Crystal structure of di(μ-3,5-dinitrobenzoato-*O*,*O*′)di(μ-3,5-dinitrobenzoato-*O*,*O*:*O*′)di(3,5-dinitrobenzoato-*O*,*O*′)di(1,10-phenanthroline-*N*,*N*′)-diterbium(III), $Tb_2(C_{12}H_8N_2)_2(C_7H_3N_2O_6)_6$

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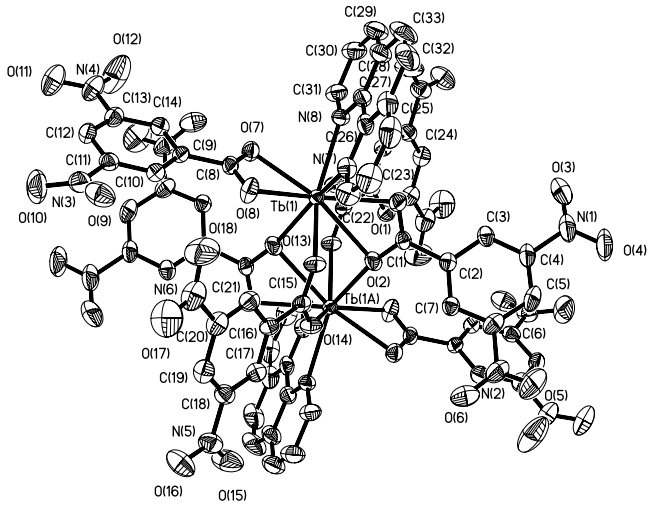

Abstract

$C_{66}H_{34}N_{16}O_{36}Tb_2$, triclinic, $P\bar{1}$ (No. 2), a = 12.027(7) Å, b = 12.908(7) Å, c = 13.210(7) Å, α = 104.086(7)°, β = 113.774(7)°, γ = 100.425(7)°, V = 1728.1 Å^3, Z = 1, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.042, T = 298 K.

Source of material

The title compound was synthesized by the hydrothermal method from a mixture of 3,5-dinitrobenzoic acid (0.5 mmol), $Tb(ClO_4)_3 \cdot 6H_2O$ (0.5 mmol), 1,10-phenanthroline (2.0 mmol) and water (20.0 mL) in a 30.0 mL teflon-lined stainless steel reactor. The solution was heated to 433 K for five days. After the reaction system was slowly cooled to room temperature, the colorless prism crystals were collected and washed with distilled water. The yield is ca. 34% based on Tb(III). The substance is insoluble in water and common organic solvents.

Discussion

In recent years, considerable efforts to novel rare earth aromatic carboxylate complexes have been actively made, owing to their interesting structures, coordination modes and functional properties [1-2]. Carboxylate anions possess versatile binding modes and lanthanide ions are well known for the variable coordination number from 3 to 12 [3], so the above anions and ions have been widely utilized in preparing many kinds of structures, such as dimeric, one-, two-, three-dimensional frameworks [4-5]. Although many complexes with benzoate or its derivatives, which were often obtained from conventional solution reactions, have been reported [6], the development of synthetic routs to systems containing 3,5-dinitrobenzoate anions is less well explored.

