研究简报

新颖的镧-2-氟苯甲酸及 2,2′-联吡啶配合物的合成与晶体结构

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关键词: 镧配合物; 2-氟苯甲酸; 2,2′-联吡啶; 晶体结构
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Synthesis, Crystal Structure and Properties of a Novel Lanthanum 2-fluorobenzoate Complex Containing 2,2′-bipyridine

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Abstract: 2-fluorobenzoic acid (2-HFBA) and 2,2′-bipyridine (2,2′-bpy) was used as ligands to react with lanthanum to obtain a complex, $[La(2\text{-}FBA)_3\cdot(2,2'\text{-}bpy)]_2$. The structure of the complex contains three independent molecules. In two of them, the two central metal ions are connected together through four 2-FBA groups by bidentate bridging and chelating-bridging two modes. In another, the two central metal ions are connected together through four bidentate bridging 2-FBA groups. CCDC: 237658.

Key words: lanthanum complex; 2-fluorobenzoate; 2,2′-bipyridine; crystal structure

0 Introduction

To our knowledge, carboxylate coordinates metal in various ways, for example, in the mode of monodentate, bidentate chelating, bidentate bridging or chelating-bridging. Lanthanide carboxylate complexes display a variety of structural types. Usually, lanthanide complexes with only monoacid ligand were obtained in the form of coordination polymer[1~4]. However, lanthanide complexes with mixed-ligands including monoacid and aromatic diimines such as 1,10-phenanthroline (phen) or 2,2′-bipyridine (2,2′-bpy) form the dimeric unit, this kind of complexes have interesting structures and high stability[5~10]. Many lanthanide complexes with benzoic acid or its derivatives containing phen or 2,2′-bipy have been reported[6~10]. Different substituents or different positions of the substituents on the benzene ring result in various structures of the lanthanide complexes. A number of these complexes have been found to be dimeric with coordination number of eight or nine, in which only one kind of configuration structure exists. However, it is very few that one complex contains several different structures, for example, complex $Dy_2(C_8H_7O_2)_6(C_{12}H_8N_2)_2$ ($C_8H_7O_2$ is 4-methylbenzoato, $C_{12}H_8N_2$ is 1,10-phenanthroline) contains two different structures[10]. We have synthesized a new lanthanum 2-fluorobenzoate complex with 2,2′-bpy. Interestingly, it has three independent mole-

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cules. In the present paper, a lanthanide complex with novel structure is reported.

1 Experimental

1.1 Materials and methods

$LaCl_3 \cdot 6H_2O$ was prepared by dissolving its oxides in hydrochloric acid, and then drying up 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 ℃·min^{-1} in air. The UV-Vis spectra of the complex in DMF solution at 1.0×10^{-4} mol·L^{-1} was measured on a UV-260 spectrophotometer.

1.2 Synthesis of the complex

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 mol·L^{-1} NaOH solution. Then the ethanolic solution of 2,2′-bipyridine (0.5 mmol) and that of $LaCl_3$ (0.5 mmol) were dropped, successively. The mixture was heated under reflux with stirring for 2 h. Single crystals the complex was obtained from the mother liquor after two weeks at room temperature. Anal. Calc. (%): C, 52.14; N, 4.22: H, 2.97. Found (%): C, 52.27; N, 3.93: H, 2.83.

1.3 Crystal structure determination

X-ray diffraction data were collected with a crystal of approximate dimensions 0.26 mm × 0.24 mm × 0.24 mm for the complex by using a Bruker Smart 1000 CCD diffractometer with monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer by using SHELXS-97 and SHELXS-97 programs [11,12]. The structure was solved by direct methods and refinement on $|F|^2$ with the full-matrix least-squares methods. Most positions of F atoms were disorder and the occupy factors for F_1/F_1', F_2/F_2', F_3/F_3', F_4/F_4', F_5/F_5', F_6/F_6', F_7/F_7', F_8/F_8', and F_9/F_9' were 0.887/0.113, 0.590/0.410, 0.808/0.192, 0.749/0.251, 0.572/0.428, 0.804/0.196, 0.846/0.154, 0.707/0.293 and 0.834/0.166, respectively. A summary of the crystallographic data and det-ails of the structure refinements are listed in Table 1 and the selected bond distances and angles in Table 2.

