Crystal structure of di(2,2′-bipyridine)tetra(μ-3-methoxylbenzoato-*O*,*O*′)-di(3-methoxybenzoato)diterbium(III), $Tb_2(C_8H_7O_3)_6(C_{10}H_8N_2)_2$

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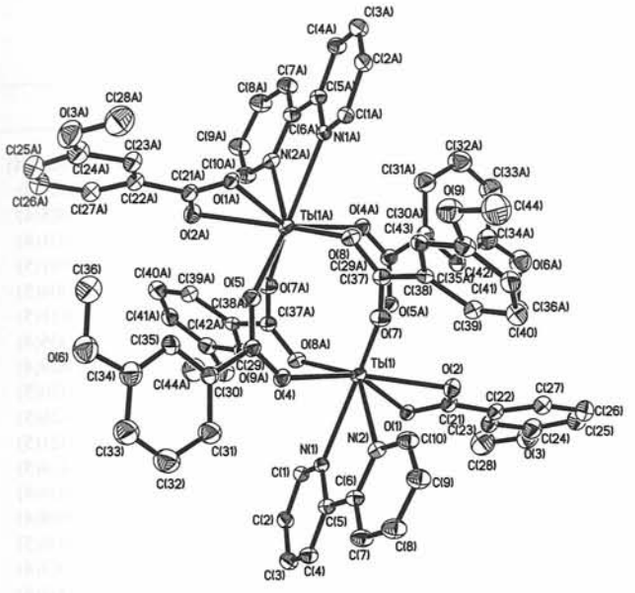

Abstract

$C_{68}H_{58}N_4O_{18}Tb_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 10.582(4)$ Å, $b = 16.149(5)$ Å, $c = 18.821(6)$ Å, $\beta = 100.554(6)°$, $V = 3161.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.058$, $wR_{ref}(F^2) = 0.178$, $T = 293$ K.

Source of material

1.5 mmol 3-methoxybenzoic acid and 0.5 mmol 2,2′-bipyridine were dissolved in 20 ml 95% ethanol. The pH of the mixed solution was controlled in a range of 6 – 7 with 2 mol NaOH solution. Then, 0.5 mmol $Tb(NO_3)_3 \cdot 6H_2O$ dissolved in 5 ml 95% ethanol were added in. The mixture was heated under reflux with stirring for 3 h. A precipitate was formed. Single crystals were obtained from the mother liquor after crystallization for 20 days at room temperature.

Discussion

The title compound $Tb_2(C_8H_7O_3)_6(C_{10}H_8N_2)_2$ (**I**) is a centrosymmetric dimeric molecule. The two Tb^{3+} ions are bridged by four bidentate-bridging carboxylate groups. Each terbium ion is eight-coordinate to six O atoms from 3-methoxybenzoate and two N atoms from 2,2′-bipyridine. The coordination modes of 3-methoxybenzoate are bidentate-chelating and bidentate-bridging. It is similar to complex $Eu(C_8H_7O_3)_3 \cdot 2H_2O$ (**II**) [1] in coordination types of carboxylate groups. But complex **II** is an infinite polymeric chain structure through bridging carboxylate groups. Generally, a lanthanide complex with organic acids and diimines is a dimeric one, such as the title complex and $Nd_2(C_9H_9O_4)_6(C_{10}H_8N_2)_2$ (**III**) [2]. The title complex differes from complex **III** by coordination modes of carboxylate groups. It is obvious that different number of the methoxyl groups on the benzene ring, making a different steric effect in the complexes, leads to the structural difference of the two complexes.

Carboxylate group O1–C21–O2 coordinate to one Tb^{3+} ion with two oxygen atoms in a bidentate-chelating mode, and the average distance for terbium-oxygen is 2.414(8)Å. Carboxylate group O7–C37–O8 coordinate to two Tb^{3+} ions with two oxygen atoms in a bidentate- bridging mode, and the average distance for terbium-oxygen is 2.333(8) Å. The average distance between terbium and oxygen from the bidentate-chelating carboxyl is larger than that from the bidentate-bridging carboxylate groups. Because O1–C21–O2–Tb1 is an unstable four-membered ring. The bond angle for O7–C37–O8 in bidentate-bridging is 125(1)°. It is larger than that of 122(1)° for O1–C21–O2 in bidentate-chelating. The 2,2′-bipyridine ligand with two N atoms chelates to Tb^{3+} ion to form a five-membered ring in complex **I**. The Tb—N distances are 2.577(9) Å and 2.569(9) Å, respectively, with a mean value of 2.573 Å.