A dimeric unit of the title compound is constituted by two rare earth atoms, six 3,5-dinitrobenzoato anions and two 1,10-phenanthroline molecules with Tb···Tb separation of 4.095 Å and a center of symmetry. The coordination of Tb atom can be described as a monocapped square antiprism with nine ligands. The coordination involves seven oxygen atoms from five 3,5-dinitrobenzoato anions and two nitrogen atoms from one 1,10-phenanthroline molecule. It is well known, carboxylate groups often have one or two binding modes and have three binding modes in the same complex containing 3,5-dinitrobenzoate anions. In the complex of $[Cu_3(C_7H_3N_2O_6)_6(CH_4O)_2]$ [7], six 3,5-dinitrobenzoate anions only have one bridging coordination mode. Within polymeric chains of complexes $[Gd_2(H_2O)_4(C_7H_3N_2O_6)_6](2H_2O)$ [8] and $[Ce_2(H_2O)_4(C_7H_3N_2O_6)_6]$ [9], the carboxylate groups also show only one bridging bidentate mode. While in the complexes of $[Ca(C_7H_3N_2O_6)(C_6H_{14}O_4)(H_2O)](C_7H_3N_2O_6) \cdot H_2O$ [10], one 3,5-dinitrobenzoate anion exhibits the bridging bidentate mode and the other is free, and in the complex of $[Co(C_7H_3N_2O_6)_2(H_2O)_4] \cdot 4H_2O$ [11], the coordination modes of two 3,5-dinitrobenzoate anions are mono-dentate. The title compound has a novel dimeric structure for six 3,5-dinitrobenzoate anions showing three coordination modes. The first mode is chelating bidentate with distances of 2.481(2) Å and 2.402(2) Å for O7—Tb1 and O8—Tb1, respectively. The second mode is bridging bidentate through O13 and O14 with distances of 2.336(2) Å and 2.356(2) Å. The third mode is bridging tridentate with distances of 2.444(2) Å, 2.344(2) Å and 2.779(2) Å for O1—Tb1, O2—Tb1 and O2—Tb1 (–x, –y, –z), respectively, which are apparently important for rational design and constitution of new framework structures.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.43 × 0.52 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.45 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, 720 frames, $\Delta\omega$ = 2°
$2\theta_{max}$:	54.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9974, 7024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6130
$N(param)_{refined}$:	609
Programs:	SHELX-97 [12], ORTEP-II [13]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	–0.201(3)	–0.286(2)	0.133(2)	0.056(9)
H(2)	2*i*	–0.561(3)	–0.301(2)	0.031(2)	0.044(9)
H(3)	2*i*	–0.352(3)	–0.086(2)	–0.026(2)	0.038(8)
H(4)	2*i*	0.372(2)	0.443(2)	0.332(2)	0.035(7)
H(5)	2*i*	0.728(2)	0.579(2)	0.393(2)	0.027(7)
H(6)	2*i*	0.583(3)	0.249(2)	0.292(2)	0.050(9)
H(7)	2*i*	–0.195(3)	0.289(2)	–0.083(2)	0.044(9)
H(8)	2*i*	–0.061(3)	0.592(2)	0.132(2)	0.045(9)
H(9)	2*i*	0.056(3)	0.346(2)	0.239(2)	0.049(8)
H(10)	2*i*	0.017(3)	0.209(2)	0.338(2)	0.037(8)
H(11)	2*i*	–0.020(3)	0.257(2)	0.503(2)	0.043(8)
H(12)	2*i*	0.081(3)	0.176(3)	0.651(3)	0.07(1)
H(13)	2*i*	0.413(4)	–0.160(3)	0.539(3)	0.10(1)
H(14)	2*i*	0.441(3)	–0.178(3)	0.367(3)	0.06(1)
H(15)	2*i*	0.339(3)	–0.084(3)	0.244(3)	0.07(1)
H(16)	2*i*	0.202(3)	0.043(3)	0.703(3)	0.09(1)
H(17)	2*i*	0.324(4)	–0.050(3)	0.668(3)	0.08(1)