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Table 1 Summary of crystalllographic data and structure refinement

Empirical formula	$C_{124}H_{80}F_{12}La_4N_8O_{24}$	Calculated density / (Mg·m^{-3})	1.677
Formula weight	2849.60	Absorption coefficient / mm^{-1}	1.581
Crystal system	Triclinic	F(000)	2816
Space group	$P\bar{1}$	Crystal size / mm	0.26 × 0.24 × 0.24
a / nm	1.144 0(5)	θ range for data collection / (°)	0.91 to 26.48
b / nm	2.199 1(8)	Limiting indices	$-14 \leqslant h \leqslant 12$, $-22 \leqslant k \leqslant 27$, $-28 \leqslant l \leqslant 28$
c / nm	2.248 8(9)	Reflections collected / unique	32 833 / 22 893 (R_{int}=0.038 1)
α / (°)	93.456(9)	Completeness to θ=26.48	97.9%
β / (°)	90.968(8)	Data / restraints / parameters	22 893 / 276 / 1 649
γ / (°)	91.511(9)	Goodness-of-fit on $|F|^2$	1.018
Volume / nm^3	5.645(4)	Final R indices [$I>2\sigma(I)$]	R_1=0.053 1, wR_2=0.088 9; R_1=0.108 8, wR_2=0.104 6
Z	2	Largest diff. peak and hole / (e·nm^{-3})	1 452 and −768

Table 2 Selected bond lengths (nm) and angles (°)

La(1)-O(1)	0.258 4(4)	La(1)-O(2)	0.255 3(4)	La(1)-O(3)	0.263 6(4)
La(1)-O(4)	0.265 9(4)	La(1)-O(5)	0.250 8(4)	La(1)-O(7)	0.247 7(4)
La(1)-O(9)	0.246 8(3)	La(1)-N(1)	0.266 2(5)	La(1)-N(2)	0.267 9(5)
La(2)-O(4)	0.247 6(3)	La(2)-O(6)	0.247 2(4)	La(2)-O(8)	0.248 5(4)
La(2)-O(9)	0.267 7(4)	La(2)-O(10)	0.262 3(4)	La(2)-O(11)	0.252 9(4)
La(2)-O(12)	0.255 3(4)	La(2)-N(3)	0.268 1(5)	La(2)-N(4)	0.268 1(5)

Continued Table 2

La(3)-O(13)	0.254 9(4)	La(3)-O(14)	0.259 3(4)	La(3)-O(15)	0.255 7(4)
La(3)-O(16)	0.287 3(4)	La(3)-O(16)#1	0.242 5(4)	La(3)-O(17)	0.249 8(4)
La(3)-O(18)#1	0.245 4(4)	La(3)-N(5)	0.272 1(5)	La(3)-N(6)	0.271 2(5)
La(4)-O(19)	0.258 4(4)	La(4)-O(20)	0.256 0(4)	La(4)-O(21)#2	0.245 2(4)
La(4)-O(22)	0.251 1(4)	La(4)-O(23)	0.247 1(4)	La(4)-O(24)#2	0.244 4(4)
La(4)-N(7)	0.268 8(5)	La(4)-N(8)	0.2.97(5)		

