution. Then the ethanolic solutions of 1,10-phenanthroline (0.5 mmol) and HoCl<sub>3</sub> (0.5 mmol) were dropped, successively. The mixture was heated under reflux with stirring for 2 h. Single crystal complex (1) was obtained from the mother liquor after a week at room temperature. Anal. calcd (%): C, 52.32; N, 3.78; H, 3.05. Found (%): C,

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Table 1 Crystal data and structure refinement for complexes (1), (2), and (3)

Empirical formula	$C_{68}H_{46}F_{6}Ho_{2}N_{4}O_{13}$	$C_{31}H_{20}F_{3}HoN_{2}O_{6}$	C31H24F3HoN2O8
Formula weight	1570.95	738.42	774.45
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	Pī	P2(1)/n	P2(1)/c
Unit cell dimensions			
a (Å)	11.241(4)	12.137(3)	9.762(3)
b (Å)	12.595(5)	17.709(5)	26.132(8)
<i>c</i> (Å)	22.717(8)	13.676(4)	13.058(4)
α (°)	81.226(6)	90	90
β (°)	78.252(5)	111.411(4)	111.299(5)
$\gamma$ (°)	80.620(6)	90	90
$V(\text{\AA}^3)$	3083.3(19)	2736.7(13)	3103.7(16)
Ζ	2	4	4
$Dc (mg/m^3)$	1.692	1.792	1.657
Absorption coefficient $(mm^{-1})$	2.635	2.961	2.619
F(000)	1548	1448	1528
Crystal size (mm)	$0.18 \times 0.16 \times 0.14$	$0.20 \times 0.20 \times 0.18$	$0.36 \times 0.16 \times 0.14$
Theta range for data collection (°)	0.92–26.38	1.97-25.01	1.85-25.01
Limiting indices	$-14 \le h \le 11$	$-14 \le h \le 14$	$-11 \le h \le 10$
	$-15 \le k \le 13$	$-19 \le k \le 21$	$-30 \le k \le 31$
	$-28 \le l \le 28$	$-16 \le l \le 9$	$-15 \le l \le 12$
Reflections collected/unique	17719/12406	14135/4828	16100/5471
	[R(int)=0.0263]	[R(int)=0.0301]	[R(int)=0.0338]
Data/restraints/parameters	12406/0/859	4828/3/397	5471/288/448
Goodness-of-fit on $F^2$	1.128	1.091	1.056
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0405	R1 = 0.0237	R1 = 0.0380
	wR2 = 0.0887	wR2 = 0.0523	wR2 = 0.0874
R indices (all data)	R1 = 0.0653	R1 = 0.0397	R1 = 0.0613
	wR2 = 0.1005	wR2 = 0.0587	wR2 = 0.0981
Largest diff. peak and hole (e $\check{A}^{-3}$ )	1.276 and -0.943	0.871  and  -0.527	0.672  and  -0.655

51.99; N, 3.56; H, 2.95. IR (KBr, cm<sup>-1</sup>): 3433(w), 1612(vs), 1462(s), 1409(vs), 845(m), 730(m), 453(w).

Synthesis of single crystal complex (2) is similar to that of complex (1), whereas 2,2'-bipydine was used instead of 1,10-phenanthroline. Anal. calcd (%): C, 50.20; N, 3.54; H, 2.68. Found (%): C, 50.44; N, 3.79; H, 2.73. IR (KBr, cm<sup>-1</sup>): 1612(vs), 1452(s), 1414(vs), 1015(m), 799(m), 454(w).

When 4,4'-bipyridine was used instead of 1,10-phenanthroline, complex (3) were obtained. Anal. calcd (%): C, 48.39; N, 3.65; H, 3.50. Found (%): C, 48.08; N, 3.62; H, 3.12. IR (KBr, cm<sup>-1</sup>): 3437(w), 1612(vs), 1462(s), 1411(vs), 460(w).

#### 2.3. Single-crystal X-ray diffraction

X-ray diffraction data of the single crystal were collected by using a Bruker Smart 1000 CCD diffractometer with monochromated Mo K $\alpha$  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 [11,12]. The structures were solved by direct methods and refinement on  $|F|^2$  used the full-matrix least-squares methods. A summary of the crystallographic data and details of the structure refinements are listed in Table 1 and the selected bond distances and angles in Tables 2–4.