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)	2*i*	0.12750(1)	0.05131(1)	0.17572(1)	0.02174(6)	0.02529(6)	0.02391(7)	0.00855(5)	0.01122(5)	0.01016(5)
N(1)	2*i*	–0.4086(3)	–0.4040(2)	0.1244(2)	0.059(2)	0.051(2)	0.054(2)	–0.002(2)	0.033(2)	0.021(1)
N(2)	2*i*	–0.5822(2)	–0.1420(2)	–0.0578(2)	0.033(2)	0.064(2)	0.059(2)	0.016(1)	0.023(1)	0.020(2)
N(3)	2*i*	0.5414(3)	0.6427(2)	0.4074(2)	0.044(2)	0.034(1)	0.045(2)	0.010(1)	0.008(1)	0.013(1)
N(4)	2*i*	0.7928(2)	0.4013(3)	0.3439(2)	0.033(2)	0.059(2)	0.060(2)	0.008(1)	0.025(1)	0.012(2)
N(5)	2*i*	–0.2133(2)	0.4817(2)	–0.0879(2)	0.047(2)	0.046(2)	0.047(2)	0.026(1)	0.025(1)	0.021(1)
N(6)	2*i*	0.0975(3)	0.5703(2)	0.3244(2)	0.050(2)	0.049(2)	0.036(2)	0.001(1)	0.021(1)	–0.002(1)
N(7)	2*i*	0.1129(2)	0.1110(2)	0.3695(2)	0.038(1)	0.032(1)	0.031(1)	0.008(1)	0.019(1)	0.009(1)
N(8)	2*i*	0.2540(2)	–0.0193(2)	0.3310(2)	0.029(1)	0.029(1)	0.027(1)	0.009(1)	0.009(1)	0.0114(9)
O(1)	2*i*	–0.0354(2)	–0.0955(2)	0.1722(2)	0.029(1)	0.045(1)	0.029(1)	0.0022(9)	0.0105(9)	0.0147(9)
O(2)	2*i*	–0.1133(2)	–0.0851(2)	–0.0051(2)	0.037(1)	0.041(1)	0.037(1)	0.0147(9)	0.0243(9)	0.0214(9)
O(3)	2*i*	–0.3180(3)	–0.4376(2)	0.1631(2)	0.078(2)	0.078(2)	0.098(2)	0.024(2)	0.048(2)	0.063(2)
O(4)	2*i*	–0.5134(2)	–0.4457(2)	0.1147(2)	0.066(2)	0.073(2)	0.075(2)	–0.009(1)	0.041(2)	0.033(1)
O(5)	2*i*	–0.6687(3)	–0.1617(3)	–0.0345(3)	0.051(2)	0.143(3)	0.164(3)	0.048(2)	0.072(2)	0.083(3)
O(6)	2*i*	–0.5764(2)	–0.0861(2)	–0.1179(2)	0.047(1)	0.066(2)	0.048(1)	0.030(1)	0.019(1)	0.015(1)
O(7)	2*i*	0.3567(2)	0.1335(1)	0.2336(2)	0.031(1)	0.028(1)	0.044(1)	0.0080(8)	0.0177(9)	0.0123(9)
O(8)	2*i*	0.2516(2)	0.2470(2)	0.2739(2)	0.034(1)	0.032(1)	0.057(1)	0.0048(9)	0.027(1)	0.0066(9)
O(9)	2*i*	0.4650(2)	0.6554(2)	0.4445(2)	0.077(2)	0.046(1)	0.049(1)	0.031(1)	0.026(1)	0.017(1)
O(10)	2*i*	0.6082(2)	0.7177(2)	0.3961(3)	0.065(2)	0.035(1)	0.137(2)	0.009(1)	0.044(2)	0.033(2)
O(11)	2*i*	0.8792(2)	0.4858(2)	0.3741(2)	0.041(2)	0.084(2)	0.093(2)	0.004(1)	0.038(1)	0.024(2)
O(12)	2*i*	0.8005(3)	0.3078(2)	0.3166(3)	0.055(2)	0.072(2)	0.162(3)	0.019(2)	0.061(2)	0.000(2)
O(13)	2*i*	–0.0220(2)	0.1482(1)	0.1317(2)	0.031(1)	0.040(1)	0.030(1)	0.0194(9)	0.0138(8)	0.0135(8)
O(14)	2*i*	–0.1399(2)	0.1133(2)	–0.0613(2)	0.035(1)	0.035(1)	0.027(1)	0.0179(9)	0.0120(8)	0.0083(8)
O(15)	2*i*	–0.2788(2)	0.4120(2)	–0.1859(2)	0.076(2)	0.058(2)	0.041(1)	0.026(1)	0.004(1)	0.016(1)
O(16)	2*i*	–0.2035(2)	0.5811(2)	–0.0646(2)	0.088(2)	0.043(1)	0.067(2)	0.034(1)	0.039(1)	0.028(1)
O(17)	2*i*	0.0902(3)	0.6655(2)	0.3442(2)	0.092(2)	0.045(2)	0.063(2)	0.011(1)	0.035(2)	–0.008(1)
O(18)	2*i*	0.1689(2)	0.5393(2)	0.3969(2)	0.072(2)	0.073(2)	0.038(1)	0.014(2)	0.002(1)	0.002(1)
C(1)	2*i*	–0.1266(2)	–0.1154(2)	0.0739(2)	0.030(1)	0.027(1)	0.031(1)	0.009(1)	0.019(1)	0.011(1)
C(2)	2*i*	–0.2585(2)	–0.1738(2)	0.0524(2)	0.031(1)	0.029(1)	0.024(1)	0.007(1)	0.015(1)	0.007(1)
C(3)	2*i*	–0.2738(3)	–0.2592(2)	0.0966(2)	0.037(2)	0.032(2)	0.031(2)	0.008(1)	0.020(1)	0.011(1)
