Crystal structure of bis(2,2'-bipyridine)bis(2-furancarboxylato)tetra[μ -(2-furancarboxylato-*O,O'*)]diterbium(III) 2,2'-bipyridine disolvate, $\text{Tb}_2(\text{C}_5\text{H}_3\text{O}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2)_2 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2$

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The ethanolic solution of 0.5 mmol $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ was dropped in. The mixture was heated under reflux with stirring for 2 h. Single crystals were obtained from the mother liquor after 20 days at room temperature.

Experimental details

The non-H atoms of the disordered 2,2'-bipyridine molecule could not be refined anisotropically. Moreover, its ring bond lengths and angles were restrained to unified values.

Discussion

Hitherto a few crystal structures of rare earth carboxylate complexes have been studied and published [1,2]. The terbium complex with 2-furancarboxylic acid and 2,2'-bipyridine, $\text{Tb}_2(\text{C}_5\text{H}_3\text{O}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2)_2$ reported here is a dimeric molecule (figure, top). Each Tb^{3+} is eight-coordinated by six oxygen atoms from five furancarboxylato groups and two nitrogen atoms from one 2,2'-bipyridine. The title complex crystallizes with one ordered and one disordered solvent bipyridine molecule in the asymmetric unit (figure, bottom). The crystal system and space group are same as $\text{Sm}_2(\text{NO}_3)_2(\text{C}_5\text{H}_3\text{O}_3)_4(\text{C}_{10}\text{H}_8\text{N}_2)_2$ [1] and $\text{Tb}_2(\text{NO}_3)_2(\text{C}_5\text{H}_3\text{O}_3)_4(\text{C}_{12}\text{H}_8\text{N}_2)_2$ [2], but the coordination mode of its carboxylato groups is different to them.

In the title complex, the carboxylato groups of furancarboxylic acids adopt two coordination modes, bidentate chelating and bidentate bridging. A O4–C6–O5 group and a O7–C11–O8 group are in bridging mode, in which two O atoms from one carboxylato group coordinate to two different Tb^{3+} ions, and a O1–C1–O2 group chelates to a same one Tb^{3+} ion with its two O atoms. The bond lengths of $\text{Tb}—\text{O}_{\text{carboxyl}}$ range from 2.320(3) Å to 2.518(3) Å, with an average of 2.392(3) Å. The O–Tb–O angles vary from 53.1(1)° to 144.5(1)°. Tb–N bond lengths are 2.580(4) Å and 2.565(4) Å, respectively.

Abstract

$\text{C}_{70}\text{H}_{50}\text{N}_8\text{O}_{18}\text{Tb}_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.405(4)$ Å, $b = 11.787(5)$ Å, $c = 14.217(6)$ Å, $\alpha = 103.479(6)^\circ$, $\beta = 103.925(6)^\circ$, $\gamma = 93.895(6)^\circ$, $V = 1631.5$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.071$, $T = 293$ K.

Source of material

1.5 mmol 2-furancarboxylic acid and 0.5 mmol 2,2'-bipyridine were dissolved in appropriate amounts of ethanol. The pH of the solution was adjusted to range 6–7 with 2 mol/l NaOH solution.

Table 1. Data collection and handling.

Crystal:	white prism, size 0.12 × 0.16 × 0.22 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	22.30 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	52.72°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	9445, 6573
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 5793
$N(\text{param})_{\text{refined}}$:	438
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(3)	2i		0.1143	0.3468	0.2343	0.071
H(4)	2i		0.2370	0.3579	0.1039	0.100
H(5)	2i		0.4044	0.2305	0.1167	0.116
H(8)	2i		-0.1726	-0.1898	0.0955	0.089
H(9)	2i		-0.0227	-0.1485	-0.0112	0.100
H(10)	2i		0.1749	-0.0268	0.0991	0.087
H(13)	2i		-0.4534	0.1830	0.4389	0.054
H(14)	2i		-0.5064	0.3913	0.4858	0.075
H(15)	2i		-0.2989	0.5154	0.5721	0.079
H(16)	2i		0.4516	0.0235	0.5852	0.052
H(17)	2i		0.6686	0.0612	0.6797	0.065
H(18)	2i		0.7499	0.2507	0.7801	0.082
H(19)	2i		0.6124	0.3959	0.7753	0.075
H(22)	2i		0.4829	0.5251	0.7611	0.074
H(23)	2i		0.3344	0.6590	0.7416	0.083
H(24)	2i		0.1171	0.5945	0.6441	0.074
H(25)	2i		0.0614	0.3986	0.5598	0.060
H(27A)	2i		0.4908	-0.0479	0.1435	0.100
H(28A)	2i		0.6717	0.0364	0.2787	0.110
H(29A)	2i		0.8438	0.1535	0.2601	0.110
H(30A)	2i		0.8285	0.1887	0.1048	0.128

