Crystal structure of di(1,10-phenanthroline-*N*,*N*′)di[μ-(2-furancarboxylato-*O*,*O*′)-μ-(2-furancarboxylato-*O*,*O*′:*O*′)]di(nitrato)diterbium(III), $Tb_2(NO_3)_2(C_5H_3O_3)_4(C_{12}H_8N_2)_2$

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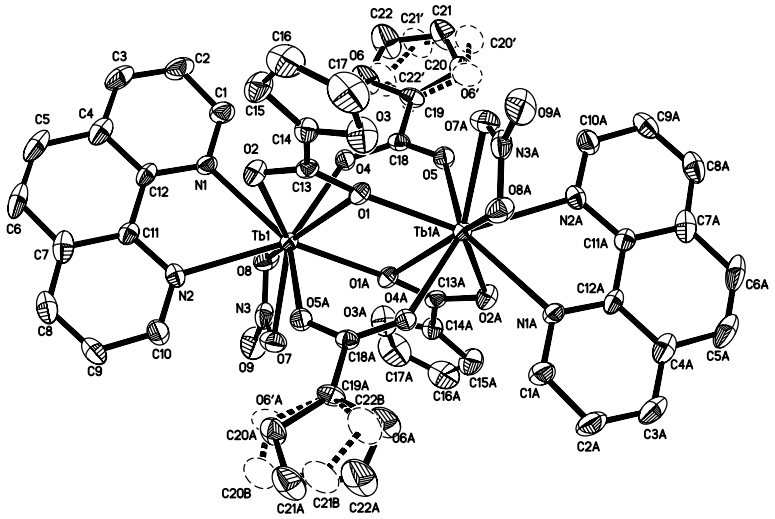
Received June 18, 2003, accepted and available on-line September 8, 2003; CCDC-No. 1267/1108



Abstract

$C_{22}H_{14}N_3O_9Tb$, triclinic, $P\bar{1}$ (No. 2), a = 10.383(3) Å, b = 10.512(3) Å, c = 11.001(3) Å, α = 81.201(6)°, β = 88.491(6)°, γ = 67.595(5)°, V = 1096.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.067, T = 293 K.

Source of material

4 mmol 2-furancarboxylic acid, 0.5 mmol 1,10-phenanthroline and 1.3 mmol 8-hydroxyquinoline were dissolved in 20 ml ethanol. The 0.5 mmol $Tb(NO_3)_3 \cdot 6H_2O$ dissolved in 10 ml ethanol - H_2O was added to the solution. Single crystal were obtained after 4 days at room temperature.

Discussion

In the title compound (**I**), each Tb^{3+} ion is coordinated to five O atoms from four furancarboxylato groups, to two O atoms from nitrato and to two *N* atoms from 1,10-phenanthroline molecule, giving a coordination number of 9. The carboxylate groups of furancarboxylic acid adopt two different coordination modes. Carboxylate groups O4–C18–O5 are in bridging mode in which two O atoms coordinate to two different Tb^{3+} ions. O1–C13–O2 groups are in a chelating-bridging coordination mode, in which two O atoms chelate one Tb^{3+} ion and one of the oxygen atoms is linked to another Tb^{3+} ion. The two central Tb^{3+} ions are connected by four carboxylate groups of furancarboxylic acid through their carboxyl oxygen atoms, forming a dimeric unit. Unlike $La(C_5H_3O_3)_3 \cdot 2H_2O$ (**II**) [1] where they form an infinite polymeric chain, the carboxylate groups of furancarboxylic acid in **I** are in three different coordination modes, chelating, bridging and bridging-chelating. The bond lengths Tb–$O_{carboxyl}$ range from 2.319(3) Å to 2.692 (3) Å, with a mean value of 2.419(3) Å. The average Tb—O distance of 2.474(3) Å for the tridentate bridging carboxyl is larger than that for the bidentate bridging carboxyl (2.338(3) Å) and the distance for Tb1—O1 is the largest one, which is reasonable. The average Tb—$O_{carboxyl}$ distance in complex **I** is shorter than that of 2.573 Å in complex **II**. This is because of the larger steric effect of 1,10-phenanthroline and the larger radius of La^{3+}. The O7 and O8 atoms from the nitrato coordinate to the Tb^{3+} ion in bidentate chelating mode. The bond distance d(Tb1—O7) is 2.514(4) Å, and d(Tb1—O8) is 2.424(4) Å. The bond distances of the N atom and O atoms from nitrato group are d(N3—O7) = 1.255(6) Å, d(N3—O8) = 1.272(6) Å and d(N3—O9) = 1.238(6) Å, respectively. The 1,10-phenanthroline chelates the Tb^{3+} ion with two N atoms. The distances Tb—N are 2.551(4) Å and 2.567(4) Å, respectively.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.18 × 0.22 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	32.86 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6409, 4475
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3525
$N(param)_{refined}$:	346
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	2*i*		0.1504	0.5383	0.0723	0.060
H(2)	2*i*		0.1348	0.3213	0.1011	0.074
H(3)	2*i*		0.0029	0.2676	0.2559	0.070
H(5)	2*i*		–0.1559	0.3426	0.4295	0.080
H(6)	2*i*		–0.2659	0.5035	0.5502	0.079
H(8)	2*i*		–0.3260	0.7457	0.6012	0.070
H(9A)	2*i*		–0.2961	0.9532	0.5631	0.064
H(10)	2*i*		–0.1613	0.9900	0.4018	0.057
H(15)	2*i*		–0.4139	0.8098	–0.0500	0.071