The crystallographic data have been deposited at Cambridge Crystallographic Data Center, CCDC-268456, 268457, and 268458 for complexes (1), (2), and (3), respectively, as the supplementary crystallographic data for this paper. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk.

## 3. Results and discussion

#### 3.1. UV–VIS spectra

UV–VIS absorption spectra of the three complexes were measured in DMF solution with  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-3}$  mol/L, respectively. Results show that UV–VIS spectral peak shapes and peak positions of the three complexes are very similar. The broad absorption band at 294 nm corresponds to the transition of the  $\pi$ – $\pi$ \* of the phen and 2-FBA group. The Hypersensitive transition of Ho<sup>3+</sup> ion was observed at 450 nm, corresponding to the transition  ${}^{5}I_{6} \rightarrow {}^{5}G_{6}$  of Ho<sup>3+</sup> ion.

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

Ho(1)–O(1)	2.277(4)	Ho(1)–O(3)	2.320(4)
Ho(1)-O(2)#1	2.329(4)	Ho(1)–O(4)#1	2.343(4)
Ho(1)-O(5)	2.346(4)	Ho(1)–O(7)	2.418(4)
Ho(1)-N(2)	2.519(5)	Ho(1)–N(1)	2.575(5)
Ho(2)-O(10)#2	2.275(4)	Ho(2)–O(8)	2.310(4)
Ho(2)-O(9)#2	2.343(4)	Ho(2)–O(12)	2.392(4)
Ho(2)–O(11)	2.408(4)	Ho(2)–O(13)	2.480(5)
Ho(2)-O(10)	2.739(4)	Ho(2)–N(3)	2.530(6)
Ho(2)–N(4)	2.631(5)		
O(1)-Ho(1)-O(3)	74.85(15)	O(1)-Ho(1)-O(2)#1	121.22(14)
O(3)-Ho(1)-O(2)#1	79.86(15)	O(1)-Ho(1)-O(4)#1	78.05(14)
O(3)-Ho(1)-O(4)#1	122.70(14)	O(2)#1-Ho(1)-O(4)#1	72.77(14)
O(1)-Ho(1)-O(5)	83.59(15)	O(3)-Ho(1)-O(5)	84.14(15)
O(2)#1-Ho(1)-O(5)	144.91(14)	O(4)#1-Ho(1)-O(5)	140.96(14)
O(1)-Ho(1)-O(7)	143.48(15)	O(3)-Ho(1)-O(7)	75.07(15)
O(2)#1-Ho(1)-O(7)	72.59(14)	O(4)#1-Ho(1)-O(7)	136.67(14)
O(5)-Ho(1)-O(7)	73.19(14)	N(2)-Ho(1)-N(1)	64.14(16)
O(10)#2-Ho(2)-O(8)	77.96(16)	O(10)#2-Ho(2)-O(9)#2	74.30(15)
O(8)-Ho(2)-O(9)#2	134.49(14)	O(10)#2-Ho(2)-O(12)	143.49(14)
O(8)-Ho(2)-O(12)	75.87(14)	O(9)#2-Ho(2)-O(12)	141.63(14)
O(10)#2-Ho(2)-O(11)	123.61(15)	O(8)–Ho(2)–O(11)	86.04(16)
O(9)#2-Ho(2)-O(11)	80.31(16)	O(12)-Ho(2)-O(11)	79.44(15)
O(10)#2-Ho(2)-O(13)	155.12(17)	O(8)-Ho(2)-O(13)	126.01(16)
O(9)#2-Ho(2)-O(13)	89.39(15)	O(12)-Ho(2)-O(13)	53.04(15)
O(11)-Ho(2)-O(13)	70.07(16)	O(10)#2-Ho(2)-O(10)	74.91(15)
O(8)-Ho(2)-O(10)	65.84(13)	O(9)#2-Ho(2)-O(10)	72.47(14)
O(12)-Ho(2)-O(10)	115.62(14)	O(11)-Ho(2)-O(10)	49.44(14)
O(13)-Ho(2)-O(10)	118.50(15)	N(3)-Ho(2)-N(4)	63.1(2)

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

## 3.2. Thermal analysis

The thermal behavior of complexes was studied in the temperature ranged from 25 to 1000 °C. The DTA-TG diagram shows that the thermal decomposition of the complex (1) occurs in the range of 146.0–454.0 °C. The total mass loss is 70.24%, which indicate the complex is