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
N(4)	2i	0.5	0.191(1)	0.4078(9)	0.8621(9)	0.118(4)
C(31)	2i	0.5	0.058(1)	0.405(1)	0.824(1)	0.138(6)
H(31)	2i	0.5	0.0133	0.3507	0.7639	0.166
C(32)	2i	0.5	-0.009(1)	0.481(2)	0.874(2)	0.20(1)
H(32)	2i	0.5	-0.1020	0.4735	0.8529	0.234
C(33)	2i	0.5	0.059(1)	0.568(2)	0.955(1)	0.19(1)
H(33)	2i	0.5	0.0123	0.6181	0.9908	0.228
C(34)	2i	0.5	0.193(1)	0.581(1)	0.983(1)	0.118(5)
H(34)	2i	0.5	0.2406	0.6484	1.0302	0.142
C(35)	2i	0.5	0.2585(9)	0.497(1)	0.9405(9)	0.092(4)
C(36)	2i	0.5	0.3924(9)	0.513(1)	0.982(1)	0.088(4)
C(37)	2i	0.5	0.464(1)	0.4221(9)	0.971(1)	0.109(5)
H(37)	2i	0.5	0.4209	0.3470	0.9358	0.131
C(38)	2i	0.5	0.598(2)	0.439(1)	1.011(3)	0.25(2)
H(38)	2i	0.5	0.6471	0.3766	1.0016	0.295
C(39)	2i	0.5	0.659(1)	0.548(2)	1.064(1)	0.130(6)
H(39)	2i	0.5	0.7499	0.5604	1.0939	0.156
C(40)	2i	0.5	0.587(1)	0.639(1)	1.072(2)	0.156(8)
H(40)	2i	0.5	0.6295	0.7136	1.1096	0.187
N(5)	2i	0.5	0.455(1)	0.6232(8)	1.027(1)	0.122(4)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Tb(1)	2i	0.15438(2)	0.12716(1)	0.52120(1)	0.02533(9)	0.02370(9)	0.0322(1)	0.00277(6)	0.00618(6)	0.00503(6)
O(1)	2i	0.2880(3)	0.1402(3)	0.4051(2)	0.037(1)	0.058(2)	0.044(2)	0.002(1)	0.010(1)	0.019(1)
O(2)	2i	0.1162(3)	0.2414(3)	0.3901(2)	0.066(2)	0.049(2)	0.054(2)	0.019(1)	0.022(2)	0.022(1)
O(3)	2i	0.3478(4)	0.1957(4)	0.2388(3)	0.088(3)	0.100(3)	0.073(3)	-0.012(2)	0.028(2)	0.021(2)
O(4)	2i	0.0053(3)	-0.0058(2)	0.3861(2)	0.046(1)	0.036(1)	0.031(1)	0.003(1)	0.002(1)	0.002(1)
O(5)	2i	-0.1615(3)	-0.1478(2)	0.3054(2)	0.041(1)	0.045(2)	0.037(1)	-0.003(1)	0.009(1)	0.007(1)
O(6)	2i	0.0930(3)	-0.0304(3)	0.2151(2)	0.049(2)	0.071(2)	0.041(2)	-0.010(2)	0.011(1)	0.012(1)
O(7)	2i	-0.0472(2)	0.1985(2)	0.5278(2)	0.028(1)	0.030(1)	0.057(2)	0.005(1)	0.009(1)	0.007(1)
O(8)	2i	-0.2244(2)	0.0583(2)	0.4737(2)	0.030(1)	0.026(1)	0.049(2)	0.0045(9)	0.007(1)	0.010(1)
O(9)	2i	-0.2036(3)	0.3685(2)	0.5524(2)	0.043(2)	0.031(1)	0.077(2)	0.007(1)	0.009(1)	0.007(1)
N(1)	2i	0.4012(3)	0.1816(2)	0.6230(2)	0.031(2)	0.033(2)	0.038(2)	0.000(1)	0.007(1)	0.006(1)
N(2)	2i	0.2330(3)	0.3453(3)	0.6106(2)	0.038(2)	0.030(2)	0.048(2)	0.001(1)	0.008(1)	0.009(1)
C(1)	2i	0.2148(4)	0.2047(3)	0.3625(3)	0.046(2)	0.039(2)	0.039(2)	-0.010(2)	0.009(2)	0.008(2)
C(2)	2i	0.2461(4)	0.2392(4)	0.2760(3)	0.056(3)	0.050(2)	0.043(2)	-0.015(2)	0.013(2)	0.008(2)
C(3)	2i	0.1870(5)	0.3083(4)	0.2243(3)	0.076(3)	0.053(3)	0.046(2)	-0.004(2)	0.006(2)	0.024(2)
C(4)	2i	0.2552(7)	0.3132(5)	0.1503(4)	0.115(5)	0.076(4)	0.050(3)	-0.031(4)	0.002(3)	0.029(3)