O(1)-La(1)-O(3)	145.11(14)	O(1)-La(1)-O(4)	161.11(13)	O(2)-La(1)-O(1)	50.65(15)
O(2)-La(1)-O(3)	142.13(14)	O(2)-La(1)-O(4)	130.74(15)	O(3)-La(1)-O(4)	48.99(11)
O(5)-La(1)-O(1)	91.75(15)	O(5)-La(1)-O(2)	128.95(14)	O(5)-La(1)-O(3)	88.83(14)
O(5)-La(1)-O(4)	73.89(13)	O(7)-La(1)-O(1)	120.89(15)	O(7)-La(1)-O(2)	70.49(15)
O(7)-La(1)-O(3)	80.34(14)	O(7)-La(1)-O(4)	66.61(13)	O(7)-La(1)-O(5)	135.68(13)
O(9)-La(1)-O(1)	89.11(14)	O(9)-La(1)-O(2)	74.14(14)	O(9)-La(1)-O(3)	123.91(12)
O(9)-La(1)-O(4)	74.95(12)	O(9)-La(1)-O(5)	71.99(13)	O(9)-La(1)-O(7)	78.93(13)
O(1)-La(1)-N(1)	81.37(15)	O(2)-La(1)-N(1)	75.39(15)	O(3)-La(1)-N(1)	75.80(14)
O(4)-La(1)-N(1)	117.52(13)	O(5)-La(1)-N(1)	139.44(14)	O(7)-La(1)-N(1)	79.08(14)
O(9)-La(1)-N(1)	146.93(14)	O(1)-La(1)-N(2)	74.26(15)	O(2)-La(1)-N(2)	113.34(16)
O(3)-La(1)-N(2)	71.60(14)	O(4)-La(1)-N(2)	113.79(13)	O(5)-La(1)-N(2)	79.16(14)
O(7)-La(1)-N(2)	134.89(14)	O(9)-La(1)-N(2)	146.17(14)	N(1)-La(1)-N(2)	60.45(15)
O(6)-La(2)-O(4)	75.16(13)	O(6)-La(2)-O(8)	134.98(14)	O(4)-La(2)-O(8)	73.74(13)
O(6)-La(2)-O(11)	75.78(15)	O(4)-La(2)-O(11)	76.41(13)	O(8)-La(2)-O(11)	125.92(14)
O(6)-La(2)-O(12)	126.83(15)	O(4)-La(2)-O(12)	94.98(14)	O(8)-La(2)-O(12)	87.71(15)
O(11)-La(2)-O(12)	51.32(14)	O(6)-La(2)-O(10)	81.81(14)	O(4)-La(2)-O(10)	123.06(13)
O(8)-La(2)-O(10)	88.70(15)	O(11)-La(2)-O(10)	145.16(15)	O(12)-La(2)-O(10)	138.89(14)
O(6)-La(2)-O(9)	66.92(13)	O(4)-La(2)-O(9)	74.49(11)	O(8)-La(2)-O(9)	73.89(13)
O(11)-La(2)-O(9)	137.22(14)	O(12)-La(2)-O(9)	160.67(14)	O(10)-La(2)-O(9)	48.57(12)
O(6)-La(2)-N(4)	78.78(15)	O(4)-La(2)-N(4)	144.88(14)	O(8)-La(2)-N(4)	140.55(15)
O(11)-La(2)-N(4)	74.65(15)	O(12)-La(2)-N(4)	82.15(16)	O(10)-La(2)-N(4)	75.07(14)
O(9)-La(2)-N(4)	115.85(13)	O(6)-La(2)-N(3)	134.14(15)	O(4)-La(2)-N(3)	150.67(15)
O(8)-La(2)-N(3)	80.85(15)	O(11)-La(2)-N(3)	108.35(15)	O(12)-La(2)-N(3)	69.24(15)
O(10)-La(2)-N(3)	69.75(15)	O(9)-La(2)-N(3)	112.44(13)	N(4)-La(2)-N(3)	59.88(17)
O(16)#1-La(3)-O(18)#1	75.59(14)	O(16)#1-La(3)-O(17)	73.04(14)	O(18)#1-La(3)-O(17)	131.35(13)
O(16)#1-La(3)-O(13)	149.87(14)	O(18)#1-La(3)-O(13)	127.78(14)	O(17)-La(3)-O(13)	96.35(14)
O(16)#1-La(3)-O(15)	120.94(14)	O(18)#1-La(3)-O(15)	86.20(16)	O(17)-La(3)-O(15)	79.29(16)
O(13)-La(3)-O(15)	83.03(14)	O(16)#1-La(3)-O(14)	145.62(14)	O(18)#1-La(3)-O(14)	77.27(14)
O(17)-La(3)-O(14)	141.33(13)	O(13)-La(3)-O(14)	50.51(13)	O(15)-La(3)-O(14)	77.49(15)
O(16)#1-La(3)-N(6)	80.31(15)	O(18)#1-La(3)-N(6)	78.24(15)	O(17)-La(3)-N(6)	130.20(15)
O(13)-La(3)-N(6)	86.18(15)	O(15)-La(3)-N(6)	149.67(16)	O(14)-La(3)-N(6)	73.79(15)
O(16)#1-La(3)-N(5)	80.17(14)	O(18)#1-La(3)-N(5)	134.38(15)	O(17)-La(3)-N(5)	74.49(14)
O(13)-La(3)-N(5)	69.77(14)	O(15)-La(3)-N(5)	139.31(16)	O(14)-La(3)-N(5)	104.95(14)
N(6)-La(3)-N(5)	59.82(16)	O(16)#1-La(3)-O(16)	74.24(14)	O(18)#1-La(3)-O(16)	68.23(13)
O(17)-La(3)-O(16)	68.03(13)	O(13)-La(3)-O(16)	128.79(13)	O(15)-La(3)-O(16)	46.99(12)
O(14)-La(3)-O(16)	114.15(13)	N(6)-La(3)-O(16)	141.81(13)	N(5)-La(3)-O(16)	139.25(14)
O(24)#2-La(4)-O(21)#2	73.68(15)	O(24)#2-La(4)-O(23)	130.67(14)	O(21)#2-La(4)-O(23)	77.42(15)
O(24)#2-La(4)-O(22)	86.43(16)	O(21)#2-La(4)-O(22)	125.28(15)	O(23)-La(4)-O(22)	78.72(15)
O(24)#2-La(4)-O(20)	135.42(16)	O(21)#2-La(4)-O(20)	87.20(16)	O(23)-La(4)-O(20)	80.81(15)

