# Synthesis, Crystal Structure and Thermal Decomposition Mechanism of a Dysprosium(III) *p*-Fluorobenzoate 1,10-Phenanthroline Complex

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Z. Naturforsch. 2007, 62b, 51-54; received June 7, 2006

A dinuclear dysprosium(III) *p*-fluorobenzoate 1,10-phenanthroline complex,  $[Dy(p-FBA)_3phen]_2$  was synthesized and characterized by elemental analysis, UV and IR spectroscopy, single crystal X-ray diffraction, molar conductance, and TG-DTG techniques. It crystallizes in the triclinic space group  $P\overline{1}$  with a = 9.895(5), b = 11.754(6), c = 14.756(10) Å;  $\alpha = 106.660(9)^{\circ}$ ,  $\beta = 107.956(9)^{\circ}$ ,  $\gamma = 101.472(7)^{\circ}$ ; Z = 1. The Dy(III) ions are eight coordinate including one terminal bidentate chelating carboxylate group, four bridging carboxylate groups and one 1,10-phenanthroline molecule. The thermal decomposition of  $[Dy(p-FBA)_3phen]_2$  has been followed by thermal analysis. The lifetime equation at weight-loss of 10 % was deduced as  $\ln \tau = -27.0798 + 19010.2434/T$  by isothermal thermogravimetric analysis.

Key words: p-Fluorobenzoic Acid, Crystal Structure, 1,10-Phenanthroline, Dysprosium Complex, Thermal Analysis

## Introduction

The rare earth carboxylate complexes have been widely studied due to their special structures and interesting luminescence properties. They are used in extraction, separation, germicide catalysis, luminescence, and functional materials [1-7]. Many types of arenecarboxylate lanthanide complexes with nitrogencontaining ligands were obtained [8-16]. Their thermal decomposition behavior has been reported in previous papers [17-28]. In this paper, we report the crystal structure, the characteristic properties and the thermal decomposition of the dysprosium *p*-fluorobenzoate complex with 1,10-phenanthroline.

## **Result and Discussion**

## Preparation

In 95% ethanol solution, reaction at r. t. of  $DyCl_3 \cdot 6H_2O$ , *p*-fluorobenzoic acid and 1,10-phenanthroline in a molar ratio of 1:3:1 gave the complex.

# Molar conductivity

The title complex is stable in air. We determined its molar conductivity in DMSO solution



Fig. 1. Molecular structure of [Dy(*p*-FBA)<sub>3</sub>phen]<sub>2</sub>.

with DMSO as a reference. It can be concluded that  $[Dy(p-FBA)_3phen]_2$  is not an electrolyte (8.55 s cm<sup>2</sup> mol<sup>-1</sup>).

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Table 2. Bond lengths [Å] and angles [deg] for

Table 1. Crystal data and structure refinement for [Dy(p-FBA)3 nhen]

