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Terbium *p*-Nitrobenzoate Hydrate

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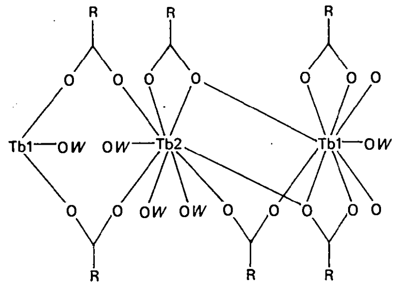
Abstract

There are no discrete molecules of the title compound, *catena*-poly[{triaquaterbium-tris-μ-(*p*-nitrobenzoato)-*O*,*O*′:*O*;*O*:*O*,*O*′;*O*:*O*′-aqua(*p*-nitrobenzoato-*O*,*O*′)terbium}-bis-μ-(*p*-nitrobenzoato-*O*:*O*′) hydrate], [$Tb_2(C_7H_4NO_4)_6(H_2O)_5$], in the crystal structure. The metal ions are bridged by the carboxylate groups to form a linear polymeric structure. There are two kinds of Tb ions which have different coordination environments. The carboxyl groups are coordinated in three modes: chelating, bridging and bridging–chelating. None of the nitro groups is coordinated.

Comment

Many types of rare earth carboxylates have been obtained (Birnbaum, 1984) and several structures have been reported. We have studied rare earth complexes with aromatic acids which exhibit polymeric network and chain structures (Ma, Jin & Ni, 1991; Jin, Xing, Duan & Ni, 1987). As part of our study we describe the structure of the title compound, (I), in this paper.



(I) $R = PhNO_2$

Fig. 1 shows the structure of the title compound (the NO_2 groups and all the other atoms of the phenyl rings are omitted for clarity except the C atoms which are bonded to the carboxylate groups). There are two kinds of metal ions in the compound. Tb(1) is coordinated by eight carboxylate O atoms [O(11), O(42), O(61), O(51), O(52), O(31^{i}), O(32^{i}), O(22^{i})] from six ligands and one O atom [O(*W*1)] from a water molecule, and Tb(2) is coordinated by six carboxylate O atoms [O(12), O(41), O(21), O(22), O(31), O(62^{ii})] from five ligands and three O atoms [O(*W*2), O(*W*3), O(*W*4)] from water molecules. Both have the same coordination number of nine. None of the NO_2 groups is coordinated to the metal ions. The carboxylate groups are coordinated in three different modes: (1) chelating [C(5), O(51), O(52)], in which the two O atoms are coordinated to the same metal ion, forming a four-membered ring; (2) bridging [C(1), O(11), O(12); C(4), O(41), O(42); C(6), O(61), O(62)], in which the two O atoms of each group are coordinated to two different metal ions, forming a carboxylate bridge; (3) bridging–chelating [C(2), O(21), O(22); C(3), O(31), O(32)], in which the two O atoms of each group chelate one metal ion, with one of the O atoms also coordinated to another metal ion. Tb(1) and Tb(2) are alternately bridged by carboxylate groups to form a linear polymeric structure. There are two bridging modes between metal ions: (1) two bridging carboxylate groups; (2) one bridging carboxylate group and two bridging–chelating carboxylate groups. Moreover, the corresponding distances between the metal ions are 5.154 (1) and 4.313 (1) Å, respectively. The Tb—O distances fall in the range 2.292 (5)–2.922 (4) Å and the average Tb—O distance is 2.459 (4) Å. The four-membered ring is unstable because of strain, *i.e.* the bridging–chelating Tb—O bonds are weaker, so the average Tb—O distance involving the chelating carboxylate groups [2.515 (4) Å] is longer than the average Tb—O distance involving the bridging carboxylate groups [2.327 (4) Å].

Although the H atoms were not located in this work, the existence of hydrogen bonds can be inferred from the distances listed in Table 2.

