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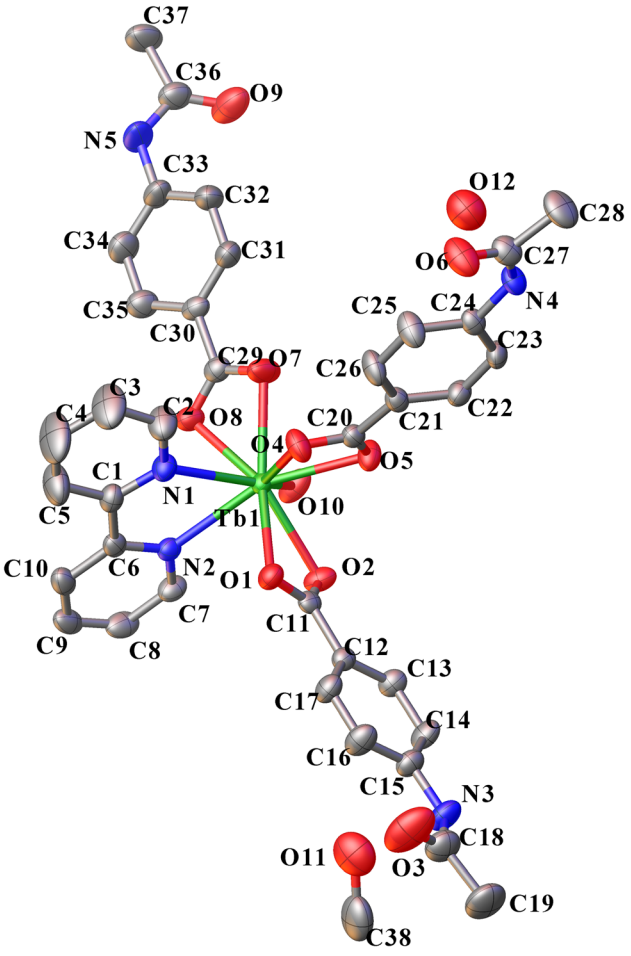
Solvothermal synthesis and crystal structure of aqua-tris(p-acetamidobenzoate-κ^{2}O,O′)-(2,2′-bipyridine-κ^{2}N,N′)terbium(III) - water - methanol (1/1/1)



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Abstract

$C_{75}H_{76}N_{10}O_{23}Tb_2$, triclinic, $P\,-\,\bar{1}$ (no. 2), a = 10.4524(13) Å, b = 12.9626(16) Å, c = 15.2003(18) Å, α = 108.674(2)°, β = 94.931(2)°, γ = 101.617(2)°, V = 1885.8(4) nm^3, Z = 1, $R_{gt}(F)$ = 0.0236, $wR_{ref}(F^2)$ = 0.0584, T = 296 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.