		[Dy(p-FBA) <sub>3</sub> phen]	2		
Empirical formula	C <sub>66</sub> H <sub>40</sub> Dy <sub>2</sub> F <sub>6</sub> N <sub>4</sub> O <sub>12</sub>	Dy(1)-O(5) <sup>#1</sup>	2.277(9)	Dy(1)-O(4) <sup>#1</sup>	2.341(8)
Formula weight	1520.02	Dy(1)-O(3)	2.327(8)	Dy(1)-O(2)	2.497(9)
Temperature [K]	293(2)	Dy(1)-O(6)	2.335(8)	Dy(1)-N(1)	2.533(10)
Wavelength [Å]	0.71073	Dy(1)-O(1)	2.338(9)	Dy(1)-N(2)	2.609(10)
Crystal system, space group	triclinic, PĪ	Dy(1)-C(13)	2.751(12)	F(2)-C(24)	1.36(2)
Unit cell dimensions		F(1)-C(17)	1.367(17)	F(3)-C(31)	1.369(19)
[Å]	a = 9.895(5)	O(4)-Dy(1) <sup>#1</sup>	2.341(8)	O(5)-Dy(1) <sup>#1</sup>	2.277(9)
	b = 11.754(6)	$O(5)^{\#1}$ -Dv(1)-O(3)	79 4(3)	O(1)-Dv(1)-O(2)	54 1(3)
	c = 14.756(10)	$O(5)^{\#1}$ -Dy(1)-O(6)	124 6(3)	$O(4)^{\#1}$ -Dv(1)-O(2)	741(3)
[°]	$\alpha = 106.660(9)$	O(3)-Dy(1)-O(6)	78.8(3)	$O(5)^{\#1}$ -Dv(1)-N(1)	85.0(3)
	$\beta = 107.956(9)$	$O(5)^{\#1}$ -Dv(1)-O(1)	132.5(3)	O(3)-Dv(1)-N(1)	80.8(3)
	$\gamma = 101.472(7)$	O(3)-Dv(1)-O(1)	145.8(3)	O(6)-Dy(1)-N(1)	139.3(3)
Volume [A <sup>3</sup> ]	1484.4(14)	O(6)- $Dv(1)$ - $O(1)$	88.3(3)	O(1)-Dv(1)-N(1)	89.3(3)
Z, Calculated density	1, 1.70 g·cm <sup>-3</sup>	$O(5)^{\#1}$ -Dv(1)-O(4)^{\#1}	76.8(3)	$O(4)^{\#1}$ -Dv(1)-N(1)	142.7(3)
Absorption coefficient [mm <sup>-1</sup> ]	2.58	O(3)-Dv(1)-O(4) <sup>#1</sup>	126.1(3)	O(2)-Dv(1)-N(1)	70.7(3)
F(000)	746	$O(6)$ - $Dv(1)$ - $O(4)^{\#1}$	76.5(3)	$O(5)^{\#1}$ -Dv(1)-N(2)	139.4(3)
Crystal size [mm]	0.22  imes 0.16  imes 0.12	$O(1)$ - $Dv(1)$ - $O(4)^{\#1}$	80.0(3)	O(3)- $Dv(1)$ - $N(2)$	71.1(3)
$\theta$ Range for data collection [°]	1.91 to 25.03	$O(5)^{\#1}$ -Dy(1)-O(2)	79.8(3)	O(6)-Dy(1)-N(2)	76.5(3)
Limiting indices	$-11 \le h \le 11,$	O(3)-Dy(1)-O(2)	145.8(3)	O(1)-Dy(1)-N(2)	75.2(3)
	$-13 \le k \le 11,$	O(6)-Dy(1)-O(2)	135.4(3)	$O(4)^{\#1}$ -Dy(1)-N(2)	143.5(3)
	$-17 \le l \le 17$	$O(5)^{\#1}$ -Dy(1)-C(13)	105.4(4)	O(2)-Dy(1)-N(2)	110.3(3)
Reflections collected / unique	$7951 / 5106 \left[ R_{(int)} = 0.0363 \right]$	O(3)-Dy(1)-C(13)	160.8(3)	N(1)-Dy(1)-N(2)	63.7(3)
Completeness to $\theta = 25.03$	97.4%	O(6)-Dy(1)-C(13)	111.5(4)	C(27)-O(5)-Dy(1) <sup>#1</sup>	164.0(9)
Absorption correction	Semi-empirical from equivalents	O(1)-Dy(1)-C(13)	27.4(3)	C(27)-O(6)-Dy(1)	124.6(8)
Max. and min. transmission	1.00 and 0.60	$O(4)^{\#1}$ -Dy(1)-C(13)	72.9(3)	C(12)-N(1)-C(1)	116.7(11)
Refinement method	Full-matrix least-squares on $F^2$	O(2)-Dy(1)-C(13)	26.9(3)	C(12)-N(1)-Dy(1)	122.2(8)
Data / restraints / parameters	5106 / 0 / 406	N(1)-Dy(1)-C(13)	81.2(3)	C(1)-N(1)-Dy(1)	121.1(8)
Goodness-of-fit on $F^2$	1.064	N(2)-Dy(1)-C(13)	95.0(3)	C(3)-N(2)-C(2)	116.9(10)
Final <i>R</i> indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0665, wR_2 = 0.1804$	C(13)-O(1)-Dy(1)	94.7(7)	C(3)-N(2)-Dy(1)	124.5(7)
<i>R</i> indices (all data)	$R_1 = 0.0814, wR_2 = 0.1873$	C(13)-O(2)-Dy(1)	88.0(7)	C(2)-N(2)-Dy(1)	118.5(8)
Largest diff. peak and hole	3.898 and $-0.845$	C(20)-O(3)-Dy(1)	139.8(8)	C(20)-O(4)-Dy(1) <sup>#1</sup>	134.7(8)
[e·A <sup>-5</sup> ]					



