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研究简报

$[La(p\text{-}OHC_6H_4CH_2COO)_3(phen)]_2\cdot 2H_2O$ 的合成和晶体结构

咸春颖* 林 苗 潘文丽
(东华大学生态纺织教育部重点实验室,上海 201620)

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Synthesis and Crystal Structure of Complex $[La(p\text{-}OHC_6H_4CH_2COO)_3(phen)]_2\cdot 2H_2O$

XIAN Chun-Ying* LIN Miao PAN Wen-Li
(*Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education, Donghua University, Shanghai* 201620)

Abstract: A complex of lanthanides formulated as $[La(p\text{-}OHC_6H_4CH_2COO)_3(phen)]_2$ was prepared from the water/ethanol solution under normal temperturate with 8-hydroxyquinoline as the acidity conditionor, the complex was characterized by elemental analysis, IR, ^{1}H NMR spectroscopy and X-ray crystal structure analysis. The crystal belongs to monoclinic crystal system, space group $P2_1/n$. The 1,10-phenanthroline and 4-hydroxyphenylacetic ligands coordinated to the center ion through O or N atoms. The structural feature of the complex were discussed. CCDC: 25305.

Key words: complex; synthesis; crytal structure

0 Introduction

Lanthanid elements has received special attention for their great applied value in such fields as electricity, magnetism, biology and iatrology process[1~3], a great deal of efforts has been put forth recently in the rational design and synthesis of mixed Lanthanide complexes, with particular emphasis given to the crystal structures of the products[4-6].

Because of the high and variety coordination numbers of the center ion as well as the coordination versatility of the carboxylate ligands, carboxylate bridged coordination complexes have been applied extensively in such areas like extraction, separation, antimicrobial peptide, photocatalysts and fluorescent materials[7]. For the complexes containing heterocyclic amines ligands, the higher thermal stability and strong fluorescence properties can be expected because of the electronic coupling function between *f*-elecreonic in center ion and the heterocyclic amines ligands[8].

The desirable application as a kind of medicament intermediate of 4-hydroxyphenylacetic acid has been recongnized for many years[9,10], they are widely used to synthesize many medical products. Only a few examples on the preparation of complexes containing 4-hydroxyphenylacetic group were known, in this paper, we report a simple method to systhesize the complex of $[La(p\text{-}OHC_6H_4CH_2COO)_3(phen)]_2\cdot 2H_2O$, as well as its

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*通讯联系人。E-mail:xiancy@dhu.edu.cn
第一作者:咸春颖,女,37 岁,副教授;研究方向:配位化学和超分子化学。

crystal structure.

1 Experimental

1.1 General methods and chemicals

The purity of lanthanide oxides exceeds 99.9%, 4-hydroxyphenylacetic acid was recrystalled from water, other commercially chemicals were of analytical purity and used as received without further purification.

Elemental analysis was performed on Carlo Erba 1106 elemental analyzer, IR spectra was collected on Nicolet 760 IR spectrometer, ^{1}H NMR was recored in DMSO on a Bruker Avance 400 instrument at 400 MHz, X-ray diffraction data was obtained using Rigaku AFC 7R diffractometer with graphite monochromated Mo $K\alpha$ radiation.

1.2 Synthesis of the complex

0.3 mmol lanthanide nitrate was dissolved in the mixed of 2 mL water and 10 mL absolute ethanol. 0.6 mmol 1,10-phenanthroline, 1.7 mmol 8-hydroxyquinoline were dissolved in another 10 mL absolute ethanol, 7.9 mol·L^{-1} 4-hydroxyphenylacetic acid was added to the latter one. The two solutions were mixed, placed at room temperature for about two days. The complexes were collected by filtration, washed with rthanol, and dried in air. Anal. Calc. For $C_{72}H_{58}La_2N_4O_{18}$(%): C, 55.97; H,3.78; N, 3.63. Found(%): C, 56.12; H,3.76; N, 3.48. Main FTIR (KBr, cm^{-1}): $\nu_{as(COOH)}$ 1 705, $\nu_{as(COO^-)}$ 1 587, $\nu_{s(COO^-)}$ 1 392; $\nu_{C\text{-}OH}$ 1 049, $\delta_{\text{-}OH}$ 1 276; $\nu_{\text{-}N=C}$ 1 545, $\delta_{C\text{-}H}$ 854[1], 725. ^{1}H NMR (500 MHz, DMSO-6d, ppm): δ_H 3.18(s, 6H, -CH_2); δ_H 6.63 (d, 6H, -C_6H_4); δ_H 6.96(d, 6H, -C_6H_4); δ_H 7.78 (q, 2H, $C_{12}H_8N_2$); δ_H 8.11 (s, 2H, $C_{12}H_8N_2$); δ_H 8.52 (d, 2H, $C_{12}H_8N_2$); δ_H 9.11 (d, 2H, $C_{12}H_8N_2$).