1 Source of material

0.3 mmol *p*–acetylamino benzoic acid, 0.2 mmol 2,2′-bipyridine (2,2′-bipy) and 0.1 mmol terbium(III) acetate hydrate were dissolved in 15 mL mixed solvent ($V_{methanol}$:V_{water} = 3:1). The pH value was adjusted to about 6.5 with 0.1 M NaOH solution. The reaction mixture was refluxed for 4 h under stirring. After that, the mixture was placed in a 25 mL hydrothermal reaction kettle. The vessel was sealed and heated at 160 °C for 48 h. Afterwards the system was cooled to room temperature. The resultant solution was filtered and the filtrate was kept untouched and evaporated slowly at room temperature. The colorless and transparent crystals were obtain.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	1.94 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19,697, 6645, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 6175
$N(param)_{refined}$:	511
Programs:	SHELX [1–3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7370 (3)	0.6218 (3)	0.2255 (2)	0.0363 (7)
C2	0.5147 (4)	0.5380 (3)	0.1996 (3)	0.0539 (9)
H2	0.431205	0.538747	0.216121	0.065*
C3	0.5278 (5)	0.4481 (4)	0.1259 (3)	0.0803 (15)
H3A	0.454582	0.390240	0.092448	0.096*
C4	0.6513 (5)	0.4458 (4)	0.1027 (4)	0.0907 (17)
H4A	0.663249	0.385814	0.053305	0.109*
C5	0.7571 (4)	0.5328 (3)	0.1531 (3)	0.0666 (12)
H5A	0.841620	0.531915	0.138636	0.080*
C6	0.8460 (3)	0.7217 (3)	0.27809 (19)	0.0314 (6)
C7	0.9069 (3)	0.9027 (3)	0.3841 (2)	0.0386 (7)
H7	0.884160	0.963728	0.425822	0.046*
C8	1.0380 (3)	0.9127 (3)	0.3702 (2)	0.0477 (9)
H8	1.101405	0.979345	0.401884	0.057*
C9	1.0722 (3)	0.8237 (3)	0.3098 (2)	0.0483 (9)
H9	1.159581	0.828410	0.300311	0.058*
C10	0.9766 (3)	0.7266 (3)	0.2627 (2)	0.0417 (8)
H10	0.998506	0.664974	0.221224	0.050*
C11	0.6909 (2)	0.8099 (2)	0.54682 (19)	0.0278 (6)
C12	0.7295 (3)	0.8140 (2)	0.64509 (18)	0.0291 (6)
C13	0.7370 (3)	0.9099 (3)	0.7218 (2)	0.0365 (7)
H13	0.721211	0.973892	0.712166	0.044*
C14	0.7679 (3)	0.9111 (3)	0.8126 (2)	0.0414 (8)
H14	0.772006	0.975729	0.863375	0.050*
C15	0.7928 (3)	0.8171 (3)	0.8287 (2)	0.0372 (7)
C16	0.7869 (4)	0.7216 (3)	0.7526 (2)	0.0475 (8)
H16	0.803797	0.657871	0.762055	0.057*
C17	0.7559 (3)	0.7216 (3)	0.6625 (2)	0.0394 (7)
H17	0.752665	0.657182	0.611835	0.047*
C18	0.8376 (4)	0.7394 (4)	0.9548 (3)	0.0566 (10)
C19	0.8738 (5)	0.7732 (4)	1.0596 (3)	0.0780 (14)
H19A	0.928184	0.848481	1.084582	0.117*
H19B	0.921556	0.723067	1.073892	0.117*
H19C	0.794652	0.769706	1.087448	0.117*
C20	0.3353 (3)	0.71162)	0.41405 (19)	0.0302 (6)
C21	0.1972 (3)	0.6633 (2)	0.42178 (19)	0.0304 (6)
C22	0.1251 (3)	0.7255 (3)	0.48031 (19)	0.0339 (7)
H22	0.165493	0.798102	0.520555	0.041*
C23	−0.0064 (3)	0.6804 (3)	0.4793 (2)	0.0352 (7)
H23	−0.054052	0.723063	0.518913	0.042*
C24	−0.0689 (3)	0.5721 (2)	0.4199 (2)	0.0318 (6)
C25	0.0040 (3)	0.5076 (3)	0.3631 (3)	0.0466 (8)
H25	−0.035321	0.434067	0.324495	0.056*
C26	0.1353 (3)	0.5542 (3)	0.3647 (2)	0.0444 (8)
H26	0.183727	0.511079	0.326300	0.053*
C27	−0.2851 (3)	0.4309 (3)	0.3804 (2)	0.0420 (8)
C28	−0.4275 (3)	0.4243 (3)	0.3931 (3)	0.0601 (10)
H28A	−0.484159	0.376665	0.335169	0.090*
H28B	−0.443214	0.498078	0.410274	0.090*
H28C	−0.445786	0.393841	0.441776	0.090*
C29	0.4749 (3)	0.8155 (2)	0.1956 (2)	0.0346 (7)
C30	0.4170 (3)	0.8238 (2)	0.10559 (19)	0.0349 (7)
C31	0.2819 (3)	0.8055 (3)	0.0819 (2)	0.0455 (8)
H31	0.226351	0.785567	0.121438	0.055*
C32	0.2283 (4)	0.8163 (4)	−0.0001 (2)	0.0567 (10)
H32	0.137079	0.804292	−0.015079	0.068*
C33	0.3088 (4)	0.8448 (4)	−0.0595 (2)	0.0579 (10)
C34	0.4442 (4)	0.8602 (4)	−0.0380 (2)	0.0581 (10)
H34	0.498978	0.877522	−0.078952	0.070*
C35	0.4981 (4)	0.8498 (3)	0.0439 (2)	0.0484 (8)
H35	0.589222	0.860294	0.057980	0.058*
C36	0.1660 (4)	0.9164 (4)	−0.1486 (2)	0.0532 (9)
C37	0.1250 (4)	0.9196 (5)	−0.2447 (3)	0.0738 (13)
H37A	0.035800	0.928062	−0.250411	0.111*
H37B	0.129744	0.850902	−0.291667	0.111*
H37C	0.183090	0.981747	−0.253424	0.111*
C38[a]	0.9571 (8)	0.4811 (7)	0.9458 (6)	0.079 (3)
H38A[a]	1.034544	0.466476	0.919417	0.119*
H38B[a]	0.950664	0.454734	0.997907	0.119*
H38C[a]	0.963143	0.560343	0.967167	0.119*
N1	0.6162 (2)	0.6243 (2)	0.24866 (16)	0.0352 (6)
N2	0.8121 (2)	0.8087 (2)	0.33960 (15)	0.0297 (5)
N3	0.8245 (3)	0.8236 (2)	0.92279 (18)	0.0485 (7)
H3	0.837028	0.889036	0.964954	0.058*
N4	−0.2056 (2)	0.5357 (2)	0.41835 (18)	0.0363 (6)
H4	−0.244010	0.587388	0.445342	0.044*
N5	0.2556 (4)	0.8580 (4)	−0.1428 (2)	0.0862 (14)
H5	0.283334	0.825779	−0.193760	0.103*
O1	0.6679 (2)	0.71730 (17)	0.47911 (13)	0.0357 (5)
O2	0.6792 (2)	0.89745 (17)	0.53178 (14)	0.0397 (5)
O3	0.8186 (4)	0.6422 (3)	0.9033 (2)	0.0978 (12)
O4	0.4011 (2)	0.64844 (17)	0.36719 (16)	0.0419 (5)
O5	0.3865 (2)	0.81601 (17)	0.45097 (14)	0.0398 (5)
O6	−0.2464 (2)	0.3479 (2)	0.3406 (2)	0.0589 (7)
O7	0.3976 (2)	0.7850 (2)	0.24712 (16)	0.0548 (7)
O8	0.5978 (2)	0.83788 (19)	0.21936 (14)	0.0408 (5)
O9	0.1211 (3)	0.9640 (3)	−0.08026 (19)	0.0765 (9)
O10	0.6173 (3)	0.99731 (18)	0.40177 (15)	0.0503 (6)
H10A	0.608751	1.033407	0.460587	0.075*
H10B	0.554676	1.013137	0.368946	0.075*
O11[a]	0.8397 (6)	0.4228 (5)	0.8742 (5)	0.0814 (18)
H11[a]	0.789970	0.464790	0.876261	0.122*
O12	−0.4135 (3)	0.1396 (3)	0.2976 (2)	0.0779 (8)
H12A	−0.372104	0.206982	0.326121	0.117*
H12B	−0.493514	0.144212	0.297781	0.117*
Tb1	0.57563 (2)	0.79869 (2)	0.36700 (2)	0.02488 (5)