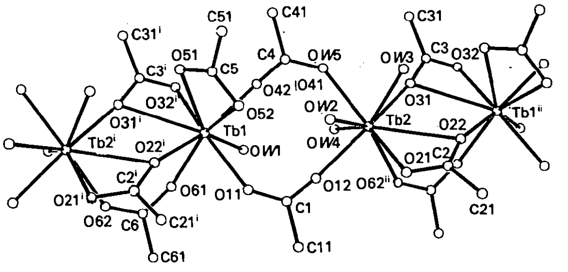


Fig. 1. Perspective view of the polymeric chain structure of the title compound.

Experimental

The title compound was obtained by the reaction of an aqueous solution of $TbCl_3$ and *p*-$NO_2C_6H_4CO_2NH_4$.

Crystal data

[$Tb_2(C_7H_4NO_4)_6(H_2O)_5$]
M_r = 1404.60

Mo *Kα* radiation
λ = 0.71069 Å

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Triclinic
$P\bar{1}$
$a = 9.405$ (1) Å
$b = 18.715$ (6) Å
$c = 15.437$ (3) Å
$\alpha = 104.52$ (3)°
$\beta = 102.29$ (3)°
$\gamma = 80.72$ (2)°
$V = 2553$ (1) Å^3
$Z = 2$
$D_x = 1.83$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 2.2$–12.0°
$\mu = 2.92$ mm^{-1}
$T = 293$ K
Needle
0.80 × 0.32 × 0.12 mm
Colourless

Data collection

Nicolet *R3m/E* diffractometer
ω scans
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.812$, $T_{\max} = 0.953$
9591 measured reflections
7077 independent reflections
6302 observed reflections [$F_o > 3\sigma(F_o)$]

$R_{\rm int} = 0.0133$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = -23 \rightarrow 23$
$l = -19 \rightarrow 19$
2 standard reflections monitored every 100 reflections
intensity variation: < 3.3%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.037$
$S = 1.101$
6302 reflections
712 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o) + 0.00046(F_o)^2]$