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

e ()	0 ()	1 ( )	
Ho(1)-O(1)	2.264(3)	Ho(1)–O(3)	2.321(3)
Ho(1)-O(2)#1	2.324(3)	Ho(1)-O(4)#1	2.327(3)
Ho(1)-O(6)	2.359(3)	Ho(1)-O(5)	2.452(3)
Ho(1)-N(1)	2.534(3)	Ho(1)-N(2)	2.568(3)
O(1)-Ho(1)-O(3)	77.82(10)	O(1)-Ho(1)-O(2)#1	126.27(10)
O(3)-Ho(1)-O(2)#1	80.22(10)	O(1)-Ho(1)-O(4)#1	79.87(10)
O(3)-Ho(1)-O(4)#1	128.45(10)	O(2)#1-Ho(1)-O(4)#1	76.74(9)
O(1)-Ho(1)-O(6)	86.78(10)	O(3)-Ho(1)-O(6)	79.13(11)
O(2)#1-Ho(1)-O(6)	135.47(10)	O(4)#1-Ho(1)-O(6)	144.74(10)
O(1)-Ho(1)-O(5)	134.81(9)	O(3)-Ho(1)-O(5)	74.01(10)
O(2)#1-Ho(1)-O(5)	82.64(9)	O(4)#1-Ho(1)-O(5)	144.99(9)
O(6)-Ho(1)-O(5)	53.84(9)	O(1)-Ho(1)-N(1)	142.35(10)
O(3)-Ho(1)-N(1)	139.13(10)	O(2)#1-Ho(1)-N(1)	77.74(10)
O(4)#1-Ho(1)-N(1)	78.71(10)	O(6)-Ho(1)-N(1)	93.20(11)
O(5)-Ho(1)-N(1)	69.37(10)	O(1)-Ho(1)-N(2)	80.69(10)
O(3)-Ho(1)-N(2)	145.70(11)	O(2)#1-Ho(1)-N(2)	134.02(10)
O(4)#1-Ho(1)-N(2)	72.47(10)	O(6)-Ho(1)-N(2)	73.23(11)
O(5)-Ho(1)-N(2)	104.19(10)	N(1)-Ho(1)-N(2)	63.47(11)

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

completely decomposed into  $Ho_2O_3$  (calcd 75.95%). The DTA-TG diagram of the complex (2) shows that the complex begins to decompose at 222 °C and ends at 484.0 °C. The first, a mass loss of 21.91% corresponds to the loss of 2,2'-bpy molecule (calcd 21.14%). This is understandable because the Ho–N(2,2'-bpy) bond length is

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

Ho(1)–O(3)	2.251(4)	Ho(1)-O(2)#1	2.258(4)
Ho(1)-O(1)	2.321(4)	Ho(1)-O(4)#2	2.340(4)
Ho(1)–O(7)	2.363(4)	Ho(1)-O(8)	2.395(4)
Ho(1)–O(6)	2.452(4)	Ho(1)-O(5)	2.468(4)
O(3)-Ho(1)-O(2)#1	157.81(15)	O(3)-Ho(1)-O(1)	88.64(15)
O(2)#1-Ho(1)-O(1)	96.22(15)	O(3)-Ho(1)-O(4)#2	99.95(15)
O(2)#1-Ho(1)-O(4)#2	88.33(15)	O(1)-Ho(1)-O(4)#2	145.31(14)
O(3)-Ho(1)-O(7)	83.74(14)	O(2)#1-Ho(1)-O(7)	77.09(14)
O(1)-Ho(1)-O(7)	72.92(14)	O(4)#2-Ho(1)-O(7)	141.08(15)
O(3)-Ho(1)-O(8)	79.50(16)	O(2)#1-Ho(1)-O(8)	83.37(15)
O(1)-Ho(1)-O(8)	141.63(14)	O(4)#2-Ho(1)-O(8)	73.02(15)
O(7)-Ho(1)-O(8)	69.61(14)	O(3)-Ho(1)-O(6)	128.71(15)
O(2)#1-Ho(1)-O(6)	73.35(15)	O(1)-Ho(1)-O(6)	75.21(15)
O(4)#2-Ho(1)-O(6)	73.26(14)	O(7)-Ho(1)-O(6)	133.26(13)
O(8)-Ho(1)-O(6)	139.20(16)	O(3)-Ho(1)-O(5)	76.02(15)
O(2)#1-Ho(1)-O(5)	126.17(14)	O(1)-Ho(1)-O(5)	76.92(14)
O(4)#2-Ho(1)-O(5)	72.80(15)	O(7)-Ho(1)-O(5)	143.86(16)
O(8) - Ho(1) - O(5)	133.23(14)	O(6) - Ho(1) - O(5)	53.11(14)