Continued Table 2

O(22)-La(4)-O(20)	135.66(16)	O(24)#2-La(4)-O(19)	87.57(15)	O(21)#2-La(4)-O(19)	84.61(15)
O(23)-La(4)-O(19)	128.47(14)	O(22)-La(4)-O(19)	145.99(15)	O(20)-La(4)-O(19)	50.12(14)
O(24)#2-La(4)-N(7)	78.22(15)	O(21)#1-La(4)-N(7)	144.23(16)	O(23)-La(4)-N(7)	138.35(15)
O(22)-La(4)-N(7)	73.61(15)	O(20)-La(4)-N(7)	97.87(16)	O(19)-La(4)-N(7)	72.39(15)
O(24)#2-La(4)-N(8)	135.04(16)	O(21)#2-La(4)-N(8)	151.20(16)	O(23)-La(4)-N(8)	81.62(16)
O(22)-La(4)-N(8)	68.38(15)	O(20)-La(4)-N(8)	70.01(16)	O(19)-La(4)-N(8)	93.33(16)
N(7)-La(4)-N(8)	59.56(17)				

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

2 Results and discussion

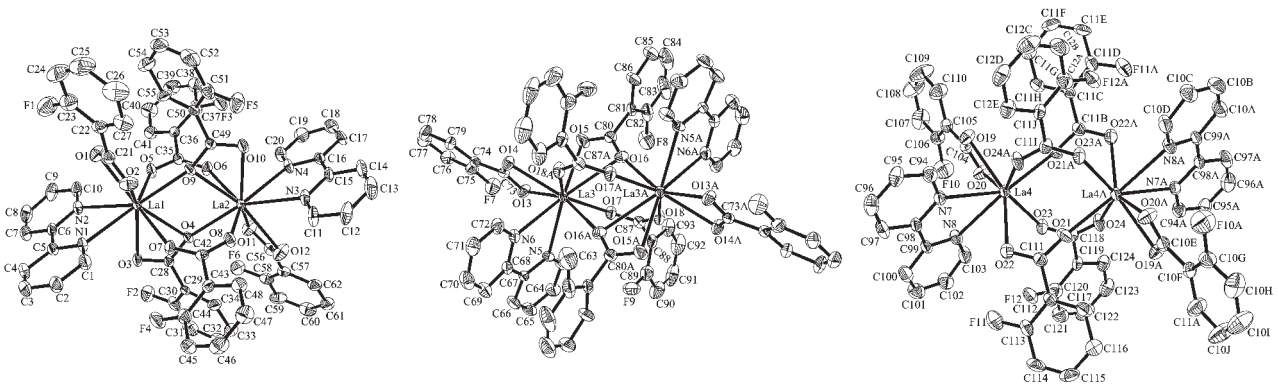
2.1 IR spectra and UV-Vis spectra

The IR spectra of the complex was determined in the range of 4 000~400 cm^{-1} as KBr pellets. The asymmetric and symmetric stretching vibration bands of 2-FBA group appear at 1 612, 1 462, and 1 402 cm^{-1}, respectively. The split of the vibration bands of 2-FBA ligand indicates that the COO^- groups are bound to the metal in different coordination modes. The ring breathing vibration bands of 2,2′-bpy at 1 011 cm^{-1}, and out- of -plane bending vibration bands at 821, 797 cm^{-1}. The weak band at 458 cm^{-1} may be assigned to the vibrations of La-O bond.