Table 1. Data collection and handling.

Crystal:	white prism, size 0.16 × 0.18 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.95 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13017, 5597
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2709
$N(param)_{refined}$:	418
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(1)	4*e*	1.4320	0.0730	0.4979	0.063
H(2)	4*e*	1.6053	0.1502	0.4813	0.074
H(3)	4*e*	1.5876	0.2319	0.3795	0.081
H(4)	4*e*	1.3974	0.2322	0.2975	0.076
H(7)	4*e*	1.2209	0.2251	0.2245	0.087
H(8)	4*e*	1.0378	0.1988	0.1389	0.102

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	4*e*	0.9056	0.0928	0.1581	0.098
H(10)	4*e*	0.9493	0.0228	0.2651	0.085
H(23)	4*e*	1.4744	–0.1887	0.4011	0.094
H(25)	4*e*	1.4398	–0.3883	0.2737	0.124
H(26)	4*e*	1.2509	–0.3450	0.2131	0.118
H(27)	4*e*	1.1533	–0.2242	0.2518	0.102
H(28A)	4*e*	1.6987	–0.2224	0.4126	0.211
H(28B)	4*e*	1.7508	–0.3059	0.4491	0.211
H(28C)	4*e*	1.6252	–0.2664	0.4672	0.211
H(31)	4*e*	1.0819	0.2638	0.4039	0.118
H(32)	4*e*	1.0629	0.4080	0.3920	0.143
H(33)	4*e*	0.9049	0.4783	0.4383	0.139

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(35)	4*e*	0.7979	0.2654	0.5209	0.079
H(36A)	4*e*	0.6001	0.3578	0.5024	0.185
H(36B)	4*e*	0.6139	0.4262	0.5625	0.185
H(36C)	4*e*	0.7025	0.3476	0.5735	0.185
H(39)	4*e*	0.8453	–0.0986	0.2786	0.085
H(40)	4*e*	0.7187	–0.1234	0.1667	0.105
H(41)	4*e*	0.5029	–0.0841	0.1531	0.096
H(43)	4*e*	0.5475	–0.0085	0.3592	0.065
H(44A)	4*e*	0.3105	0.0069	0.1512	0.209
H(44B)	4*e*	0.2101	–0.0325	0.1930	0.209
H(44C)	4*e*	0.3131	–0.0886	0.1665	0.209

