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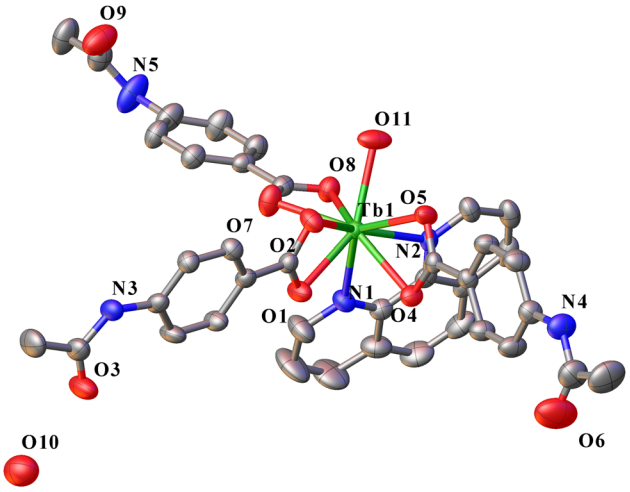
Hydrothermal synthesis and crystal structure of aqua-tris(4-acetamidobenzoato-κ^2*O*,*O*′)-(1,10-phenanthroline-κ^2*N*,*N*′)terbium(III) hydrate $C_{39}H_{36}N_5O_{11}Tb$



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Abstract

$C_{39}H_{36}N_5O_{11}Tb$, triclinic, $P\bar{1}$ (no. 2), a = 10.3365(12) Å, b = 13.0194(15) Å, c = 15.2064(18) Å, α = 108.769(2)°, β = 94.694(2)°, γ = 100.882(2)°, V = 1880.2(4) Å^3, Dc = 1.607 g/cm^3, Z = 2, $R_{gt}(F)$ = 0.0315, $wR_{ref}(F^2)$ = 0.0836, T = 296.15 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.95 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	25°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19,718, 6629, 0.084
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 6210
$N(param)_{refined}$:	511
Programs:	Olex2 [8], Shelx [9, 10]

1 Introduction

Complexes constructed by aromatic carboxylic acids and metal ions have shown potential application value in many fields [1–4]. p-Acetamidobenzoic acid is not only an important chemical raw material, widely used in fuel, medicine and other industries and other fields, but also as an important organic synthesis intermediate, which can be esterified to produce a series of compounds [1, 5]. It is also an important material for the synthesis of quinazolin-4-one derivatives of non-barbiturate hypnosedative drugs, fluorescent whitening agents and anti-asthmatic drugs N-cinnamyl anthranilic acid [6]. p-Acetamidobenzoic acid also acts as an aromatic carboxylic acid ligand, which can coordinate with metal ions due to its multiple coordination sites (nitrogen and oxygen atoms), and is also the giver and acceptor of hydrogen bonds to form functional complexes with stable structures [7]. The single crystal structure analysis revealed that the title compound crystallized in the orthorhombic space group $P\bar{1}$. The Ortep diagram is presented in the figure. Bond lengths and angles are all in the expected ranges. There is only one molecule in the asymmetric unit. As shown in figure, complex **1** consists of one Tb ion, three p-acetamidobenzoate anions, one 1,10-phenanthroline molecule, one coordinating water molecule and one free water molecule. The central Tb