C(4)	2*i*	–0.3927(3)	–0.3081(2)	0.0833(2)	0.040(2)	0.037(2)	0.038(2)	0.001(1)	0.022(1)	0.013(1)
C(5)	2*i*	–0.4943(3)	–0.2710(3)	0.0349(3)	0.035(2)	0.052(2)	0.050(2)	0.003(2)	0.028(2)	0.013(2)
C(6)	2*i*	–0.4759(3)	–0.1861(2)	–0.0079(2)	0.029(2)	0.049(2)	0.038(2)	0.010(1)	0.017(1)	0.009(1)
C(7)	2*i*	–0.3600(3)	–0.1378(2)	–0.0023(2)	0.031(2)	0.032(2)	0.030(2)	0.009(1)	0.016(1)	0.011(1)
C(8)	2*i*	0.3503(2)	0.2303(2)	0.2693(2)	0.028(1)	0.035(2)	0.025(1)	0.002(1)	0.012(1)	0.012(1)
C(9)	2*i*	0.4608(2)	0.3319(2)	0.3060(2)	0.023(1)	0.031(1)	0.025(1)	0.004(1)	0.008(1)	0.010(1)
C(10)	2*i*	0.4505(3)	0.4386(2)	0.3397(2)	0.028(2)	0.033(2)	0.031(2)	0.007(1)	0.012(1)	0.012(1)
C(11)	2*i*	0.5529(3)	0.5298(2)	0.3730(2)	0.036(2)	0.029(1)	0.028(1)	0.008(1)	0.008(1)	0.010(1)
C(12)	2*i*	0.6662(3)	0.5206(3)	0.3757(3)	0.031(2)	0.040(2)	0.037(2)	0.000(1)	0.011(1)	0.016(1)
C(13)	2*i*	0.6730(3)	0.4146(2)	0.3419(2)	0.031(2)	0.041(2)	0.033(2)	0.007(1)	0.015(1)	0.012(1)
C(14)	2*i*	0.5731(3)	0.3185(2)	0.3069(2)	0.034(2)	0.033(2)	0.033(2)	0.010(1)	0.014(1)	0.013(1)
C(15)	2*i*	–0.0800(2)	0.1757(2)	0.0447(2)	0.024(1)	0.033(1)	0.029(1)	0.013(1)	0.016(1)	0.011(1)
C(16)	2*i*	–0.0741(2)	0.2972(2)	0.0715(2)	0.026(1)	0.031(1)	0.030(1)	0.012(1)	0.014(1)	0.010(1)
C(17)	2*i*	–0.1461(3)	0.3329(2)	–0.0171(2)	0.032(2)	0.033(2)	0.028(2)	0.010(1)	0.014(1)	0.008(1)
C(18)	2*i*	–0.1387(3)	0.4451(2)	0.0083(2)	0.036(2)	0.038(2)	0.039(2)	0.017(1)	0.021(1)	0.018(1)
C(19)	2*i*	–0.0607(3)	0.5237(3)	0.1190(3)	0.039(2)	0.031(2)	0.043(2)	0.011(1)	0.023(1)	0.008(1)
C(20)	2*i*	0.0111(3)	0.4864(2)	0.2055(2)	0.037(2)	0.034(2)	0.030(2)	0.006(1)	0.015(1)	–0.000(1)
C(21)	2*i*	0.0069(3)	0.3760(2)	0.1841(2)	0.032(2)	0.041(2)	0.030(2)	0.010(1)	0.015(1)	0.013(1)
C(22)	2*i*	0.0492(3)	0.1798(3)	0.3920(3)	0.047(2)	0.043(2)	0.039(2)	0.018(2)	0.024(2)	0.013(2)
C(23)	2*i*	0.0342(3)	0.2055(3)	0.4934(3)	0.058(2)	0.051(2)	0.049(2)	0.015(2)	0.035(2)	0.006(2)
C(24)	2*i*	0.0880(3)	0.1579(3)	0.5756(3)	0.062(2)	0.054(2)	0.035(2)	–0.003(2)	0.031(2)	0.001(2)
C(25)	2*i*	0.1595(3)	0.0879(2)	0.5573(2)	0.049(2)	0.041(2)	0.028(2)	–0.003(2)	0.016(1)	0.004(1)
C(26)	2*i*	0.1692(3)	0.0664(2)	0.4525(2)	0.037(2)	0.031(1)	0.024(1)	–0.001(1)	0.014(1)	0.008(1)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(27)	2*i*	0.2432(3)	–0.0044(2)	0.4316(2)	0.035(2)	0.031(1)	0.026(1)	0.002(1)	0.007(1)	0.010(1)
C(28)	2*i*	0.3029(3)	–0.0519(2)	0.5156(3)	0.050(2)	0.038(2)	0.035(2)	0.004(2)	0.006(1)	0.018(1)
C(29)	2*i*	0.3746(3)	–0.1190(3)	0.4913(3)	0.056(2)	0.046(2)	0.050(2)	0.014(2)	0.007(2)	0.026(2)
C(30)	2*i*	0.3871(3)	–0.1341(3)	0.3910(3)	0.046(2)	0.041(2)	0.046(2)	0.017(2)	0.005(2)	0.015(2)
C(31)	2*i*	0.3277(3)	–0.0803(2)	0.3147(3)	0.032(2)	0.039(2)	0.039(2)	0.015(1)	0.009(1)	0.012(1)
C(32)	2*i*	0.2199(4)	0.0364(3)	0.6392(3)	0.082(3)	0.058(2)	0.028(2)	0.003(2)	0.024(2)	0.017(2)
C(33)	2*i*	0.2881(4)	–0.0298(3)	0.6196(3)	0.087(3)	0.056(2)	0.030(2)	0.015(2)	0.014(2)	0.025(2)