Fig. 2. Coordination geometry about the Dy(III) ion.

*Crystal structure of* [*Dy*(*p*-*FBA*)<sub>3</sub>*phen*]<sub>2</sub>

The crystal data, experimental details and structure refinement are summarized in Table 1. Selected bond

lengths are given in Table 2. The structure is shown in Fig. 1. The cluster is centrosymmetric, and composed of two phen ligands, six p-FBA anions and two Dy cations. Each Dy(III) ion is coordinated by eight atoms in a distorted square antiprism geometry as shown in Fig. 2, which includes six oxygen atoms of the *p*-FBA ligands and two nitrogen atoms of the phen molecule. The two Dy(III) ions are linked in the mode of four bidentate bridges. The Dy-O bond lengths are in the range from 2.277 to 2.497 Å, with a mean bond length of 2.369 Å; the average of Dy-O bond length formed by the bridging carboxylates is slightly shorter than the bond lengths formed by the chelating carboxylate groups. Dy-N bond lengths are in the range from 2.533 to 2.609 Å, with an average distance of 2.595 Å.

# Spectral characteristics

The bands of asymmetric and symmetric vibrations of the COO<sup>-</sup> groups occur at 1610-1560 and 1440-1360 cm<sup>-1</sup>. The band at 410 cm<sup>-1</sup> is assigned to the metal-oxygen ionic bond. All these indicate



Fig. 3. TG-DTG curves of the title complex.

that the carboxylate groups are coordinated to the Dy(III) ion [29]. The band of the v (C=N) vibration at 1646 cm<sup>-1</sup> in the 1,10-phenanthroline ligand spectrum shifts to 1590 cm<sup>-1</sup> in the spectrum of the complex, demonstrating the coordination of the ligand. The UV spectra of the ligands and the complex were obtained in DMSO solution with DMSO as a reference. The strong absorption band of *p*-fluorobenzoic acid at 282 nm is shifted to 265 nm in the complex. The strong absorption band of 1,10-phenanthroline at 265.54 nm is similar to that in the complex.

#### Thermal behavior

The thermal stability of the complex was investigated in the range from 25 to 900 °C. The TG-DTG curves at  $\beta = 7$  °C min<sup>-1</sup> are shown in Fig. 3. In the first stage, 24.5% of weight was lost in the range of 281–367 °C, which is ascribed to the release of the phen molecules from the complex (calculated: 23.7%). The IR absorption band of  $v_{C=N}$  at 1590 cm<sup>-1</sup> disappears. The second stage of weight loss is from 367 to 860 °C, with a mass loss 51.2% (theoretical mass loss: 51.8%), which is attributed to the loss of C<sub>42</sub>H<sub>24</sub>F<sub>6</sub>O<sub>9</sub> units. The special absorption of  $v_{C-F}$  at 1000–1100 cm<sup>-1</sup> disappears. The IR spectrum of the residue is the same as that of Dy<sub>2</sub>O<sub>3</sub>. On the basis of experimental and calculated results, the thermal decomposition process is as follows:

$$[Dy(p-FBA)_3phen]_2 \rightarrow [Dy(p-FBA)_3]_2 \rightarrow Dy_2O_3$$

#### Lifetime

The general lifetime formula of materials has been proposed and proved by Dakin [30]. It is represented

Table 3. The lifetime of  $[Dy(p-FBA)_3phen]_2$  by isothermal TG.

