Crystal structure of di(2,2′-bipyridine)di[μ-(2,3-dimethoxylbenzoato-*O*,*O*′)]di[μ-(2,3-dimethoxylbenzoato-*O*,*O*′:*O*′)]di(nitrato)diterbium(III), $Tb_2(NO_3)_2(C_9H_9O_4)_4(C_{10}H_8N_2)_2$

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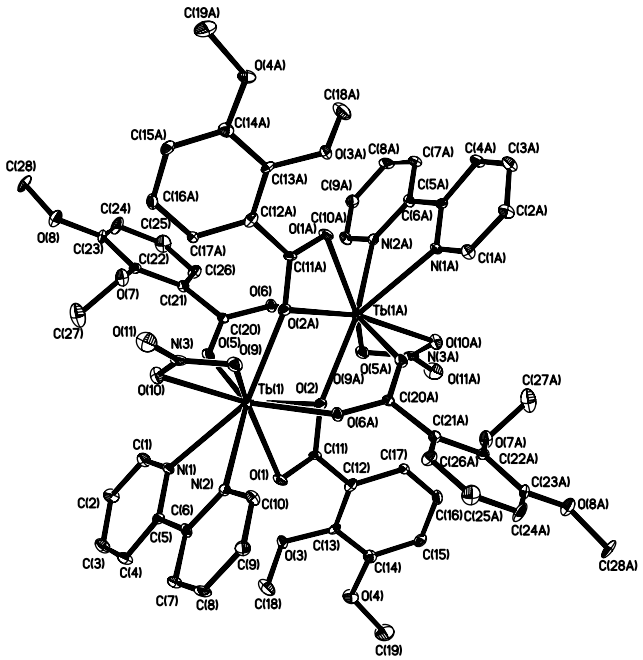

Abstract

$C_{28}H_{26}N_3O_{11}Tb$, triclinic, $P\bar{1}$ (No. 2), a = 10.620(7) Å, b = 10.766(7) Å, c = 13.182(8) Å, α = 76.11(1)°, β = 79.51(1)°, γ = 74.39(1)°, V = 1398.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.062, $wR_{ref}(F^2)$ = 0.151, T = 293 K.

Source of material

1.5 mmol 2,3-dimethoxybenzoic acid and 0.5 mmol 2,2′-bipyridine was dissolved in 25 ml ethanol. The pH of the mixed solution was controlled in a range of 6-7 with 2 mol·dm^{-3} NaOH solution. The 6 ml ethanol solution of 0.5 mmol $Tb(NO_3)_3$ was dropped into the mixed solution. The mixture was heated under reflux with stirring for 3 h. Single crystals were obtained from the mother liquor after 10 days at room temperature.

Discussion

The mixed ligand lanthanide complexes with organic acids and 1,10-phenanthroline or 2,2′-bipyridine have been extensively studied. A few quaternary lanthanide complex with organic acids and 2,2′-bipyridine have been reported. This paper reports the structure of a quaternary terbium complex with 2,3-dimethoxybenzoic acid and 2,2′-bipyridine, $Tb_2(NO_3)_2(C_9H_9O_4)_4(C_{10}H_8N_2)_2$ (**I**). In complex **I**, two central Tb^{3+} ions are connected by four carboxylate groups and coordinated by two 2,2′-bipyridine and two NO_3^-. The Tb^{3+} ion is 9 coordinated. Carboxylate groups O5–C20–O6 adopt a bridging mode. O1–C11–O2 groups adopt a bridging-chelating mode. A similar coordination environment has been observed in complexes $Nd_2(NO_3)_2(C_9H_9O_4)_4(C_{12}H_8N_2)_2$ (**II**) [1] and $Sm_2(NO_3)_2(C_5H_3O_3)_4(C_{10}H_8N_2)_2$ (**III**) [2]. In complex **I**, the distance of Tb^{3+}—Tb^{3+} is 3.907(2) Å. The Tb—$O_{carboxyl}$ distances range from 2.324(7) Å to 2.606(7) Å, with a mean value of 2.408(7) Å. They are smaller than those in complex **II**. This is because the radius of the Nd^{3+} ion is greater than that of Tb^{3+}. The O–Tb–O angles vary from 51.2(2)° to 137.9(2)°. O9 and O10 atoms from the nitrato coordinate to the Tb^{3+} ion in bidentate chelating mode. The bond distances of Tb1—O9 and Tb1—O10 are 2.504(7) Å, 2.459(7) Å, respectively. They are smaller than the distance of Sm—$O_{nitrato}$ in complex **III**. The bond distances of N and O from the nitrato group are 1.27(1) Å, 1.27(1) Å and 1.22(1) Å, respectively. The 2,2′-bipyridine ligand with two N atoms chelates to the Tb^{3+} ion. The average distance of Tb—N is 2.565(7) Å.