[a]Occupancy: 0.5.

2 Experimental details

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 (aromatic), with U_{iso}(H) = 1.2U_{eq}(C).

3 Comment

In the domain of rare earth chemistry, the study of rare earth-organic complexes has attracted much attention due to their potential applications in many fields such as organic electroluminescent materials, agricultural light conversion

film, high efficiency fluorescent powder for compact lamp, luminescence labeling, magnetic molecular materials, catalysis and so on [4–6]. Nowadays, much attention has been focused on Tb(III) and Eu(III) complexes with carboxylates as ligands [7–9]. *p*–Acetamidobenzoic acid is a widely used aromatic carboxylic acid: it is the raw material for the synthesis of non-barbiturate hypnotic sedative quinazoline-4-one derivatives [10], and also the raw material for the synthesis of fluorescent whitening agent and anti-asthma drug N-cinnamyl anthranilic acid [11]. As a ligand, p-acetaminobenzoate and the paracetaminobenzoic acid can coordinate with transition metal ions as end-group ligand or bridging ligand, and is also the donor and acceptor of hydrogen bond, which is conducive to the formation of structurally stable complexes [12] The ORTEP diagram is presented in the Figure. As shown in Figure, complex 1 consists of one Tb ion, three p-acetamidobenzoate anions (AAB), one 2,2′-bipy molecules, two water molecules and one methanol molecule. The central Tb ion is coordinated with two nitrogen atoms from 2,2′-bipy, and seven oxygen atoms from three AAB anions and one water molecule. The Tb(III) ion adopts a single-capped square antiprism coordination geometry, where the cap position is occupied by O10. Atoms O1, O4, N1 and N2 give the upper plane of the square antiprism, and atoms O2, O5, O7 and O8 determine the plane below. Their plane equations are $-3.215x + 12.632y - 1.730z = 8.2531$ and $-4.989x + 12.392y + -3.405z = 4.3340$. The average distance of the atoms in the plane is 0.0310 Å and 0.04631 Å, respectively, and their dihedral angle is 13.5°. The bond lengths Tb1–O1, Tb1–O2, Tb1–O4, Tb1–O5, Tb1–O7, Tb1–O8 and Tb1–O10 are 2.495(2), 2.4509(19), 2.386(2), 2.453(2), 2.428(2), 2.474(2) and 2.395(2) Å, respectively, which are in the normal ranges [11, 12]. The bond lengths of Tb1–N1 and Tb1–N2 are 2.537(2) and 2.527(2) Å, with the average to be 2.532 Å. Otherwise, the shortest center distance between aromatic cycles of 2-(tert-pentyl)anthracene group is 3.736 Å, little longer than 3.700 Å, indicating π–π stacking interaction between the aromatic rings.

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