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

the longest, and easy to be broken down. The mass of the final product, 27.71%, indicates the remaining Ho<sub>2</sub>O<sub>3</sub> (calcd 25.59%). Thermal decomposition of the complex (3) occurs at 80.0–454.0 °C. The first weight loss of 26.06% in the temperature ranged from 80.0 to 225.0 °C corresponds to

the 4,4'-bpy+2H<sub>2</sub>O, calcd 24.80%. This decomposition process can be explained by the bond length comparisons obtained from the structural analysis. The 4,4'-bpy uncoordinated to metal exists in crystal only by hydrogen bond, and the Ho–O (water) bond length is the longer than



Fig. 1. Molecular structures of the complex (1). (a) [Ho(2-FBA)<sub>3</sub>·phen·CH<sub>3</sub>CH<sub>2</sub>OH]<sub>2</sub>, (b) [Ho(2-FBA)<sub>3</sub>·phen]<sub>2</sub>.

average distance Ho–O (carboxyl), which indicate 4,4'-bpy and  $H_2O$  easy to be removed. A total mass loss is 73.83%, which indicates the complex is completely changed into Ho<sub>2</sub>O<sub>3</sub> (calcd 75.60%).

## 3.3. Structural description of complex (1)

The crystal structure of the complex (1) is shown in Fig. 1. Interestingly, the two kinds of binuclear molecules,  $[Ho(2-FBA)_3 \cdot phen \cdot CH_3CH_2OH]_2$  and  $[Ho(2-FBA)_3 \cdot Phen \cdot CH_3CH_2OH]_2$ phen]<sub>2</sub>, exist in an asymmetric unit. Both binuclear molecules are centrosymmetric, but their molecular formula and structures are different. The complex (1) has two molecules with different composition, unlike previously reported complex Dy<sub>2</sub>(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COO)phen<sub>2</sub> [3], in which two different kinds of molecules exist owing to different coordination mode of carboxyl groups. The complex containing different molecules is very rare.

In binuclear molecule [Ho(2-FBA)<sub>3</sub>·phen·CH<sub>3</sub>CH<sub>2</sub> OH]<sub>2</sub>, Ho1<sup>3+</sup> ion is coordinated to eight atoms, five O atoms from five 2-FBA groups, two N atoms from the phen molecule and one O atom from ethanol molecule (Fig. 1a). A coordinated polyhedron around Ho1<sup>3+</sup> ion is a distorted square-antiprism; atoms O1, O3, O2A, O4A and O5, O7, N1, N2, O4A form upper and lower square planes, respectively, with a dihedral angle between them of  $2.7^{\circ}$ (Fig. 2a). 2-FBA groups linked to  $Ho1^{3+}$  ion are in monodentate and bridging coordination modes. O5-C15-O6 group is in a monodentate mode, in which an oxygen atom (O5) coordinates Ho<sup>3+</sup> ion. O1-C1-O2 group is in bidentate bridging mode, in which two oxygen atoms coordinate  $Ho^{3+}$  ion to form a bidentate bridge. The phen ligand coordinates to Ho<sup>3+</sup> ion in chelating mode, in which two N atoms coordinate Ho<sup>3+</sup> ion forming a five-membered ring. The bond distances of Ho1-Ocarboxyl (on average), Ho1-Oethanol and Ho1-N (on average) are 2.323, 2.418 and 2.547 Å, respectively. The distance of  $Ho1^{3+}$ ... $Ho1A^{3+}$  is 4.416 Å. Bond angles of O-Ho1-O range from 72.77(14) to 144.91(14)°, and that of N-Ho1-N is 64.14(16)°. The hydrogen bond exists between the ethanol and uncoordinated carboxyl oxygen atom, O7-H7...O6, in which the O7-H7 distance is 0.930 Å, H7...O6, 1.807 Å and  $\angle 07H706 = 137.14^{\circ}$ .