Table 1. Data collection and handling.

Crystal:	white square prism, size 0.06 × 0.10 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.97 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	53.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8164, 5708
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3865
$N(param)_{refined}$:	392
Programs:	SHELXS-97 [3] SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(10)	2*i*	0.3976	0.3784	0.1345	0.038
H(26)	2*i*	0.3987	–0.2489	–0.2296	0.037
H(17)	2*i*	0.5074	–0.2488	0.2602	0.030
H(16)	2*i*	0.4866	–0.4060	0.4102	0.040
H(15)	2*i*	0.2829	–0.4281	0.4946	0.038
H(8)	2*i*	0.0675	0.5991	0.2541	0.043
H(9)	2*i*	0.2940	0.5422	0.2263	0.041
H(1)	2*i*	0.0969	0.1135	–0.0837	0.036
H(7)	2*i*	–0.0515	0.4990	0.1860	0.038
H(2)	2*i*	–0.1257	0.1404	–0.0602	0.037

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	2*i*	–0.1490	0.3840	0.1312	0.042
H(3)	2*i*	–0.2508	0.2748	0.0541	0.052
H(19A)	2*i*	0.0711	–0.4489	0.5486	0.118
H(19B)	2*i*	–0.0583	–0.3409	0.5676	0.118
H(19C)	2*i*	0.0771	–0.3232	0.5860	0.118
H(27A)	2*i*	0.1939	0.3156	–0.4013	0.094
H(27B)	2*i*	0.2129	0.3329	–0.2907	0.094
H(27C)	2*i*	0.1459	0.2230	–0.2987	0.094
H(28A)	2*i*	0.3606	0.0669	–0.6437	0.093
H(28B)	2*i*	0.2804	0.2133	–0.6715	0.093
H(28C)	2*i*	0.2064	0.1011	–0.6201	0.093
H(18A)	2*i*	–0.0051	–0.0369	0.3814	0.083
H(18B)	2*i*	–0.0860	0.0176	0.2852	0.083
H(18C)	2*i*	0.0428	0.0630	0.2839	0.083
H(24)	2*i*	0.3136	–0.0996	–0.5213	0.057
H(25)	2*i*	0.3598	–0.2804	–0.3840	0.059