1.3 Crystal structure determination

A colorless prismatic crystal of [La(p-$OHC_6H_4CH_2COO)_3$(phen)]$_2$·$2H_2O$ having approximate dimensions of 0.478 mm×0.345 mm×0.169 mm was selected for the structural analysis. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The data were collected at a temperature of 20±1 ℃ using the ω-2θ scan technique (1.87°~27.0°). Over the course of data collection, a linear correction factor was applied to the data to account for this phenomenon. An empirical absorption, Lp and correction for secondary extinction were applied. The structure was solved by heave-atom Patterson methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atom were included but not refined. The final cycle of full-matrix least-squares refinement was based on the observed unique reflections. A summary of crystal data, data collection and refinement is given in Table 1.

CCDC: 25305.

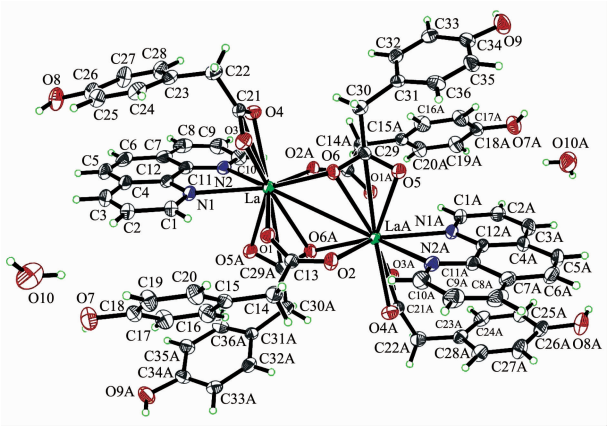
Table 1　Crystal data and structure refinement for complex of [La(p-$OHC_6H_4CH_2COO)_3$(phen)]$_2$·$2H_2O$

Formula	$C_{72}H_{62}La_2N_4O_{20}$	Z	2
Formula weight	1 581.08	D_c / (g·cm^{-3})	1.612
Crystal size / mm	0.478×0.345×0.169	μ(Mo $K\alpha$) / cm^{-1}	13.75
Crystal system	Monoclinic	F(000)	1 592
Space group	$P2_1/n$	Reflections collected	18832
a / nm	1.347 95(9)	Unique reflections (R_{int})	7 066 (0.103 0)
b / nm	1.415 24(9)	Reflections [$I>2\sigma(I)$]	5 349
c / nm	1.734 17(11)	R_1, wR_2 [$I>2\sigma(I)$]	0.040 2, 0.088 1
β / (°)	100.101(1)	S	0.925
V / nm^3	3.257 0(4)	$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	1 176, −797

2 Results and discussion

The crystal structure and the packing in a cell [La(p-$OHC_6H_4CH_2COO)_3$(phen)]$_2$·$2H_2O$ were shown in Fig.1 and Fig.2, selected bond lengths and bond angles of non-hydrogen atoms are listed in Table 2.

The complex is dinuclear and each La(Ⅲ) ion is nine-coordinate, the coordination sphere around each La(Ⅲ) ion consists of seven O atoms from five 4-hydroxy phenylacetic ligands and two N atoms from one 1,10-



Symmetry code A: $-x$, $-y+2$, $-z$

Fig.1 Perspective view of the structure of the complex

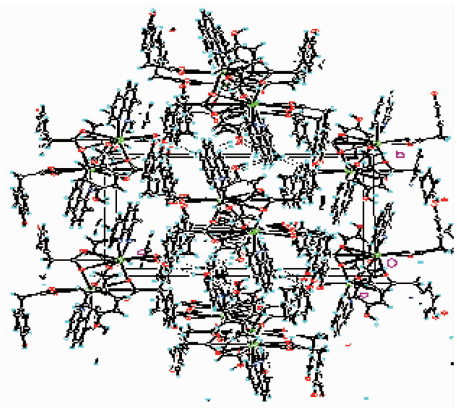


Fig.2 Packing view of the complex

Table 2 Selected bond length (nm) and bond angle (°)

La-O(1)	0.244 3(2)	La-N(1)	0.266 8(3)	O(2)-C(13)	0.126 7(4)
La-O(2)A	0.243 5(2)	La-N(2)	0.269 7(3)	O(3)-C(21)	0.126 0(4)
La-O(3)	0.263 9(3)	La-LaA	0.400 12(4)	O(4)-C(21)	0.126 5(4)
La-O(4)	0.258 6(2)	N(2)-C(10)	0.132 9(5)	O(5)-C(29)	0.125 2(4)
La-O(5)A	0.260 4(3)	N(2)-C(11)	0.135 3(5)	O(6)-C(29)	0.125 1(4)
La-O(6)	0.248 3(3)	N(1)-C(1)	0.132 9(4)		
La-O(6)A	0.269 0(2)	O(1)-C(13)	0.125 2(4)		