In  $[Ho(2-FBA)_3 \cdot phen]_2$ ,  $Ho2^{3+}$  ion is coordinated to nine atoms, seven oxygen atoms from five 2-FBA groups and two N atoms from the phen molecule (Fig. 1b). A distorted monocapped square-antiprism is found. Atoms O8, O11, O9A, O10A and O12, O13, N3, N4 form upper and lower square planes, respectively, with a dihedral angle between them of 7.3°. O10 atom occupies the cap position (Fig. 2b). 2-FBA ligands coordinate the  $Ho2^{3+}$  ion in three different coordination modes. Carboxyl group O12-C50-O13 adopts bidentate chelating mode, in which two oxygen atoms coordinate the same Ho<sup>3+</sup> ion. The O8-C36-O9 group acts in a bidentate bridging fashion, in which two oxygen atoms coordinate two different holmium ions to form

011 010A 013

Fig. 2. The coordination polyhedron of the  $Ho^{3+}$  ion in the complex (1), (a) and (b) show two different coordination environments.

a bidentate bridge. O10-C43-O11 group is in bridgingchelating mode, in which two O atoms chelate one holmium ion and one of them also simultaneously links another holmium ion to form a tridentate bridge. This kind of crystal structure is common in lanthanide carboxylate complexes. Obviously, the two molecules of the complex (1) are different in composition, coordination mode of carboxylate groups, and coordination number of central ion. The average distance of Ho2–O(carboxyl) is 2.421 Å and that of Ho2… Ho2A is 3.990 Å. The phen ligand chelates  $Ho2^{3+}$  ion with Ho2-N bond lengths of 2.530(6) and 2.631(5) Å, respectively. The bond angles of O-Ho2-O range from 49.44(14) to 155.12(17)°, and that of N-Ho2-N is 63.1°.

The relationships of d(Ho2-O(carboxyl)) > d(Ho1-O(carboxyl)) and  $d(Ho2\cdots Ho2A) < d(Ho1\cdots Ho1A)$  in the two molecules of complex (1) were observed. This is due to carboxyl groups adopt different coordination modes linking





Fig. 3. Molecular structure of the complex (2).

two  $\text{Ho}^{3+}$  ions in the two molecules. The fact that  $\text{Ln}^{3+}$  ions are bridged by chelating-bridging carboxylate groups results in a larger Ln–O distance and a smaller Ln–Ln distance.

### 3.4. Structural description of complex (2)

The crystal structure of the complex (2) is shown in Fig. 3. The complex is dimeric one with an inversion center. The two Ho<sup>3+</sup> ions are linked together by four 2-FBA ligands in bridging coordination mode. Each Ho<sup>3+</sup> ion is eight-coordinated by six oxygen atoms of 2-FBA ligands and two nitrogen atoms of a 2,2'-bpy molecule. The coordination sphere of  $Ho^{3+}$  ion is in a square antiprism with atoms O5, O6, N1, N2 and O1, O3, O2A, O4A as the two square planes, respectively, with a dihedral angle of  $0.5^{\circ}$  between them. Carboxyl groups act as bidentate chelating and bidentate bridging coordination modes. The 2,2'-bpy ligand chelates  $Ho^{3+}$  ion with two N atoms forming a five-membered ring. The two pyridyl rings are not coplanar with the dihedral angle of  $6.6^{\circ}$  in the dimmer. The crystal structure of complex (2) is similar to that of previously reported samarium (III) complex [4]. The average distances of Ho-O (carboxyl), Ho-N, and Ho…Ho are 2.341, 2.551, and 4.133 Å, respectively. These distances are shorter than the corresponding distances in samarium (III) complex [4] because the ionic radius of  $\text{Sm}^{3+}$  ion is longer than that of Ho<sup>3+</sup> ion. The bond angles O-Ho-O vary considerably in the range of  $53.84(9)-144.99(9)^{\circ}$ . The angle of N–Ho–N is 63.47(11)°. This is a common structure of lanthanide carboxylate complexes containing phen or 2,2'-bpy.