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}
Tb(1)	4*e*	1.13386(5)	0.00001(4)	0.42732(3)	0.0494(3)	0.0474(3)	0.0438(3)	0.0089(4)	0.0176(2)	0.0069(4)
N(1)	4*e*	1.3143(9)	0.1006(6)	0.4092(5)	0.047(4)	0.050(4)	0.045(4)	–0.003(4)	0.011(4)	0.000(4)
N(2)	4*e*	1.1083(9)	0.0783(6)	0.3067(5)	0.053(5)	0.064(5)	0.051(5)	0.004(4)	0.012(4)	0.005(4)
C(1)	4*e*	1.425(1)	0.1045(7)	0.4559(6)	0.055(5)	0.050(5)	0.053(5)	–0.002(4)	0.011(4)	0.001(4)
C(2)	4*e*	1.530(1)	0.1513(7)	0.4471(7)	0.064(5)	0.059(5)	0.061(5)	–0.006(5)	0.007(5)	0.001(5)
C(3)	4*e*	1.519(1)	0.1990(8)	0.3872(7)	0.069(5)	0.068(5)	0.065(5)	–0.009(5)	0.008(5)	0.004(5)
C(4)	4*e*	1.407(1)	0.1983(8)	0.3380(7)	0.067(5)	0.066(5)	0.057(5)	–0.003(5)	0.013(5)	0.011(5)
C(5)	4*e*	1.307(1)	0.1465(7)	0.3488(6)	0.052(5)	0.054(5)	0.054(5)	0.002(4)	0.014(4)	0.006(4)
C(6)	4*e*	1.190(1)	0.1371(7)	0.2943(7)	0.057(5)	0.059(5)	0.057(5)	0.001(4)	0.014(4)	0.009(4)
C(7)	4*e*	1.165(1)	0.1831(8)	0.2322(7)	0.071(5)	0.083(6)	0.063(5)	–0.010(5)	0.007(5)	0.020(5)
C(8)	4*e*	1.056(1)	0.1673(9)	0.1809(8)	0.081(6)	0.101(6)	0.071(6)	–0.005(5)	0.006(5)	0.026(5)
C(9)	4*e*	0.978(1)	0.1063(9)	0.1925(8)	0.076(6)	0.094(6)	0.073(6)	–0.004(5)	0.005(5)	0.021(5)
C(10)	4*e*	1.006(1)	0.0642(8)	0.2564(7)	0.067(5)	0.081(6)	0.064(5)	–0.004(5)	0.009(5)	0.018(5)
O(1)	4*e*	1.3133(7)	–0.0798(5)	0.4062(4)	0.055(4)	0.052(4)	0.054(4)	0.005(4)	0.020(4)	–0.004(4)
O(2)	4*e*	1.1308(8)	–0.1037(5)	0.3327(4)	0.063(5)	0.074(5)	0.056(5)	0.004(4)	0.007(4)	–0.009(4)
O(3)	4*e*	1.599(1)	–0.3201(7)	0.3714(7)	0.123(6)	0.115(6)	0.134(6)	0.028(5)	0.045(5)	–0.008(5)
C(21)	4*e*	1.245(1)	–0.1221(8)	0.3576(7)	0.065(5)	0.063(5)	0.058(5)	0.003(4)	0.022(4)	–0.003(4)
C(22)	4*e*	1.306(1)	–0.1972(8)	0.3304(7)	0.077(5)	0.065(5)	0.070(5)	–0.003(5)	0.035(4)	–0.008(4)
C(23)	4*e*	1.428(1)	–0.2193(8)	0.3634(8)	0.087(6)	0.070(6)	0.084(6)	0.004(5)	0.035(5)	–0.010(5)
C(24)	4*e*	1.477(1)	–0.291(1)	0.3367(9)	0.106(6)	0.096(6)	0.104(6)	0.007(5)	0.039(5)	–0.006(5)
C(25)	4*e*	1.407(2)	–0.338(1)	0.2855(9)	0.116(6)	0.093(6)	0.109(6)	–0.001(6)	0.042(6)	–0.017(5)
C(26)	4*e*	1.294(2)	–0.314(1)	0.2518(9)	0.110(6)	0.092(6)	0.100(6)	–0.009(6)	0.036(6)	–0.021(5)
C(27)	4*e*	1.235(2)	–0.2411(9)	0.2741(8)	0.094(6)	0.081(6)	0.087(6)	–0.008(5)	0.037(5)	–0.012(5)
C(28)	4*e*	1.675(2)	–0.275(1)	0.4299(9)	0.130(9)	0.15(1)	0.15(1)	0.022(8)	0.034(8)	0.000(8)
O(4)	4*e*	1.0543(8)	0.1290(5)	0.4524(4)	0.069(5)	0.054(4)	0.067(5)	0.012(4)	0.023(4)	0.000(4)
O(5)	4*e*	0.8917(8)	0.1251(5)	0.5130(4)	0.075(5)	0.055(4)	0.063(5)	0.004(4)	0.022(4)	0.008(4)
O(6)	4*e*	0.751(1)	0.4278(7)	0.5060(6)	0.125(6)	0.109(6)	0.127(6)	0.012(5)	0.028(5)	–0.004(5)
