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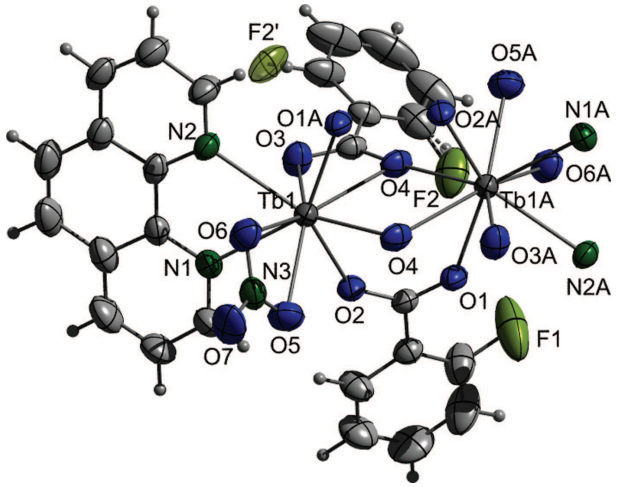
Crystal structure of bis(μ$_2$-2-fluorobenzoato-κ^2*O*:*O*:*O*′) bis(μ$_2$-2-fluorobenzoato-κ^2*O*:*O*′) dinitrato-κ^2*O*,*O*′ bis(1,10-phenathroline-κ^2*N*,*N*′) diterbium(III), $C_{52}H_{32}F_4N_6O_{14}Tb_2$



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Abstract

$C_{52}H_{32}F_4N_6O_{14}Tb_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.745(2)$ Å, $b = 10.993(2)$ Å, $c = 11.141(2)$ Å, $\alpha = 84.45(3)°$, $\beta = 81.22(3)°$, $\gamma = 69.46(3)°$, $V = 1216.6(4)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0345$, $wR_{ref}(F^2) = 0.0992$, $T = 293(2)$ K.

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Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Stoichiometric amounts of $Tb(NO_3)_3 \cdot 6H_2O$, *o*-fluorobenzoic acid and 1,10-phenanthroline (1:2:1) were dissolved separately in ethanol solvent. The ethanol solutions of the ligands were mixed and then the mixture was added dropwise to the ethanolic $Tb(NO_3)_3$ solution under stirring. The mixture was adjusted to pH 6–7 by adding 0.1 M NaOH solution, while a white precipitate appeared.

Table 1: Data collection and handling.

Crystal:	Light yellow, block, size 0.280×0.330×0.410 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	29.75 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	54.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5377, 5377
$N(param)_{refined}$:	362
Programs:	Bruker programs [10], PLATON [11], SHELX [12], Diamond [13]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	−0.2039	0.2860	−0.3358	0.062
H(4)	2*i*	−0.3646	0.4531	−0.4249	0.079
H(5)	2*i*	−0.5691	0.5508	−0.3187	0.093
H(6)	2*i*	−0.6090	0.4936	−0.1145	0.109
H(10)	2*i*	0.1360	−0.3535	−0.1583	0.073
H(11)	2*i*	0.1700	−0.5302	−0.2624	0.108
H(12)	2*i*	−0.0082	−0.6041	−0.2614	0.126
H(13)	2*i*	−0.2132	−0.5002	−0.1464	0.108
H(14)	2*i*	−0.2291	−0.3320	−0.0360	0.073
H(15)	2*i*	0.0055	0.1499	−0.4098	0.061
H(16)	2*i*	0.0398	0.2748	−0.5830	0.072
H(17)	2*i*	0.2409	0.3106	−0.6295	0.080
H(19)	2*i*	0.4796	0.2548	−0.5875	0.079
H(20)	2*i*	0.6365	0.1622	−0.4638	0.079
H(22)	2*i*	0.7098	0.0254	−0.2760	0.066
H(23)	2*i*	0.6591	−0.0918	−0.1060	0.075
H(24)	2*i*	0.4466	−0.1063	−0.0646	0.063

