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The crystal structure of [(tetra- μ_2 -2,6-difluorobenzoato- $\kappa^2 O:O'$)-bis-(2,6-difluorobenzoato- $\kappa^2 O:O'$)-bis-(1,10-phenanthroline- $\kappa^2 N:N')$]dierbium(III) $C_{66}H_{34}N_4O_{12}F_{12}Er_2$

<https://doi.org/10.1515/ncrs-2019-0777>

Received October 18, 2019; accepted November 11, 2019; available online December 3, 2019

Abstract

$C_{66}H_{34}N_4O_{12}F_{12}Er_2$, triclinic, $P\bar{1}$ (no. 2), $a = 11.8934(5)$ Å, $b = 12.0041(4)$ Å, $c = 12.4578(5)$ Å, $\alpha = 68.718(4)^\circ$, $\beta = 64.205(4)^\circ$, $\gamma = 87.053(3)^\circ$, $V = 1480.09(12)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0326$, $wR_{ref}(F^2) = 0.0626$, $T = 293(2)$ K.

CCDC no.: 1954675

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Pink rod
Size:	$0.15 \times 0.10 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.92 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ϕ and ω
$\theta_{\max}$, completeness:	29.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13931, 6822, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5935
$N(\text{param})_{\text{refined}}$:	433
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3]

Source of material

A $H_2O/EtOH$ solution (12 mL, $V_{H_2O} : V_{EtOH} = 10 : 2$) of 2,6-difluorobenzoic acid (50 mg, 0.30 mmol) and $NaHCO_3$ (25 mg, 0.28 mmol) were added into $Er(NO_3)_3 \cdot 6H_2O$ (65 mg, 0.14 mmol) which was dissolved in 8 mL EtOH. Then a 5 mL EtOH dissolving 1,10-phenanthroline (20 mg, 0.10 mmol) was added into the above solution. The solvent was partially evaporated and pink crystals were obtained after one week. Yield: 40 mg (35%) based on Er^{3+} .

Experimental details

H atoms bound to C atoms were placed in calculated positions and refined as riding on their parent atoms, with $C-H = 0.93$ Å (aromatic), $C-H = 0.96$ Å (methylene), $C-H = 0.97$ Å (ethylene), and with $U_{\text{iso}}(H) = 1.5 U_{\text{eq}}(C)$ for methyl H atoms and $1.2 U_{\text{eq}}(C)$ for all other H atoms.

Comment

In the last two decades, lanthanide complexes have attracted much interest because of their diverse applications as functional materials such as molecular sensors, photo-catalysts and luminescent materials [4]. A key step in the construction of lanthanide complexes is to use appropriate organic ligands. O- and N-donor ligands are usually employed to assemble lanthanide complexes because of their various coordination modes. Among O-donor organic bridging ligands, benzoic acid and its derivatives are used to connect metal centers, yielding some fantastic structures of polynuclear clusters. Especially, the fluorine substituted organic molecules are good candidates for construction of