C(29)	4*e*	0.964(1)	0.1606(8)	0.4771(7)	0.063(5)	0.053(5)	0.058(5)	0.008(4)	0.019(4)	0.004(4)
C(30)	4*e*	0.943(1)	0.2518(8)	0.4650(7)	0.069(5)	0.055(5)	0.070(5)	0.003(4)	0.024(4)	0.003(4)
C(31)	4*e*	1.022(2)	0.293(1)	0.4247(8)	0.104(6)	0.084(6)	0.112(6)	0.006(5)	0.035(5)	0.010(5)
C(32)	4*e*	1.008(2)	0.379(1)	0.4166(9)	0.127(7)	0.104(6)	0.132(7)	0.001(6)	0.038(6)	0.017(6)
C(33)	4*e*	0.916(2)	0.422(1)	0.444(1)	0.125(7)	0.099(6)	0.125(7)	0.008(6)	0.031(6)	0.012(6)
C(34)	4*e*	0.841(1)	0.375(1)	0.4819(9)	0.100(6)	0.086(6)	0.107(6)	0.014(5)	0.026(5)	–0.001(5)
C(35)	4*e*	0.851(1)	0.2928(8)	0.4942(7)	0.070(5)	0.055(5)	0.075(5)	0.004(5)	0.018(5)	–0.002(5)
C(36)	4*e*	0.660(2)	0.387(1)	0.5387(9)	0.126(9)	0.125(9)	0.123(9)	0.004(8)	0.033(7)	–0.005(7)
O(7)	4*e*	0.9163(8)	–0.0212(5)	0.3968(5)	0.056(4)	0.071(5)	0.077(5)	0.001(4)	0.015(4)	0.010(4)
O(8)	4*e*	0.7512(7)	–0.0227(5)	0.4546(4)	0.057(4)	0.069(5)	0.052(4)	0.003(3)	0.015(3)	0.006(3)
O(9)	4*e*	0.386(1)	–0.0212(6)	0.2541(6)	0.099(5)	0.110(6)	0.099(6)	–0.006(5)	0.017(5)	0.009(5)
C(37)	4*e*	0.799(1)	–0.0298(7)	0.3996(7)	0.050(4)	0.056(5)	0.058(5)	0.002(4)	0.013(4)	0.006(4)
C(38)	4*e*	0.711(1)	–0.0489(7)	0.3305(6)	0.061(5)	0.049(4)	0.053(5)	–0.009(4)	0.020(4)	0.002(4)
C(39)	4*e*	0.759(1)	–0.0847(8)	0.2714(7)	0.076(6)	0.071(5)	0.070(5)	–0.006(5)	0.027(5)	–0.004(5)
C(40)	4*e*	0.685(2)	–0.1001(9)	0.2044(8)	0.092(6)	0.083(6)	0.089(6)	–0.014(5)	0.017(5)	–0.006(5)
C(41)	4*e*	0.558(2)	–0.0785(8)	0.1976(8)	0.095(6)	0.075(6)	0.070(6)	–0.014(5)	0.014(5)	–0.007(5)
C(42)	4*e*	0.512(1)	–0.0494(9)	0.2543(8)	0.077(5)	0.071(5)	0.078(5)	–0.008(5)	0.014(5)	0.008(5)
C(43)	4*e*	0.584(1)	–0.0312(7)	0.3223(6)	0.062(5)	0.050(5)	0.052(5)	–0.008(4)	0.012(4)	0.002(4)
C(44)	4*e*	0.297(2)	–0.035(1)	0.1852(8)	0.133(9)	0.151(9)	0.130(9)	–0.009(8)	0.014(8)	–0.005(8)

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References

1. Li, X.; Jin, Q.-H.; Zou, Y.-Q.; Yu, K.-B.: Crystal structure of *catena*-poly [(diaqua(3-methoxybenzato-*O*,*O'*)europium-bis-μ-3-methoxybenzato-*O*,*O'*:*O'*-diaqua(3-methoxybenzato-*O*,*O'*)-europium-bis-μ-3-methoxybenzato-*O*,*O'*:*O'*], $C_{24}H_{25}EuO_{11}$. Z. Kristallogr. NCS **216** (2001) 285-286.
2. Li, X; Zou Y.-Q.: Crystal structure of di(2,2′-bipyridine)di(μ-2,3-dimethoxylbenzoato-*O*,*O'*)di(μ-2,3-dimethoxylbenzoato-*O*,*O'*:*O'*)di(2,3-dimethoxylbenzoato)dineodymium(III), $Nd_2(C_9H_9O_4)_6(C_{10}H_8N_2)_2$. Z. Kristallogr. NCS **218** (2003) 213-215.
3. Sheldrick,G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
4. Sheldrick,G.M.: SHELXL-97, program for the refinement of crystal structure. University of Göttingen, Germany 1997.