$(\Delta/\sigma)_{\max} = 0.034$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Tb(1)	0.2172 (1)	0.1904 (1)	0.1940 (1)	0.031 (1)
Tb(2)	0.7606 (1)	0.2182 (1)	0.2147 (1)	0.031 (1)
N(1)	0.687 (1)	0.3549 (7)	0.7362 (5)	0.149 (6)
N(2)	1.3219 (7)	0.5177 (4)	0.6107 (5)	0.091 (3)
N(3)	0.7139 (7)	0.1167 (4)	−0.3216 (4)	0.082 (3)
N(4)	0.1748 (9)	0.2793 (5)	−0.2780 (4)	0.118 (4)
N(5)	0.1935 (7)	0.5201 (3)	−0.1046 (4)	0.076 (3)
N(6)	0.3027 (9)	0.0327 (4)	0.6613 (4)	0.113 (4)
O(*W*1)	0.3947 (4)	0.0766 (2)	0.2021 (3)	0.051 (2)
O(*W*2)	0.5757 (4)	0.3296 (2)	0.2283 (3)	0.052 (2)
O(*W*3)	0.8050 (4)	0.3057 (2)	0.1315 (3)	0.047 (2)
O(*W*4)	0.7064 (5)	0.0872 (2)	0.1760 (3)	0.050 (2)
O(*W*5)	0.6534 (6)	0.0104 (3)	0.0027 (3)	0.086 (2)
O(11)	0.3792 (4)	0.2285 (2)	0.3274 (2)	0.047 (2)
O(12)	0.6115 (4)	0.2061 (3)	0.3094 (3)	0.051 (2)
O(13)	0.600 (1)	0.3733 (6)	0.7832 (4)	0.170 (6)
O(14)	0.819 (1)	0.3531 (9)	0.7652 (5)	0.32 (1)
O(21)	0.8558 (4)	0.3136 (2)	0.3393 (3)	0.047 (2)
O(22)	1.0466 (4)	0.2740 (2)	0.2701 (2)	0.042 (1)
O(23)	1.4011 (6)	0.5530 (4)	0.5888 (5)	0.128 (4)
O(24)	1.3085 (9)	0.5250 (4)	0.6884 (4)	0.139 (4)
O(31)	0.9184 (4)	0.1588 (2)	0.1120 (2)	0.045 (2)
O(32)	1.1164 (4)	0.0996 (2)	0.0630 (2)	0.041 (1)
O(33)	0.7677 (8)	0.0758 (4)	−0.3813 (3)	0.122 (3)
O(34)	0.6058 (7)	0.1615 (4)	−0.3355 (4)	0.123 (4)
O(41)	0.5852 (4)	0.2031 (2)	0.0816 (2)	0.045 (2)
O(42)	0.3790 (4)	0.1668 (2)	0.0921 (3)	0.049 (2)
O(43)	0.1986 (9)	0.3373 (5)	−0.2875 (5)	0.174 (5)
O(44)	0.089 (1)	0.2421 (5)	−0.3286 (4)	0.214 (5)
O(51)	0.0870 (4)	0.2714 (2)	0.0878 (2)	0.040 (1)
O(52)	0.2819 (4)	0.3131 (2)	0.1823 (2)	0.044 (2)
O(53)	0.3013 (7)	0.5528 (3)	−0.0872 (4)	0.107 (3)
O(54)	0.0924 (7)	0.5277 (4)	−0.1653 (4)	0.106 (3)
O(61)	0.1455 (4)	0.1259 (2)	0.2823 (3)	0.045 (2)
O(62)	−0.0762 (4)	0.1545 (2)	0.3195 (3)	0.048 (2)
O(63)	0.2187 (9)	0.0192 (4)	0.7038 (4)	0.130 (4)
O(64)	0.4375 (9)	0.0206 (5)	0.6790 (5)	0.181 (5)
C(1)	0.5134 (6)	0.2297 (3)	0.3570 (3)	0.037 (2)
C(11)	0.5594 (6)	0.2618 (4)	0.4571 (4)	0.043 (2)
C(12)	0.4557 (7)	0.2865 (4)	0.5129 (4)	0.055 (3)
C(13)	0.4979 (8)	0.3178 (4)	0.6040 (4)	0.068 (3)
C(14)	0.644 (1)	0.3218 (5)	0.6371 (4)	0.084 (4)
C(15)	0.7485 (9)	0.2974 (6)	0.5844 (5)	0.109 (5)
C(16)	0.7044 (7)	0.2671 (5)	0.4934 (4)	0.074 (4)
C(2)	0.9876 (6)	0.3164 (3)	0.3337 (4)	0.040 (2)
C(21)	1.0741 (6)	0.3705 (3)	0.4056 (4)	0.039 (2)
C(22)	1.0459 (7)	0.3883 (4)	0.4928 (4)	0.050 (3)
C(23)	1.1281 (7)	0.4364 (4)	0.5613 (4)	0.056 (3)
C(24)	1.2321 (7)	0.4675 (4)	0.5382 (5)	0.056 (3)
C(25)	1.2612 (7)	0.4520 (4)	0.4514 (5)	0.069 (3)
C(26)	1.1807 (7)	0.4019 (4)	0.3843 (4)	0.056 (3)
C(3)	0.9821 (6)	0.1241 (3)	0.0474 (3)	0.033 (2)
C(31)	0.9054 (6)	0.1171 (3)	−0.0485 (4)	0.037 (2)
C(32)	0.7931 (8)	0.1698 (5)	−0.0690 (4)	0.083 (4)
C(33)	0.7307 (7)	0.1694 (5)	−0.1587 (4)	0.083 (4)
C(34)	0.7794 (7)	0.1151 (4)	−0.2249 (4)	0.057 (3)
C(35)	0.8890 (9)	0.0618 (4)	−0.2080 (4)	0.072 (3)
C(36)	0.9526 (8)	0.0634 (4)	−0.1179 (4)	0.050 (3)
C(4)	0.4554 (6)	0.1926 (3)	0.0529 (3)	0.035 (2)
C(41)	0.3842 (6)	0.2127 (3)	−0.0364 (4)	0.037 (2)
C(42)	0.4372 (7)	0.2671 (4)	−0.0639 (4)	0.050 (3)
C(43)	0.3672 (8)	0.2891 (4)	−0.1418 (5)	0.066 (3)
C(44)	0.2511 (9)	0.2553 (5)	−0.1923 (4)	0.075 (3)
C(45)	0.1959 (8)	0.2008 (5)	−0.1688 (5)	0.080 (4)
C(46)	0.2614 (7)	0.1796 (4)	−0.0877 (4)	0.060 (3)
C(5)	0.1809 (6)	0.3170 (3)	0.1137 (4)	0.036 (2)
C(51)	0.1790 (6)	0.3732 (3)	0.0593 (4)	0.038 (2)
C(52)	0.2815 (7)	0.4235 (4)	0.0862 (4)	0.054 (3)
C(53)	0.2858 (8)	0.4725 (4)	0.0328 (5)	0.063 (3)
C(54)	0.1859 (8)	0.4688 (4)	−0.0468 (4)	0.053 (3)
C(55)	0.0809 (7)	0.4217 (4)	−0.0737 (4)	0.050 (3)
C(56)	0.0786 (6)	0.3734 (4)	−0.0203 (4)	0.045 (2)
C(6)	0.0581 (6)	0.1328 (3)	0.3358 (4)	0.037 (2)
C(61)	0.1195 (6)	0.1121 (3)	0.4253 (4)	0.042 (2)
C(62)	0.0285 (7)	0.0997 (4)	0.4781 (4)	0.054 (3)
C(63)	0.0875 (9)	0.0746 (4)	0.5562 (4)	0.069 (3)
C(64)	0.2382 (9)	0.0635 (4)	0.5794 (4)	0.073 (3)
C(65)	0.3320 (8)	0.0765 (5)	0.5294 (5)	0.081 (4)
C(66)	0.2703 (7)	0.1014 (4)	0.4515 (4)	0.064 (3)