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
Tb1	1.07767 (2)	0.30084 (2)	0.36652 (2)	0.02586 (8)
O8	1.1005 (2)	0.3378 (2)	0.21827 (18)	0.0419 (6)
O4	1.1685 (2)	0.21834 (18)	0.47830 (16)	0.0345 (5)
O2	0.8872 (2)	0.3166 (2)	0.45265 (18)	0.0401 (6)
O7	0.8991 (3)	0.2941 (3)	0.25006 (19)	0.0503 (7)
O11	1.1183 (3)	0.4987 (2)	0.40126 (19)	0.0547 (8)
H11A	1.123930	0.542416	0.366189	0.082*
H11B	1.117799	0.546726	0.456899	0.082*
O5	1.1813 (3)	0.39790 (19)	0.53090 (17)	0.0412 (6)
O1	0.9043 (2)	0.15059 (19)	0.3663 (2)	0.0427 (6)
O3	0.2572 (3)	−0.1510 (2)	0.3414 (3)	0.0640 (9)
O6	1.3110 (5)	0.1404 (4)	0.9029 (3)	0.1039 (14)
O9	0.6163 (4)	0.4661 (3)	−0.0810 (3)	0.0804 (11)
N2	1.3189 (3)	0.3096 (2)	0.34066 (19)	0.0296 (6)
N1	1.1193 (3)	0.1272 (2)	0.2479 (2)	0.0374 (7)
N3	0.2954 (3)	0.0352 (2)	0.4200 (2)	0.0381 (7)
H3	0.255328	0.086276	0.447158	0.046*
N4	1.3214 (4)	0.3214 (3)	0.9214 (2)	0.0509 (8)
H4	1.336464	0.386896	0.963228	0.061*
N5	0.7547 (4)	0.3608 (4)	−0.1425 (3)	0.0724 (12)
H5	0.784286	0.329110	−0.193211	0.087*
C22	1.1911 (3)	0.3104 (3)	0.5469 (2)	0.0283 (7)
C12	1.3497 (3)	0.2198 (3)	0.2776 (2)	0.0321 (7)
C31	0.9765 (4)	0.3183 (3)	0.1955 (3)	0.0340 (8)
C3	1.0400 (6)	−0.0525 (4)	0.1278 (4)	0.0846 (18)
H3A	0.968186	−0.110445	0.093447	0.102*
C39	0.6233 (5)	0.4222 (5)	−0.2447 (3)	0.0719 (14)
H39A	0.700952	0.452884	−0.266478	0.108*
H39B	0.560153	0.468249	−0.241220	0.108*
H39C	0.583700	0.348314	−0.287575	0.108*
C17	0.4337 (3)	0.0716 (3)	0.4229 (3)	0.0343 (7)
C4	1.1674 (6)	−0.0562 (4)	0.1103 (4)	0.0807 (17)
H4A	1.182693	−0.118263	0.064716	0.097*
C34	0.7265 (4)	0.3209 (4)	0.0012 (3)	0.0477 (9)
H34	0.634573	0.309481	−0.013304	0.057*
C23	1.2282 (3)	0.3141 (3)	0.6443 (2)	0.0312 (7)
C29	1.3304 (5)	0.2380 (4)	0.9548 (3)	0.0623 (12)
C14	0.7008 (3)	0.1642 (3)	0.4258 (2)	0.0322 (7)
C8	1.4814 (4)	0.2191 (3)	0.2583 (3)	0.0398 (8)
C19	0.6236 (3)	0.2270 (3)	0.4803 (2)	0.0353 (7)
H19	0.660976	0.300454	0.518191	0.042*
C9	1.5809 (4)	0.3163 (4)	0.3056 (3)	0.0471 (10)
H9	1.668663	0.319430	0.295059	0.056*
C13	0.8381 (3)	0.2132 (3)	0.4156 (2)	0.0310 (7)
C25	1.2861 (5)	0.2215 (3)	0.7517 (3)	0.0469 (10)
H25	1.303370	0.157944	0.761090	0.056*
C32	0.9179 (4)	0.3270 (3)	0.1061 (2)	0.0350 (8)
C18	0.4914 (3)	0.1814 (3)	0.4788 (3)	0.0356 (8)
H18	0.440278	0.224494	0.515464	0.043*
C1	1.2447 (3)	0.1239 (3)	0.2287 (2)	0.0354 (7)
C37	0.9992 (4)	0.3500 (3)	0.0432 (3)	0.0456 (9)
H37	1.090907	0.358755	0.056469	0.055*
C11	1.4158 (4)	0.3987 (3)	0.3828 (3)	0.0400 (8)
H11	1.395103	0.460471	0.425567	0.048*
C33	0.7816 (4)	0.3109 (3)	0.0832 (3)	0.0406 (8)
H33	0.725868	0.292932	0.123729	0.049*
C35	0.8085 (5)	0.3480 (4)	−0.0588 (3)	0.0537 (11)
C2	1.0210 (5)	0.0401 (3)	0.1985 (3)	0.0579 (12)
H2	0.934988	0.041343	0.211828	0.069*
C24	1.2560 (4)	0.2210 (3)	0.6620 (3)	0.0403 (8)
H24	1.254019	0.156854	0.611511	0.048*
C38	0.6623 (4)	0.4176 (4)	−0.1495 (3)	0.0519 (10)
C26	1.2910 (4)	0.3162 (3)	0.8285 (3)	0.0403 (8)
C28	1.2349 (4)	0.4088 (3)	0.7212 (3)	0.0393 (8)
H28	1.219055	0.472728	0.711807	0.047*
C20	0.2168 (4)	−0.0684 (3)	0.3806 (3)	0.0462 (10)
C10	1.5474 (4)	0.4054 (4)	0.3668 (3)	0.0472 (9)
H10	1.611893	0.470595	0.397883	0.057*
C15	0.6432 (3)	0.0528 (3)	0.3729 (3)	0.0402 (8)
H15	0.694951	0.009081	0.337474	0.048*
C5	1.2740 (5)	0.0322 (3)	0.1602 (3)	0.0534 (10)
C27	1.2644 (4)	0.4095 (3)	0.8110 (3)	0.0458 (9)
H27	1.266818	0.473745	0.861389	0.055*
C7	1.5083 (5)	0.1224 (4)	0.1929 (3)	0.0533 (11)
H7	1.595703	0.120420	0.183346	0.064*
C16	0.5120 (4)	0.0062 (3)	0.3720 (3)	0.0441 (9)
H16	0.476110	−0.068621	0.337388	0.053*
C30	1.3616 (7)	0.2708 (5)	1.0590 (4)	0.0810 (17)
H30A	1.414128	0.345832	1.084764	0.121*
H30B	1.410634	0.221481	1.074180	0.121*
H30C	1.280076	0.266143	1.085059	0.121*
C36	0.9452 (4)	0.3600 (4)	−0.0386 (3)	0.0570 (11)
H36	1.000321	0.374699	−0.080561	0.068*
C21	0.0722 (4)	−0.0748 (4)	0.3920 (4)	0.0628 (13)
H21A	0.016688	−0.124007	0.334526	0.094*
H21B	0.054311	−0.001919	0.406769	0.094*
H21C	0.053432	−0.102733	0.441964	0.094*
C6	1.4081 (5)	0.0330 (4)	0.1442 (4)	0.0613 (12)
H6	1.427070	−0.028346	0.099899	0.074*
O10	0.0912 (4)	−0.3562 (3)	0.2993 (4)	0.0839 (12)
H10A	0.118998	−0.286100	0.314716	0.126*
H10B	0.008815	−0.365329	0.304157	0.126*