O(2)A-La-O(6)A	74.09(8)	O(6)-La-O(3)	77.14(8)	O(3)-La-N(2)	61.15(10)
O(4)-La-O(3)	49.25(8)	O(6)-La-LaA	41.25(5)	N(1)-La-N(2)	112.45(8)
O(5)A-La-O(3)	139.29(9)	O(4)-La-LaA	125.69(7)	O(2)A-La-C(21)	107.37(10)
O(2)A-La-N(1)	138.09(9)	O(5)A-La-LaA	86.10(6)	O(1)-La-C(21)	99.74(10)
O(1)-La-N(1)	81.75(9)	O(3)-La-LaA	112.55(6)	O(6)-La-C(21)	83.59(9)
O(2)A-La-N(2)	76.94(9)	N(1)-La-LaA	147.03(7)	O(4)-La-C(21)	24.74(9)
O(1)-La-N(2)	138.91(9)	O(6)A-La-LaA	37.49(6)	O(5)A-La-C(21)	147.21(10)
O(6)-La-N(1)	144.36(8)	N(2)-La-LaA	139.36(7)	O(3)-La-C(21)	24.74(9)
O(4)-La-N(1)	82.04(9)	C(21)-La-LaA	124.52(7)	N(1)-La-C(21)	72.21(10)
O(5)A-La-N(1)	75.31(9)	C(29)A-La-LaA	61.73(8)	O(6)A-La-C(21)	161.08(9)
O(2)A-La-O(1)	136.89(9)	C(21)-La-C(29)A	167.32(10)	N(2)-La-C(21)	85.91(10)
O(2)A-La-O(6)	73.61(9)	O(3)-La-N(1)	69.90(9)	O(2)A-La-C(29)A	85.05(9)
O(1)-La-O(6)	76.92(9)	O(1)-La-O(6)A	69.80(8)	O(1)-La-LaA	68.12(6)
O(2)A-La-O(4)	84.87(8)	O(6)-La-O(6)A	78.74(8)	O(1)-La-C(29)A	71.60(9)
O(1)-La-O(4)	124.18(8)	O(4)-La-O(6)A	157.04(8)	O(6)-La-C(29)A	102.96(10)
O(6)-La-O(4)	86.71(9)	O(5)A-La-O(6)A	48.75(9)	O(4)-La-C(29)A	163.53(10)
O(2)A-La-O(5)A	93.76(9)	O(3)-La-O(6)A	140.88(8)	O(5)A-La-C(29)A	24.37(9)
O(1)-La-O(5)A	79.75(9)	N(1)-La-O(6)A	119.86(8)	O(3)-La-C(29)A	145.58(9)
O(6)-La-O(5)A	127.20(8)	O(6)-La-N(2)	144.01(9)	N(1)-La-C(29)A	96.95(9)
O(4)-La-O(5)A	144.26(9)	O(4)-La-N(2)	70.35(9)	O(6)A-La-C(29)A	24.50(9)
O(2)A-La-O(3)	126.35(9)	O(5)A-La-N(2)	74.54(9)	N(2)-La-C(29)A	94.67(10)
O(1)-La-O(3)	75.02(8)	O(3)-La-N(2)	105.16(8)	O(2)A-La-LaA	68.94(6)

Symmetry code: A $-x$, $-y+2$, $-z$.

phenanthroline ligands. The La-N bonds are provided by bidentate ligands forming a five membered chelate ring, and the La-O bonds by three different types: one bidentate ligands just like La-N and two bridged ones in different modes by two pairs of oxygen atoms from chelating carboxylates with a second La(Ⅲ) ion.

The La-N bond lengths are 0.266 8(3) nm and 0.269 7(3) nm respectively, the La-O bond lengehs from five 4-hydroxyphenylacetic group are in the range of 0.243 5(2) nm to 0.269 0(2) nm: the bond lengths of La-O(1), La-O(2)A, La-O(3), La-O(4), La-O(5)A, La-O(6) and La-O(6)A are 0.244 3(2), 0.243 5(2), 0.263 9(3), 0.258 6(2), 0.260 4(3), 0.248 3(3) and 0.269 0(2) nm correspondingly, which is slightly shorter compared with that of La-N, so more stable coordinating of 4-hydroxyphenylacetic group would be expected.

According to Pauling, in the conjugated system like 1,10-phenanthroline, the C-C bond lengths are in the range of 0.132 9 ~0.146 9 nm and the C-N bond lengths are 0.132 9 nm or 0.137 3 nm, respectively. In the complex, the slightly shorter C-C bond length (0.132 9~0.143 8 nm) and C-N bond length (0.132 9 nm or 0.135 6 nm) compared with the free one indicates the more stability of coordinated 1,10-phenanthroline, but the lower conjugacy and different conjugated degree in two 1,10-phenanthroline ring were observed, which was consis-tant with the results of ^{1}H NMR spectra.

3 Conclusions

A solid complex of lanthanide nitrate with 1,10-phenanthroline and 4-hydroxyphenylacetic group has been synthesized with a new method at the ordinary condition. The single structure shows that the complex was nine-coordinate with the O atoms from 4-hydroxyphenylacetic group and N atoms from 1,10-phenanthroline, the 4-hydroxyphenylacetic ligands exhibit three kinds of coordination modes.

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