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(16)	2*i*		–0.5967	0.9431	–0.2202	0.088
H(17)	2*i*		–0.5484	1.1411	–0.3098	0.098
H(20A)	2*i*	0.64(2)	0.3677	0.7458	–0.3238	0.059
H(21A)	2*i*	0.64	0.5269	0.5020	–0.3198	0.082
H(22A)	2*i*	0.64	0.4890	0.3652	–0.1302	0.108
H(22B)	2*i*	0.36	0.3845	0.5001	–0.0325	0.090
H(20B)	2*i*	0.36	0.4896	0.5905	–0.3757	0.081
H(21B)	2*i*	0.36	0.5437	0.4068	–0.1952	0.078

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tb(1)	2*i*		0.01391(3)	0.86697(2)	0.15173(2)	0.0310(1)	0.0252(1)	0.0291(1)	–0.0121(1)	0.0030(1)	–0.0047(1)
N(1)	2*i*		0.0244(4)	0.6166(4)	0.2029(4)	0.050(3)	0.027(2)	0.035(3)	–0.017(2)	–0.003(2)	–0.003(2)
N(2)	2*i*		–0.1134(4)	0.8146(4)	0.3424(4)	0.034(2)	0.045(2)	0.032(3)	–0.016(2)	0.006(2)	–0.004(2)
N(3)	2*i*		0.2113(5)	0.8172(6)	0.3504(5)	0.058(4)	0.066(4)	0.035(3)	–0.041(3)	–0.010(3)	0.010(3)
O(1)	2*i*		–0.1301(3)	0.9948(3)	–0.0617(3)	0.036(2)	0.043(2)	0.043(2)	–0.026(2)	0.003(2)	–0.008(2)
O(2)	2*i*		–0.1853(3)	0.8429(3)	0.0657(4)	0.039(2)	0.039(2)	0.050(3)	–0.019(2)	–0.005(2)	0.002(2)
O(3)	2*i*		–0.3780(4)	1.0722(4)	–0.1937(4)	0.049(3)	0.079(3)	0.060(3)	–0.023(2)	–0.009(2)	0.003(3)
O(4)	2*i*		0.1433(3)	0.7586(3)	–0.0054(3)	0.052(2)	0.026(2)	0.036(2)	–0.012(2)	0.012(2)	–0.006(2)
O(5)	2*i*		0.1484(3)	0.9096(3)	–0.1712(3)	0.040(2)	0.030(2)	0.040(2)	–0.010(2)	0.007(2)	–0.005(2)
O(7)	2*i*		0.1081(4)	0.9306(4)	0.3314(4)	0.054(3)	0.061(3)	0.047(3)	–0.025(2)	0.003(2)	–0.022(2)
O(8)	2*i*		0.2216(4)	0.7292(4)	0.2794(4)	0.054(2)	0.036(2)	0.053(3)	–0.015(2)	–0.013(2)	–0.002(2)
O(9)	2*i*		0.2984(5)	0.7906(5)	0.4349(4)	0.092(4)	0.103(4)	0.049(3)	–0.057(3)	–0.040(3)	0.020(3)
C(1)	2*i*		0.0947(6)	0.5182(5)	0.1337(6)	0.067(4)	0.034(3)	0.050(4)	–0.018(3)	–0.002(3)	–0.007(3)
C(2)	2*i*		0.0867(7)	0.3865(5)	0.1513(6)	0.084(5)	0.030(3)	0.071(5)	–0.020(3)	–0.008(4)	–0.010(3)
C(3)	2*i*		0.0079(7)	0.3552(6)	0.2423(6)	0.072(4)	0.032(3)	0.073(5)	–0.025(3)	–0.023(4)	0.005(3)
C(4)	2*i*		–0.0656(6)	0.4549(6)	0.3151(6)	0.051(4)	0.047(3)	0.056(4)	–0.028(3)	–0.023(3)	0.014(3)
C(5)	2*i*		–0.1479(7)	0.4287(7)	0.4141(7)	0.075(5)	0.054(4)	0.084(6)	–0.047(4)	–0.022(4)	0.019(4)
C(6)	2*i*		–0.2142(7)	0.5248(7)	0.4856(7)	0.066(5)	0.073(4)	0.067(5)	–0.050(4)	–0.009(4)	0.026(4)
C(7)	2*i*		–0.2069(6)	0.6589(6)	0.4644(6)	0.036(3)	0.070(4)	0.046(4)	–0.028(3)	–0.011(3)	0.017(3)