Table 2. *Selected geometric parameters* (Å)

Tb(1)—O(*W*1)	2.498 (4)	Tb(1)—O(11)	2.312 (3)
Tb(1)—O(42)	2.331 (4)	Tb(1)—O(51)	2.505 (4)
Tb(1)—O(52)	2.525 (5)	Tb(1)—O(61)	2.292 (5)
Tb(1)—O(22$^{\rm i}$)	2.340 (4)	Tb(1)—O(31$^{\rm i}$)	2.915 (4)
Tb(1)—O(32$^{\rm i}$)	2.420 (3)	Tb(2)—O(*W*2)	2.486 (4)
Tb(2)—O(*W*3)	2.452 (5)	Tb(2)—O(*W*4)	2.483 (4)
Tb(2)—O(12)	2.300 (5)	Tb(2)—O(21)	2.397 (4)
Tb(2)—O(22)	2.922 (4)	Tb(2)—O(31)	2.354 (4)
Tb(2)—O(41)	2.333 (3)	Tb(2)—O(62$^{\rm ii}$)	2.391 (4)
O(42)···O(*W*1)	2.646 (7)	O(*W*5)···O(*W*4)	2.686 (6)
O(12)···O(*W*4)	2.798 (6)	O(61)···O(*W*1)	2.801 (6)
O(31)···O(*W*3)	2.749 (5)	O(52)···O(*W*2)	2.750 (5)
O(*W*2)···O(*W*3)	2.795 (6)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$.