C(5)	2i	0.3474(8)	0.2448(7)	0.1582(4)	0.110(5)	0.117(6)	0.052(3)	-0.046(4)	0.028(4)	0.010(3)
C(6)	2i	-0.0620(4)	-0.0804(3)	0.3070(3)	0.038(2)	0.035(2)	0.028(2)	0.006(2)	0.005(2)	0.008(1)
C(7)	2i	-0.0241(4)	-0.0899(3)	0.2134(3)	0.040(2)	0.043(2)	0.035(2)	-0.005(2)	0.007(2)	0.006(2)
C(8)	2i	-0.0889(6)	-0.1449(5)	0.1179(3)	0.077(3)	0.086(4)	0.039(2)	-0.033(3)	0.011(2)	-0.005(2)
C(9)	2i	-0.0051(6)	-0.1215(5)	0.0581(4)	0.109(5)	0.091(4)	0.039(3)	-0.026(3)	0.026(3)	0.000(3)
C(10)	2i	0.1024(5)	-0.0543(5)	0.1189(4)	0.068(3)	0.101(4)	0.051(3)	-0.013(3)	0.028(3)	0.018(3)
C(11)	2i	-0.1699(3)	0.1635(3)	0.5024(2)	0.030(2)	0.029(2)	0.033(2)	0.006(1)	0.008(1)	0.009(1)
C(12)	2i	-0.2602(3)	0.2547(3)	0.5063(3)	0.035(2)	0.027(2)	0.046(2)	0.007(1)	0.012(2)	0.011(2)
C(13)	2i	-0.3926(4)	0.2500(3)	0.4729(3)	0.033(2)	0.037(2)	0.065(3)	0.005(2)	0.012(2)	0.017(2)
C(14)	2i	-0.4223(5)	0.3668(4)	0.4992(4)	0.045(2)	0.053(3)	0.099(4)	0.026(2)	0.024(3)	0.029(3)
C(15)	2i	-0.3078(5)	0.4343(4)	0.5464(4)	0.066(3)	0.034(2)	0.098(4)	0.026(2)	0.024(3)	0.013(2)
C(16)	2i	0.4843(4)	0.0995(3)	0.6247(3)	0.034(2)	0.040(2)	0.052(2)	0.006(2)	0.010(2)	0.007(2)
C(17)	2i	0.6144(4)	0.1208(4)	0.6810(4)	0.035(2)	0.056(3)	0.066(3)	0.009(2)	0.004(2)	0.013(2)
C(18)	2i	0.6627(5)	0.2333(4)	0.7395(4)	0.041(2)	0.067(3)	0.072(3)	0.002(2)	-0.013(2)	0.000(3)
C(19)	2i	0.5803(4)	0.3193(4)	0.7373(4)	0.044(2)	0.051(3)	0.067(3)	-0.005(2)	-0.007(2)	-0.006(2)
C(20)	2i	0.4492(4)	0.2925(3)	0.6784(3)	0.037(2)	0.038(2)	0.039(2)	-0.001(2)	0.006(2)	0.003(2)
C(21)	2i	0.3571(4)	0.3825(3)	0.6698(3)	0.040(2)	0.037(2)	0.043(2)	-0.004(2)	0.009(2)	0.006(2)
C(22)	2i	0.3965(5)	0.5003(4)	0.7202(4)	0.053(3)	0.038(2)	0.074(3)	-0.004(2)	0.000(2)	-0.002(2)
C(23)	2i	0.3079(5)	0.5797(4)	0.7093(4)	0.074(3)	0.031(2)	0.087(4)	-0.004(2)	0.017(3)	-0.007(2)
C(24)	2i	0.1797(5)	0.5423(4)	0.6505(4)	0.063(3)	0.034(2)	0.088(4)	0.008(2)	0.020(3)	0.013(2)
C(25)	2i	0.1472(4)	0.4244(3)	0.6014(3)	0.044(2)	0.033(2)	0.069(3)	0.004(2)	0.009(2)	0.013(2)
N(3)	2i	0.6561(6)	0.0945(6)	0.0326(4)	0.112(5)	0.123(5)	0.073(3)	0.022(4)	0.043(3)	0.034(3)
C(26)	2i	0.5568(6)	0.0246(5)	0.0443(4)	0.092(4)	0.089(4)	0.060(3)	0.044(3)	0.042(3)	0.033(3)
C(27)	2i	0.5601(7)	0.0007(6)	0.1364(4)	0.103(4)	0.106(5)	0.061(3)	0.044(4)	0.030(3)	0.042(3)
C(28)	2i	0.6685(8)	0.0508(6)	0.2166(5)	0.112(5)	0.110(5)	0.069(4)	0.050(4)	0.027(4)	0.040(4)
C(29)	2i	0.7698(8)	0.1203(6)	0.2064(5)	0.108(5)	0.096(5)	0.076(4)	0.056(4)	0.022(4)	0.022(3)
C(30)	2i	0.7594(8)	0.1403(7)	0.1125(6)	0.107(5)	0.118(6)	0.097(5)	0.016(5)	0.041(5)	0.018(4)

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