C(8)	2*i*		–0.2713(6)	0.7616(7)	0.5369(6)	0.052(4)	0.086(5)	0.041(4)	–0.036(4)	0.007(3)	0.003(4)
C(9)	2*i*		–0.2545(6)	0.8845(6)	0.5143(5)	0.053(4)	0.073(4)	0.035(4)	–0.023(3)	0.012(3)	–0.015(3)
C(10)	2*i*		–0.1735(6)	0.9059(6)	0.4160(5)	0.051(4)	0.057(4)	0.039(4)	–0.026(3)	0.008(3)	–0.008(3)
C(11)	2*i*		–0.1269(5)	0.6897(5)	0.3673(5)	0.036(3)	0.040(3)	0.034(3)	–0.021(2)	–0.010(3)	0.001(3)
C(12)	2*i*		–0.0545(5)	0.5856(5)	0.2920(5)	0.044(3)	0.034(3)	0.040(3)	–0.023(3)	–0.015(3)	0.009(3)
C(13)	2*i*		–0.2103(5)	0.9318(5)	–0.0293(5)	0.030(3)	0.027(3)	0.041(3)	–0.010(2)	0.006(3)	–0.013(3)
C(14)	2*i*		–0.3341(5)	0.9589(5)	–0.1046(5)	0.032(3)	0.042(3)	0.042(3)	–0.015(3)	0.000(3)	–0.005(3)
C(15)	2*i*		–0.4203(6)	0.8903(6)	–0.1026(6)	0.049(4)	0.070(4)	0.073(5)	–0.039(3)	0.008(4)	–0.014(4)
C(16)	2*i*		–0.5234(7)	0.9658(8)	–0.1975(7)	0.039(4)	0.120(6)	0.080(6)	–0.043(4)	0.001(4)	–0.036(5)
C(17)	2*i*		–0.4952(7)	1.0731(8)	–0.2468(7)	0.042(4)	0.120(7)	0.069(5)	–0.018(4)	–0.028(4)	–0.004(5)
C(18)	2*i*		0.1884(5)	0.7914(5)	–0.1068(5)	0.029(3)	0.037(3)	0.035(3)	–0.013(2)	0.001(2)	–0.013(3)
O(6)	2*i*	0.64(2)	0.341(1)	0.549(1)	–0.0920(8)	0.074(7)	0.041(4)	0.058(5)	0.013(4)	0.019(4)	–0.010(4)
C(19)	2*i*	0.64	0.299(1)	0.680(1)	–0.158(1)	0.033(8)	0.038(8)	0.041(8)	–0.002(8)	0.005(8)	–0.018(8)
C(20)	2*i*	0.64	0.375(2)	0.672(1)	–0.262(1)	0.041(7)	0.049(6)	0.052(6)	–0.010(5)	0.018(5)	–0.013(5)
C(21)	2*i*	0.64	0.464(1)	0.537(2)	–0.260(1)	0.058(7)	0.061(9)	0.057(9)	0.011(6)	0.015(7)	–0.009(8)
C(22)	2*i*	0.64	0.442(1)	0.4605(9)	–0.155(1)	0.10(1)	0.053(7)	0.08(1)	0.017(7)	0.032(8)	–0.008(7)
C(22′)	2*i*	0.36	0.387(3)	0.548(3)	–0.111(2)	0.06(1)	0.06(1)	0.07(1)	0.01(1)	0.02(1)	–0.01(1)
C(19′)	2*i*	0.36	0.302(3)	0.682(2)	–0.155(2)	0.04(1)	0.04(1)	0.05(1)	–0.02(1)	0.01(1)	–0.01(1)
O(6′)	2*i*	0.36	0.338(2)	0.713(2)	–0.273(2)	0.032(9)	0.050(9)	0.07(1)	0.001(7)	0.015(7)	–0.031(7)
C(20′)	2*i*	0.36	0.445(2)	0.598(3)	–0.301(2)	0.05(1)	0.07(1)	0.08(2)	–0.01(1)	0.03(1)	–0.03(1)
C(21′)	2*i*	0.36	0.475(2)	0.496(2)	–0.201(2)	0.05(1)	0.05(1)	0.06(2)	0.025(9)	0.01(1)	–0.01(1)

Acknowledgment. We are grateful to the Natural Science Foundation of Beijing for the grant No.2022007 and the Science Technology Foundation of Beijing for financing studies abroad.

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