ion is coordinated with two nitrogen atoms from 1,10-phenanthroline molecules, and seven oxygen atoms from three acid anions and one water molecule. The Tb(III) ion adopts a single-capped square antiprism coordination geometry, where the cap position is occupied by O8. Atoms N1, O7, O11 and N2 give the upper plane of the square antiprism, and atoms O1, O2, O5 and O4 determine the plane below. Their plane equations are $-3.321x + -5.831y + 14.384z = 1.5663$ and $-2.969x + -6.064y + 14.479z = -0.6825$, where the average distance of all the atoms in the plane is 0.1556 Å and 0.1635 Å

respectively, and their dihedral angle is 2.1°. The bond lengths Tb1–O1, Tb1–O2, Tb1–O4, Tb1–O5, Tb1–O7, Tb1–O8 and Tb1–O11 are 2.389(2), 2.457(2), 2.494(2), 2.452(2), 2.419(3), 2.472(2) and 2.402(2) Å, respectively, which are in the normal ranges. The bond lengths of Tb1–N1 and Tb1–N2 are 2.534(3) and 2.543(3) Å, with the average to be 2.5385 Å. Otherwise, the shortest center distance between aromatic cycles of 2-(tert-pentyl)anthracene group is 3.610 Å, shorter than 3.700 Å, indicating π–π stacking interaction between the aromatic cycles [8].

2 Experimental

The H atoms bound to C atoms were placed in idealized positions and treated as riding on their parent atoms, with d (C–H) = 0.96 Å (methylene), with U_{iso}(H) = 1.5U_{eq}(C), and d(C–H) = 0.93 Å (aromtic), with U_{iso}(H) = 1.2U_{eq}(C).

2.1 Refinement

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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