## 3.5. Structural description of complex (3)

A fragment of the structure of the complex {[Ho(2- $FBA_{3} \cdot 2H_{2}O] \cdot (4,4'-bpy)_{n}$  (3) is shown in Fig. 4a, where it can be seen that each  $Ho^{3+}$  ion is bonded to eight atoms, two oxygen atoms from the chelating carboxylate group, two oxygen atoms from two water molecules, and four oxygen atoms from bidentate bridging carboxyl groups. The crystal structure  $[Ho(2-FBA)_3 \cdot 2H_2O] \cdot (4,4'-bpy)$  is built as coordination polymer that is typical for many lanthanide carboxylate complexes such as  $\{[Eu(m-MOBA)_3 \cdot 2H_2O] \cdot 1/$ 2(4,4'-bpy)<sub>n</sub> (*m*-MOBA: *m*-methoxybenzoate) [7], {[Eu(*p*-MOBA)<sub>3</sub>·2H<sub>2</sub>O]1/2 H<sub>2</sub>O·1/2 (4,4'-bpy) $_n$  (*p*-MOBA: *p*-methoxybenzoate) [8], and  $\{Eu(\alpha-FURA)_3 \cdot 2H_2\}$ O}]NO<sub>3</sub>(4,4'-Hbpy)}<sub>n</sub> ( $\alpha$ -FURA:  $\alpha$ -furoate) [9]. These complexes are an infinite polymeric structure by bridging carboxyl groups, 4,4'-bpy molecule is uncoordinated in the polymer. Two neighbouring Ho<sup>3+</sup> ions are linked bidentate bridging carboxyl groups to form a zigzag chain (Fig. 4a). Ho<sup>3+</sup> ions are coplanar and the angle Ho1A–Ho1–Ho1B is 159.7°. The distances between two neighbouring  $Ho^{3+}$  ions are 4.991 and 4.927 Å, respectively. Viewed along *a*-axis the  $\pi$ - $\pi$  stacking interactions of aromatic rings and pyridine ring are observed in the 1D chain (Fig. 4b). The complex (3) is different from coordination polymer [La(2-FC<sub>6</sub>H<sub>4-</sub>  $COO_3 \cdot (4,4'-bpy) \cdot H_2O_n$ , in which 4,4'-bpy coordinate La<sup>3+</sup> ion in monodentate coordination mode, carboxyl groups adopt bidentate bridging and chelating-bridging coordination modes [10]. Coordination number of  $La^{3+}$  ion, nine, is larger than that of  $Ho^{3+}$  ion in complex (3) because the radius of  $La^{3+}$  ion is larger than that of  $Ho^{3+}$  ion as a consequence of lanthanide contraction. The complex (3) is also different from the eight-coordinated binuclear complex



Fig. 4. Polymeric structure of the complex (3). (a) A fragment of structure of the complex, (b) 1D chain viewed along the *a*-axis, and (c) 3D-network by  $\pi$ - $\pi$  stacking interaction and hydrogen bonding interaction viewed along the *a*-axis.

(2). In complex (2) 2,2'-bpy molecule chelates the Ho<sup>3+</sup> ion since 2,2'-bpy is likely to form a chelated ring, however 4,4'-bpy molecule is not involved in coordination for complex (3). The Ho–O (carboxyl) bond lengths vary from 2.251(4) to 2.468(4) Å with an average distance of 2.348 Å, which is in agreement with that in complex (1) due to the same coordination modes of carboxyl groups in

the two complexes. There are two nitrogen atoms of uncoordinated 4,4'-bpy molecule at a distances of 4.541 and 6.418 Å to the Ho<sup>3+</sup> ion, respectively, and the dihedral angle between the two pyridyl rings is 7.7 Å. The neighbouring 1D chains are interlinked through 4,4'-bpy molecules by hydrogen bonds (Fig. 4c). The uncoordinated 4,4'-bpy molecules form hydrogen bonds with coordinated

water, O7–H7B···N1 [X, Y–1, Z], with  $d(O7 \cdots N1) = 2.662 \text{ Å}$  and  $\angle O7H7BN1 = 124.83^{\circ}$ , and O8–H8B···N1 [X, -Y+1/2, Z-1/2], with  $d(O8 \cdots N2) = 2.740 \text{ Å}$  and  $\angle O8H8BN2 = 135.28^{\circ}$ . The  $\pi-\pi$  stacking interactions can be found, as shown in Fig. 4c. As a result, 3D supramolecular structure is formed by the hydrogen bonds and  $\pi-\pi$  stacking interactions (Fig. 4c). Furthermore, these intermolecular interactions increase the stability of the crystal packing.

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