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References

1. Reineke, T. M.; Eddaoudi, M.; Keefe, M. O.; Yaghi, O. M.: A microporous lanthanide-organic framework. Angew. Chem. Int. Ed. Engl. **39** (1999) 2590-2594.
2. Pan, L.; Zheng, N. W.; Wu, Y. G.; Han, S.; Yang, R. Y.; Huang, X. Y.; Li, J.: Synthesis, characterization and structural transformation of a condensed rare earth metal coordination polymer. Inorg. Chem. **40** (2001) 828-830.
3. Wan, Y. H.; Jin, L. P.; Wang, K. Z.: Ytterbium Coordination Polymer with Different Coordination Numbers: The First Structural Characterization of Lanthanide Phthalate Complex. Chin. J. Chem. **20** (2002) 813-815.
4. Li, X.; Jin, L. P.; Zheng, X. J.; Lu, S. Z.; Zhang, J. H.: Synthesis, structure and luminescence property of the three ternary and quaternary europium complexes. J. Mol. Struct. **607** (2002) 59-67.
5. Sun, D. F.; Bi, W. H.; Cao, R.; Li, X.; Shi Q.; Hong, M. C.: Hydrothermal synthesis and structure of a new 3D lanthanide-carboxylate framework, $[La(btec)_{1/2}(H_2btec)_{1/2}(H_2O)]_n$ (H_4btec = 1,2,4,5-benzenetetracarboxylic acid). Chin. J. Chem. **21** (2003) 405-408.
6. Shi, Q.; Hu, M. L.; Cao, R.; Liang Y.; Hong, M. C.: Tetra-μ-benzoato-*O*:*O*′-bis[(benzoato-*O*,*O*′)(1,10-phenanthroline-*N*,*N*′)lanthanum(III)]. Acta. Crystallogr. E**57** (2001) m122-m123.
7. Hökelek, T.; Mert, Y.; Ünaleroglu, C.: *Catena*-poly[[tetrakis(μ-3,5-dinitrobenzoato-*O*:*O*′)dicopper(II)]bis [(μ-3,5-dinitrobenzoato-*O*:*O*′)(methanol-*O*)copper(II)]]. Acta Crystallogr. C**54** (1998) 310-313.
8. Ülkü, D.; Arici, C.; Tahir, M. N.; Ünaleroglu, C.: Crystal Structure of Gadolinium 3,5-Dinitrobenzoate Dihydrate. Analytical Sciences. **15** (1999) 929-930.
9. Tahir, M. N.; Ülkü, D.; Ünaleroglu, C.; Mövsümov, E. M.: Cerium 3,5-Dinitrobenzoate Dihydrate. Acta Crystallogr. C**52** (1996) 1449-1451.
10. Hundal, G.; Ripoll, M. M.; Hundal, M. S.; Poonia, N. S.: Dimeric Aqua(3,5-dinitrobenzoato)(triethylene glycol)calcium(II) 3,5-Dinitrobenzoate Hydrate. Acta Crystallogr. C**52** (1996) 786-789.
11. Tahir, M. N.; Ülkü, D.; Mövsümov, E. M.: Tetraaquabis(3,5-dinitrotobenzoato-*O*)-cobalt(II) Tetrahydrate. Acta Crystallogr. C**52** (1996) 1392-1394.
12. Sheldrick, G. M.: SHELX-97. Programs for crystal structure analysis (Release 97-2). University of Göttingen, Germany 1997.
13. Johnson, C. K.: ORTEP-II. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA 1976.