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Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb(1)	2*i*	0.12758(2)	−0.00570(2)	−0.15019(2)	0.0269(1)	0.0344(1)	0.0291(1)	−0.01116(8)	−0.00312(7)	0.00009(7)
O(1)	2*i*	−0.2328(3)	0.1233(3)	−0.0133(3)	0.033(2)	0.053(2)	0.042(2)	−0.016(1)	−0.011(1)	0.011(1)
O(2)	2*i*	−0.0877(3)	0.1369(3)	−0.1759(3)	0.030(1)	0.046(2)	0.039(2)	−0.006(1)	−0.008(1)	0.005(1)
O(3)	2*i*	−0.1468(4)	−0.1830(3)	0.0794(3)	0.052(2)	0.046(2)	0.053(2)	−0.024(2)	0.004(2)	−0.010(2)
O(4)	2*i*	−0.0020(3)	−0.1287(3)	−0.0555(3)	0.047(2)	0.041(2)	0.053(2)	−0.027(1)	−0.015(2)	0.006(1)
O(5)	2*i*	0.0607(4)	−0.0954(4)	−0.3195(4)	0.057(2)	0.060(2)	0.054(2)	−0.021(2)	−0.015(2)	−0.009(2)
O(6)	2*i*	0.2610(4)	−0.1876(4)	−0.2739(4)	0.043(2)	0.058(2)	0.058(2)	−0.015(2)	−0.001(2)	−0.017(2)
O(7)	2*i*	0.1983(5)	−0.2595(5)	−0.4206(4)	0.086(3)	0.097(3)	0.058(3)	−0.049(3)	0.016(2)	−0.044(3)
N(1)	2*i*	0.1775(4)	0.1142(4)	−0.3516(3)	0.040(2)	0.044(2)	0.033(2)	−0.015(2)	−0.003(2)	−0.000(2)
N(2)	2*i*	0.3709(4)	−0.0012(4)	−0.2031(4)	0.031(2)	0.046(2)	0.046(2)	−0.017(2)	−0.004(2)	0.002(2)
N(3)	2*i*	0.1733(5)	−0.1829(4)	−0.3410(4)	0.051(2)	0.055(2)	0.040(2)	−0.025(2)	0.006(2)	−0.008(2)
C(1)	2*i*	−0.2022(4)	0.1734(4)	−0.1137(4)	0.030(2)	0.036(2)	0.037(2)	−0.012(2)	−0.009(2)	−0.000(2)
C(2)	2*i*	−0.3095(4)	0.2848(4)	−0.1702(4)	0.034(2)	0.033(2)	0.045(2)	−0.009(2)	−0.009(2)	0.000(2)
C(3)	2*i*	−0.2862(6)	0.3264(5)	−0.2905(5)	0.055(3)	0.045(2)	0.042(3)	−0.001(2)	−0.012(2)	0.004(2)
C(4)	2*i*	−0.3828(7)	0.4265(6)	−0.3443(6)	0.074(4)	0.059(3)	0.054(3)	−0.009(3)	−0.021(3)	0.015(3)
C(5)	2*i*	−0.5031(7)	0.4860(6)	−0.2810(8)	0.056(4)	0.052(3)	0.110(6)	0.003(3)	−0.032(4)	0.019(4)
C(6)	2*i*	−0.5281(7)	0.4504(7)	−0.1605(9)	0.046(3)	0.074(4)	0.116(7)	0.008(3)	0.011(4)	0.023(4)
C(7)	2*i*	−0.4311(6)	0.3499(6)	−0.1093(6)	0.047(3)	0.060(3)	0.072(4)	−0.002(3)	0.006(3)	0.016(3)
C(8)	2*i*	−0.0684(4)	−0.2034(4)	−0.0166(4)	0.038(2)	0.032(2)	0.041(2)	−0.015(2)	−0.013(2)	0.003(2)