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(6)	2*i*	0.4901(6)	–0.1287(6)	–0.1236(5)	0.027(4)	0.022(4)	0.031(4)	0.001(3)	–0.008(3)	–0.007(3)
Tb(1)	2*i*	0.36482(5)	0.16384(5)	0.00157(4)	0.0195(3)	0.0149(2)	0.0180(2)	0.0003(2)	–0.0011(2)	–0.0041(2)
O(2)	2*i*	0.4253(7)	–0.0850(7)	0.0897(5)	0.031(4)	0.027(4)	0.023(4)	–0.005(3)	0.000(3)	–0.002(3)
N(3)	2*i*	0.3964(9)	0.4149(9)	–0.1279(7)	0.037(6)	0.020(5)	0.030(5)	0.002(5)	0.015(5)	–0.005(4)
O(5)	2*i*	0.3310(6)	0.0559(7)	–0.1204(5)	0.028(4)	0.031(4)	0.034(4)	0.008(3)	–0.008(3)	–0.021(3)
C(11)	2*i*	0.3282(9)	–0.065(1)	0.1610(7)	0.017(5)	0.031(6)	0.020(5)	–0.010(5)	0.005(4)	–0.009(5)
O(4)	2*i*	0.0538(7)	–0.2913(9)	0.4385(6)	0.026(4)	0.067(6)	0.045(5)	–0.023(4)	0.009(4)	0.008(4)
C(20)	2*i*	0.3968(9)	–0.0375(9)	–0.1625(7)	0.017(5)	0.019(5)	0.025(5)	–0.005(4)	0.000(4)	–0.007(4)
C(10)	2*i*	0.306(1)	0.403(1)	0.1439(8)	0.026(6)	0.026(6)	0.041(7)	0.000(5)	–0.005(5)	–0.009(5)
N(1)	2*i*	0.1107(7)	0.2293(8)	0.0048(6)	0.017(4)	0.025(5)	0.029(5)	–0.002(4)	0.000(4)	–0.006(4)
O(1)	2*i*	0.2519(6)	0.0467(7)	0.1547(5)	0.023(4)	0.021(4)	0.038(4)	0.002(3)	0.009(3)	0.000(3)
O(7)	2*i*	0.3380(7)	0.1800(7)	–0.3372(6)	0.040(5)	0.027(4)	0.045(5)	–0.006(4)	–0.018(4)	–0.009(4)
C(26)	2*i*	0.377(1)	–0.176(1)	–0.2834(8)	0.044(7)	0.025(6)	0.026(6)	–0.010(5)	–0.006(5)	–0.008(5)
N(2)	2*i*	0.2389(8)	0.3419(8)	0.1025(6)	0.027(5)	0.017(4)	0.021(4)	0.000(4)	–0.006(4)	–0.007(4)
C(14)	2*i*	0.178(1)	–0.283(1)	0.3951(9)	0.027(6)	0.038(7)	0.036(6)	–0.014(5)	–0.002(5)	–0.010(5)
C(17)	2*i*	0.424(1)	–0.257(1)	0.2938(7)	0.021(5)	0.028(6)	0.021(5)	0.001(5)	–0.001(4)	–0.003(4)
O(3)	2*i*	0.0763(6)	–0.1160(7)	0.2585(5)	0.019(4)	0.043(5)	0.033(4)	–0.003(3)	–0.006(3)	0.000(4)
O(10)	2*i*	0.3071(7)	0.3612(7)	–0.1364(6)	0.032(4)	0.026(4)	0.045(5)	–0.010(4)	–0.009(4)	0.000(4)
C(13)	2*i*	0.188(1)	–0.187(1)	0.3033(7)	0.034(6)	0.028(6)	0.013(5)	–0.012(5)	0.001(5)	0.001(4)
C(16)	2*i*	0.411(1)	–0.350(1)	0.3833(8)	0.028(6)	0.032(6)	0.035(6)	–0.003(5)	–0.012(5)	0.004(5)
C(15)	2*i*	0.290(1)	–0.364(1)	0.4338(8)	0.039(7)	0.032(6)	0.022(6)	–0.016(5)	–0.003(5)	0.004(5)