T/K	$ au_{ m 10\%}/ m min$	T/K	$ au_{10\%}/{ m min}$
523.15	180.94	543.15	45.25
533.15	83.81	553.15	25.15

by:

$$\ln \tau = a + b/T \tag{1}$$

where  $\tau$  is the lifetime at temperature *T*(K), *a* and *b* are constants. We measured the mass-loss of 10% lifetime by isothermal TG at 523.15, 533.15 543.15 and 553.15 K as listed in Table 3. By substituting these values into eq. (1), the constants *a*, *b* and the linear correlation coefficients *r* were obtained by the linear least squares method. The lifetime equation is  $\ln \tau = -27.0798 + 19010.2434/T$ . The linear correlation coefficient *r* is 0.9985.

#### **Experimental Section**

#### Material and apparatus

All reagents were obtained from commercial supplies with analytical grade and used without further purification. All manipulation was carried out in the laboratory atmosphere.

Analyses of C, H, and N were performed on a Carlo-Erba model 1106 element analyzer, and the metal content was assayed using EDTA titration. Infrared spectra were recorded using KBr pellets in the range of 4000-400 cm<sup>-1</sup> on a Bio-Rad FTS-135 spectrometer. UV spectra were depicted on a SHIMADZU 2501 spectrometer. Molar conductivity was determined by a DDS-307 conductometer of the Shanghai exactitude apparatus factory. TG and DTG experiments were performed using a Perkin-Elmer TGA7 thermogravimetric analyzer, and air was used as a static atmosphere. X-Ray diffraction data were obtained by a Bruker Apex II CCD diffractometer with graphite-monochromated Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 293 K. A semi-empirical absorption correction based on SADABS was applied. Unique data  $(R_{int} = 0.0363)$  were used to solve the structure by Direct Methods using the SHELXS-97 program, and refined on  $F^2$ by full-matrix least squares methods using the SHELXL-97 program.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-603953. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

### Synthesis

DyCl<sub>3</sub> · 6H<sub>2</sub>O was obtained from the reaction of Dy<sub>2</sub>O<sub>3</sub> (99.95 %) and HCl (6.0 mol  $1^{-1}$ ). Stoichiometric amounts of *p*-fluorobenzoic acid and 1,10-phenanthroline were mixed and then dissolved in 95 % ethanol solution. The pH value of the mixture was adjusted to 6 – 7 by adding 1.0 M NaOH solution before it was added dropwise to the ethanolic DyCl<sub>3</sub> solution. The mixture was stirred for 8 h at r.t. and then deposited for a day. The precipitate was filtered out and washed with deionized water and 95 % ethanol. Colorless crystals for X-ray diffraction analysis were obtained by slow evaporation of the solvent for a month. Yield: 83.9 %. – UV/vis:  $\lambda_{max}(\lg \epsilon) = 265$  nm (0.25). – IR (film):  $\tilde{\nu} = 1634,$  1602, 1547, 1519, 1479, 1417, 1346, 1090, 410 cm $^{-1}$ . – C<sub>66</sub> H<sub>40</sub> Dy<sub>2</sub> F<sub>6</sub> N<sub>4</sub> O<sub>12</sub> (1520.02): calcd. C 52.15, H 2.65, N 3.69, Dy 21.38; found C 51.38, H 2.49, N 4.41, Dy 21.59.

#### Acknowledgements

This project was supported by the Natural Science Foundation of Hebei Province, Hebei Education Department and Hebei Normal University.

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