C(9)	2*i*	−0.0503(5)	−0.3196(4)	−0.0853(4)	0.054(3)	0.034(2)	0.035(2)	−0.016(2)	−0.014(2)	0.003(2)
C(10)	2*i*	0.0652(7)	−0.3844(5)	−0.1547(6)	0.072(4)	0.045(3)	0.052(3)	−0.004(3)	−0.009(3)	−0.002(2)
C(11)	2*i*	0.087(1)	−0.4891(7)	−0.2186(7)	0.136(7)	0.052(3)	0.056(4)	0.005(4)	−0.018(4)	−0.010(3)
C(12)	2*i*	−0.019(1)	−0.5332(7)	−0.2166(7)	0.21(1)	0.050(4)	0.062(4)	−0.041(6)	−0.053(6)	−0.007(3)
C(13)	2*i*	−0.141(1)	−0.4724(7)	−0.1483(8)	0.169(9)	0.062(4)	0.079(5)	−0.075(5)	−0.057(6)	0.011(4)
C(14)	2*i*	−0.1488(7)	−0.3707(6)	−0.0847(6)	0.091(4)	0.055(3)	0.058(3)	−0.044(3)	−0.031(3)	0.009(3)
C(15)	2*i*	0.0866(6)	0.1647(6)	−0.4275(5)	0.051(3)	0.062(3)	0.037(2)	−0.017(2)	−0.007(2)	0.005(2)
C(16)	2*i*	0.1068(6)	0.2393(6)	−0.5330(5)	0.065(3)	0.066(3)	0.043(3)	−0.017(3)	−0.018(3)	0.015(2)
C(17)	2*i*	0.2265(7)	0.2591(7)	−0.5612(6)	0.088(5)	0.070(4)	0.043(3)	−0.035(3)	−0.006(3)	0.015(3)
C(18)	2*i*	0.3263(6)	0.2020(6)	−0.4877(5)	0.068(3)	0.056(3)	0.041(3)	−0.028(3)	0.003(2)	0.003(2)
C(19)	2*i*	0.4592(7)	0.2097(7)	−0.5166(6)	0.083(4)	0.082(4)	0.050(3)	−0.056(4)	0.007(3)	0.001(3)
C(20)	2*i*	0.5527(7)	0.1535(7)	−0.4439(6)	0.066(4)	0.083(4)	0.063(4)	−0.050(3)	0.012(3)	−0.005(3)
C(21)	2*i*	0.5279(5)	0.0805(5)	−0.3368(5)	0.043(2)	0.055(3)	0.053(3)	−0.027(2)	0.005(2)	−0.010(2)
C(22)	2*i*	0.6249(5)	0.0187(6)	−0.2586(6)	0.041(3)	0.067(3)	0.068(4)	−0.031(2)	−0.001(2)	−0.014(3)
C(23)	2*i*	0.5953(6)	−0.0503(6)	−0.1580(6)	0.043(3)	0.075(4)	0.075(4)	−0.025(3)	−0.015(3)	0.003(3)
C(24)	2*i*	0.4661(5)	−0.0582(5)	−0.1336(6)	0.037(2)	0.059(3)	0.064(3)	−0.018(2)	−0.016(2)	0.012(3)
C(25)	2*i*	0.3997(4)	0.0684(4)	−0.3038(4)	0.038(2)	0.037(2)	0.042(2)	−0.020(2)	0.004(2)	−0.009(2)
C(26)	2*i*	0.2977(5)	0.1300(4)	−0.3815(4)	0.042(2)	0.041(2)	0.035(2)	−0.019(2)	0.004(2)	−0.006(2)
F(1)	2*i*	−0.4600(6)	0.3232(5)	0.0125(5)	0.103(4)	0.110(4)	0.092(3)	0.025(3)	0.046(3)	0.031(3)
F(2)[a]	2*i*	0.179(1)	−0.360(1)	−0.136(1)	0.057(7)	0.059(6)	0.10(1)	−0.001(5)	0.017(6)	0.002(6)
F(2')[b]	2*i*	−0.2659(6)	−0.3216(6)	−0.0123(7)	0.057(3)	0.078(4)	0.108(5)	−0.043(3)	−0.015(3)	0.002(3)