Intensity data were corrected for Lp factors. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. All non-H atoms were refined anisotropically. H atoms on the benzene rings were placed at calculated positions. All calculations were performed using the *SHELXTL* program system (Sheldrick, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond angles and *p*-nitrobenzoate geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71835 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1099]

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Yttrium Salicylate Tetrahydrate

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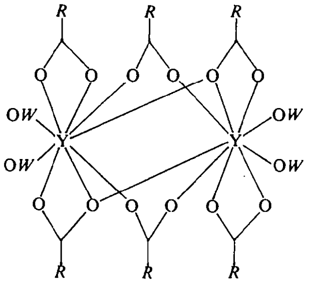
Abstract

The structure of tetraaqua-1κ^2O,2κ^2O-tetrakis-(μ-salicylato)-1:2κ^2O,1$\kappa O'$;1:2κ^2O,2$\kappa O'$;1κO:2$\kappa O'$;1κO:2$\kappa O'$-bis(salicylato)-1κ^2O,O';2κ^2O,O'-diyttrium tetrahydrate, [$Y_2(C_7H_5O_3)_6(H_2O)_4$].$4H_2O$, is composed of dimeric Y_2(o-$HOC_6H_4CO_2)_6(H_2O)_4$ units in which the two metal ions are bridged by carboxylate groups. The carboxylate groups coordinate in three different modes: bridging, chelating and bridging–chelating. None of the phenolic O atoms is coordinated.

Comment

As rare earth complexes can be used as bonding models for the study of the interaction of rare earth elements with humic materials, structural information for these complexes is important. The structures of Sm(o-$HOC_6H_4CO_2)_3.H_2O$ (Burns & Baldwin, 1977) and [M(o-$HOC_6H_4CO_2)_3(H_2O)_2$].$2H_2O$ [M = Tb, Ho (Ma, Jin & Ni, 1991)] have been determined. In this paper we describe the structure of the title compound (I).



(I) R = 2-HO-C_6H_4—

Each Y ion is coordinated to seven carboxylate O atoms [O(11), O(12^i), O(21), O(22), O(31), O(31^i) and O(32^i)] from five salicylate ions and two O atoms [O(W1) and O(W2)] from water molecules. There are also two lattice water molecules per metal ion which are not coordinated to the metal ions. The coordination number of each Y ion is nine. None of the phenolic O atoms is coordinated to the metal ions. The carboxylate groups coordinate in three different modes. In the bridging mode two O atoms are coordinated to two different metal ions, forming a carboxylate bridge [C(17), O(11), O(12)]. In the chelating mode two O atoms are coordinated to the same metal ion, forming a four-membered ring [C(27), O(21), O(22)]. In the bridging–chelating mode two O atoms chelate one metal ion, with one of the O atoms also coordinated to another metal ion. Pairs of Y ions are bridged by two bridging carboxylate groups and two bridging–chelating carboxylate groups to form a dimeric molecule in which the Y···Y distance is 4.029 (1) Å.

The title compound has a different structure from those of the compounds of samarium (Burns & Baldwin, 1977), terbium and holmium (Ma, Jin & Ni, 1991), which have infinite chain structures. The Y—O distances are in the range 2.296 (4)–2.732 (4) Å, with an average value of 2.418 (4) Å. The average Y—O bond length within the bridging carboxylate groups [2.352 (4) Å] is shorter than the average Y—O bond length within the chelating carboxylate groups [2.433 (4) Å], as the four-membered chelate ring is less stable. The dihedral angles between the carboxylate planes and the benzene rings in the three salicylate ions are 19.3 (5), 5.7 (9) and 13.0 (7)°, respectively.

Although the H atoms were not located in this work, the existence of some hydrogen bonds can be inferred from the distances listed in Table 2. Both the coordinated and lattice water molecules can form hydrogen bonds with the carboxylate O atoms, and hydrogen bonds also exist between the water molecules. The dimers are connected by hydrogen bonds

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