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Er1	0.58933(2)	0.91167(2)	0.62121(2)	0.02413(5)
N1	0.5682(3)	0.8862(3)	0.8366(3)	0.0330(7)
C1	0.4734(4)	0.8152(3)	0.9447(4)	0.0413(10)
H1	0.413343	0.774390	0.938756	0.050*
C2	0.4589(5)	0.7986(4)	1.0671(4)	0.0517(12)
H2	0.391530	0.746939	1.140492	0.062*
C3	0.5441(5)	0.8585(4)	1.0769(4)	0.0603(14)
H3	0.534254	0.850318	1.157794	0.072*
C4	0.6469(5)	0.9326(4)	0.9669(4)	0.0498(11)
C5	0.6571(4)	0.9443(3)	0.8461(4)	0.0365(9)
C6	0.7616(4)	1.0177(3)	0.7296(4)	0.0373(9)
C7	0.8551(4)	1.0778(4)	0.7372(5)	0.0478(11)
C8	0.8401(5)	1.0664(5)	0.8612(6)	0.0697(16)
H4	0.900492	1.107632	0.866377	0.084*
C9	0.7424(6)	0.9986(5)	0.9690(6)	0.0714(16)
H5	0.735869	0.993765	1.047738	0.086*
C10	0.9571(4)	1.1454(4)	0.6222(6)	0.0628(14)
H6	1.020628	1.186584	0.623035	0.075*
C11	0.9642(4)	1.1513(4)	0.5083(5)	0.0599(13)
H7	1.032499	1.195900	0.430868	0.072*
C12	0.8674(4)	1.0894(3)	0.5093(4)	0.0462(10)
H8	0.872942	1.094043	0.430961	0.055*
N2	0.7682(3)	1.0246(2)	0.6162(3)	0.0344(7)
O1	0.5549(2)	0.6915(2)	0.7538(2)	0.0349(6)
C13	0.6702(4)	0.6931(3)	0.7085(4)	0.0342(9)
O2	0.7456(2)	0.7852(2)	0.6190(3)	0.0408(7)
C14	0.7264(4)	0.5842(3)	0.7639(4)	0.0419(10)
C15	0.8152(5)	0.5311(4)	0.6903(5)	0.0566(12)
F1	0.8494(3)	0.5757(2)	0.5619(3)	0.0811(9)
C16	0.8696(5)	0.4332(4)	0.7393(7)	0.0769(17)
H9	0.929028	0.399026	0.686274	0.092*
C17	0.8318(6)	0.3886(4)	0.8701(7)	0.0788(18)
H10	0.867265	0.323205	0.905583	0.095*
C18	0.7455(5)	0.4364(4)	0.9480(6)	0.0672(15)
H11	0.720613	0.404635	1.036228	0.081*
C19	0.6947(5)	0.5336(3)	0.8939(5)	0.0504(11)
F2	0.6117(3)	0.5841(2)	0.9714(3)	0.0729(8)
O3	0.5198(3)	1.0909(2)	0.6383(2)	0.0407(7)
C20	0.4772(3)	1.1747(3)	0.5782(3)	0.0296(8)
O4	0.4548(3)	1.1805(2)	0.4882(2)	0.0438(7)
C21	0.4502(4)	1.2808(3)	0.6196(3)	0.0326(9)
C22	0.3340(5)	1.3187(4)	0.6588(4)	0.0492(11)
F3	0.2386(3)	1.2561(3)	0.6650(3)	0.0791(9)
C23	0.3076(6)	1.4163(4)	0.6952(5)	0.0728(16)
H12	0.227022	1.439137	0.721645	0.087*
C24	0.4032(7)	1.4785(4)	0.6913(5)	0.0763(19)
H13	0.387375	1.545068	0.714724	0.092*
C25	0.5195(6)	1.4457(4)	0.6544(4)	0.0642(15)
H14	0.583758	1.488764	0.652272	0.077*
C26	0.5420(5)	1.3468(3)	0.6195(4)	0.0469(11)
F4	0.6576(3)	1.3140(2)	0.5824(3)	0.0768(9)
O5	0.3723(2)	0.8650(2)	0.7376(2)	0.0390(6)
C27	0.2917(3)	0.8878(3)	0.6978(3)	0.0282(8)
O6	0.3065(2)	0.9603(2)	0.5896(2)	0.0394(6)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C28	0.1618(3)	0.8201(3)	0.7893(3)	0.0319(8)
C29	0.1231(4)	0.7158(4)	0.7853(5)	0.0550(12)
F5	0.2063(3)	0.6790(2)	0.6938(3)	0.0930(12)
C30	0.0070(5)	0.6513(4)	0.8652(6)	0.0795(18)
H15	−0.015188	0.582381	0.857519	0.095*
C31	−0.0764(5)	0.6906(5)	0.9571(6)	0.0804(17)
H16	−0.156109	0.647664	1.012778	0.097*
C32	−0.0440(4)	0.7924(5)	0.9682(5)	0.0688(15)
H17	−0.100163	0.818423	1.031469	0.083*
C33	0.0735(4)	0.8547(4)	0.8833(4)	0.0444(10)
F6	0.1054(3)	0.9579(3)	0.8889(3)	0.0745(9)

functional lanthanide complexes because they are found to be more stable to oxidation and show thermal stability [5]. There are some reports about the use of 2-fluorobenzoate [6–8], 2,3-difluorobenzoate [9], 2,4-difluorobenzoate [10, 11], 2,5-difluorobenzoate [12], 2,3,4,5-tetrafluorobenzoate [13, 14], 2,3,5,6-tetrafluorobenzoate [15], and 2,3,4,5,6-pentafluorobenzoate [16] as ligands, however, there is only one example of 2,6-difluorobenzoate as ligand to coordinate with Ln(III) ions [17]. Herein, we select 2,6-difluorobenzoic acid to react with Er(III) ions and 1,10-phenanthroline to obtain a new complex {[Er(2,6-dfba)(phen)](μ₂-2,6-dfba)₂}₂.

X-ray analysis showed that there are one Er(III) ion, one 1,10-phenanthroline ligand and three 2,6-difluorobenzoate anions in the asymmetric unit of the title complex. Each Er(III) ion is coordinated by six O atoms from three 2,6-difluorobenzoate ligands, and two N atoms from one 1,10-phenanthroline molecule. The 2,6-dfba[−] ligands have two different coordination modes. The carboxylate group of O1–C13–O2 coordinates in a chelating mode, whereas the carboxylate groups of O3–C20–O4 and O5–C27–O6 adopt bridging mode. Two adjacent Er³⁺ ions are bridged by two 2,6-dfba[−] ligands with the Er...Er distance of 4.3134(4) Å to form a dimeric unit. Each 1,10-phenanthroline molecule coordinates to one Er³⁺ ion using two N atoms. The distances of Er–O are in the range of 2.265(2)–2.497(2) Å. The distances of Er1–N1 and Er1–N2 are 2.486(3)–2.546(3) Å, respectively. The O–Er–O bond angles range from 53.83(8)° to 146.28(9)°. The phenanthroline molecule is a little distorted, the dihedral angle between N1C1C2C3C4C5 ring and C4C5C6C7C8C9 ring is 1.5(2)°, and it is 1.6(2)° between C4C5C6C7C8C9 ring and N2C6C7C10C11C12 ring. The carboxylate groups are almost twisted out of the benzene ring planes, and the dihedral angles between the carboxylate groups and their benzene rings are 54.1(3)°, 57.6(4)°, and 83.7(2)°, respectively.

Acknowledgements: We gratefully acknowledge support by the National Nature Foundation of China [Nos. 21461011, 31960720, 31560712], the Natural Science Foundation of Jiangxi Province (Nos. 20192ACBL21018, 20112BBF60023), and the Education Department of Jiangxi Province (Nos. GJJ170245, GJJ170257).

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