[a]Disordered, occupancy factor: 0.35.
[b]Disordered, occupancy factor: 0.65.

The reaction mixture was stirred for 4 h at room temperature and filtered. Light yellow transparent crystals were obtained by slow evaporation of the filtrate for several days. Calcd. for $C_{52}H_{32}F_4N_6O_{14}Tb_2$ (1358.67) (%): C, 45.97; H, 2.37; N, 6.19. Found (%): C, 45.58; H, 2.18; N, 6.67.

Experimental details

All the H atoms of carbon were treated as riding-model, with C—H = 0.93–0.97 Å, and their $U_{iso} = 1.2U_{eq}$ (carrier sp^2 carbon atom). The fluor atom attached to one benzene ring was disordered at the positions from C10 and C14 with occupancy factors of 0.35 (F2) and 0.65 (F2′), respectively. The C—F2 and the C—F2′ distances were fixed at 1.81 Å.

Discussion

Rare earth complexes with benzoate ligands and its derivatives are intensively investigated for their potential applications on new fluorescent materials, electroluminescent materials and luminescent probes. Binuclear lanthanide complex is the common structure type, which can be formed by the benzoate or its derivatives and diamine ligands (ternary complex), and even by the third ligands (quaternary complex). The reported quantity of the ternary

complexes is much more than that of the quaternary complexes, and the quaternary complexes are generally prepared by the lanthanum nitrate. Rare earth complexes with the fluoro benzoate ligand are rarely reported. They are almost ternary complexes, which exhibited the typical binuclear structure [1–7], and some quaternary complexes were reported [8, 9]. This work presented a quaternary binuclear terbium complex synthesized by *o*-fluorobenzoic acid (*o*-FBA), 1,10-phenanthroline (Phen) and terbium nitrate.

The title complex is binuclear centrosymmetric, which is typical for quaternary lanthanide benzoate complexes. Two Tb^{3+} ions are linked by four *o*-FBA ligands, of which two ligands are in bridging-bidentate coordination mode and the other two in bridging-chelating tridentate mode (see the figure). Each Tb^{3+} ion is nine-coordinated with five oxygen atoms of four *o*-FBA, two nitrogen atoms of Phen and two oxygen atoms of nitrate. The TbO_7N_2 coordination polyhedron around the Tb^{3+} ion can be described as distorted mono-capped square-antiprism. Atoms O2, O4, O6, N3 and O1′, O3′, O4′(′ = $-x$, $-y$, $-z$), N2 form the top and bottom planes of the prism, respectively, and the O5 atom acts as the capped site. Dihedral angle between the two square best planes is 3.47°. The title complex has a Tb—Tb distance of 3.9712(14) Å. The Tb—O (carboxyl) distances are in range of 2.327(3)–2.751(4) Å, the Tb—O(nitrate) bonds are 2.423(4)–2.513(4) Å, and the Nd—N separation are 2.572(4)–2.608(4) Å. All of the above bond lengths are consistent with their relative bond in the ternary and quaternary terbium complexes with the *o*-FBA ligand [1, 4, 8, 9].

There are no classical hydrogen bonds found in the crystal structure of title complex. However, there are some weak intra- and inter C—H···F and C—H···O hydrogen bonds, which play the roles of stabilizing and assembling the molecules into a supramolecular structure. The two intramolecular hydrogen bonds are C24—H24···F1′ with length of 3.1074(6) Å and angle of 137° and C24—H24···O1′ with length of 3.0413(6) Å and angle of 127°, and the two intermolecular are C6—H6···F2″(″ = $-1+x$, $1+y$, z) with length of 3.1109(6) Å and angle of 140° and C20—H20···O7‴(‴ = $1-x$, $-y$, $-1-z$) with length of 3.3781(6) Å and angle of 155°.

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