C(22)	2*i*	0.3366(9)	0.056(1)	–0.3477(7)	0.021(5)	0.032(6)	0.021(5)	–0.009(5)	0.000(4)	–0.007(5)
C(8)	2*i*	0.111(1)	0.535(1)	0.2155(8)	0.034(7)	0.031(6)	0.037(7)	0.004(5)	0.008(5)	–0.020(5)
O(9)	2*i*	0.4737(7)	0.3529(7)	–0.0601(6)	0.027(4)	0.036(5)	0.041(5)	–0.009(4)	0.000(4)	–0.003(4)
C(9)	2*i*	0.245(1)	0.501(1)	0.1998(8)	0.039(7)	0.032(6)	0.034(6)	–0.002(5)	–0.007(5)	–0.015(5)
C(12)	2*i*	0.310(1)	–0.172(1)	0.2529(8)	0.046(7)	0.020(5)	0.022(6)	–0.010(5)	–0.007(5)	–0.005(4)
C(21)	2*i*	0.3676(9)	–0.0513(9)	–0.2655(7)	0.025(6)	0.019(5)	0.025(5)	–0.003(4)	–0.006(4)	–0.012(4)
C(1)	2*i*	0.047(1)	0.169(1)	–0.0397(8)	0.029(6)	0.024(6)	0.040(7)	–0.005(5)	–0.007(5)	–0.015(5)
O(11)	2*i*	0.4062(9)	0.5210(8)	–0.1826(7)	0.062(6)	0.024(5)	0.072(7)	–0.010(4)	0.008(5)	0.009(5)
C(7)	2*i*	0.040(1)	0.475(1)	0.1753(8)	0.022(6)	0.035(6)	0.033(6)	–0.002(5)	0.004(5)	–0.011(5)
C(5)	2*i*	0.037(1)	0.310(1)	0.0678(7)	0.025(6)	0.023(5)	0.019(5)	–0.006(5)	0.001(4)	–0.001(4)
C(2)	2*i*	–0.086(1)	0.184(1)	–0.0260(8)	0.024(6)	0.034(6)	0.044(7)	–0.022(5)	0.001(5)	–0.010(5)
C(6)	2*i*	0.106(1)	0.377(1)	0.1166(8)	0.024(6)	0.017(5)	0.034(6)	0.003(4)	–0.003(5)	0.004(5)
C(4)	2*i*	–0.100(1)	0.328(1)	0.0870(9)	0.023(6)	0.041(7)	0.041(7)	–0.003(5)	0.002(5)	–0.019(6)
C(3)	2*i*	–0.160(1)	0.264(1)	0.0407(9)	0.023(6)	0.052(8)	0.052(8)	–0.004(6)	–0.002(6)	–0.012(7)
C(19)	2*i*	0.034(1)	–0.356(2)	0.543(1)	0.07(1)	0.09(1)	0.053(9)	–0.020(9)	0.017(8)	0.016(9)
O(8)	2*i*	0.2930(8)	0.1483(8)	–0.5217(6)	0.060(6)	0.047(5)	0.028(4)	–0.010(4)	–0.016(4)	0.001(4)
C(27)	2*i*	0.212(1)	0.270(1)	–0.332(1)	0.07(1)	0.039(8)	0.09(1)	0.007(7)	–0.045(9)	–0.030(8)
C(28)	2*i*	0.284(1)	0.131(2)	–0.6222(8)	0.08(1)	0.09(1)	0.012(6)	–0.004(8)	–0.017(6)	–0.001(6)
C(18)	2*i*	0.001(1)	–0.009(1)	0.306(1)	0.030(7)	0.051(9)	0.07(1)	0.002(6)	0.000(7)	–0.010(7)
C(24)	2*i*	0.327(1)	–0.087(1)	–0.4570(9)	0.073(9)	0.049(8)	0.023(6)	–0.006(7)	–0.024(6)	–0.011(6)
C(23)	2*i*	0.318(1)	0.037(1)	–0.4446(8)	0.031(6)	0.037(7)	0.022(6)	0.002(5)	–0.012(5)	0.001(5)
C(25)	2*i*	0.356(1)	–0.196(1)	–0.375(1)	0.062(9)	0.038(7)	0.055(8)	–0.008(6)	–0.016(7)	–0.023(7)

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