The UV absorption spectra for the complex was obtained. The broad absorption band at 266 nm corresponding to the transition of the π-π^* of the 2,2′-bpy and 2-FBA groups were observed.

2.2 Structural description of the complex

The molecular structure of the complex is shown in Fig.1 (a, b and c). There are three different molecules in the asymmetric unit, in which each molecule is a dimer with an inversion center. Fig.1a and Fig.1b show that the two central metal ions are connected together through four 2-FBA groups, in which two of them are in the bidentate bridging mode, and the other two are in the chelating-bridging mode, and each lanthanum ion is further bonded to two oxygen atoms of the chelating one 2-FBA group and two nitrogen of one 2,2′-bpy molecule, making a coordination number of nine. The coordination sphere of the lanthanum ion is distorted monocapped square antiprism. The 2-FBA ligands act as the chelating, bidentate bridging and chelating-bridging modes. In the two molecules, the environments of $La1^{3+}$ in Fig.1a and $La3^{3+}$ in Fig.1b ion are quite similar but with slight difference. For example, the distances between two central lanthanum ions are 0.408 64(11) nm for La1…La2 and 0.423 32 nm for La3…La3A in Fig.1a and Fig.1b, respectively. The average lengths of lanthanum-carboxyl oxygen are 0.255 5 nm for La1-O and 0.256 4 nm for La3-O. The average length of La1-



(a) (b) (c)

(a), (b), and (c) show three different structures, respectively

All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level

Fig.1 Molecular structure of the complex

N and that of La3-N is 0.267 05(5) and 0.271 65 nm, respectively. The bond angles of O-La1-O and that of O-La3-O rang from 48.99 (11)° ~161.11 (13)° and 50.51(13)°~149.87(14)°, respectively. The bond angle of N-La1-N and that of N-La3-N is 60.45 (15)° and 59.88(1)°, respectively.

Fig.1c shows that $La4^{3+}$ ion is eight-coordinated with six oxygen atoms from five 2-FBA ligands and two nitrogen atoms from one 2,2′-bpy molecule. The coordination sphere of the $La4^{3+}$ ion is distorted square antiprism. The 2-FBA ligands act as the chelating and bidentate bridging modes. The two central metal ions are connected together through four bidentate bridging 2-FBA groups. The structure shown in Fig.1c is different from those in Fig.1a and Fig.1b owing to different bonding mode of carboxyl groups, resulting in different distances of La-O (carboxyl) and La…La. For example, the distances of La4-O and La4…La4A are 0.250 4(4) nm and 0.424 6 nm, respectively. The bond angles of O-La4-O rang from 50.12(14)° to 145.99 (15)°. The average bond length of La4-N is 0.269 25(5) nm, and the bond angle of N-La4-N is 59.56(17)°.

The title complex contains three different kinds of molecules, one of them is different from another two owing to different coordination mode of carboxyl groups, this case is similar to the $Dy_2(C_8H_7O_2)_6(C_{12}H_8N_2)_2$ containing two different structures[10]. However, the structure of similarity to the title complex is rare in lanthanide complexes.

2.3 Themogravimetric analysis

The thermal behavior of the complex was studied from 25 to 1 000 ℃. The results indicate that the complex involve two steps of weight losses. The first weight losses is 20.38% (228 ℃, peak). The weight losses ascribe to the removal of coordination 2,2′-bpy molecule (calculated, 21.92%). The degradation process can be explained by structural data. In the complex, the distances of La-N (2,2′-bpy) are longer than those of La-O(carboxyl). These bonds seem to be less stable and easy to be broken down. The second weight losses is 54.19% (474 ℃, peak), corresponds to the removal of 2-FBA ligands. The weight of the residue is 25.43%. Supposing La_2O_3 as final residue, calculated residue weight of the complex is 22.87%, which is in coincidence with experimental values. Results indicate that the complex degraded to oxide, completely.

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