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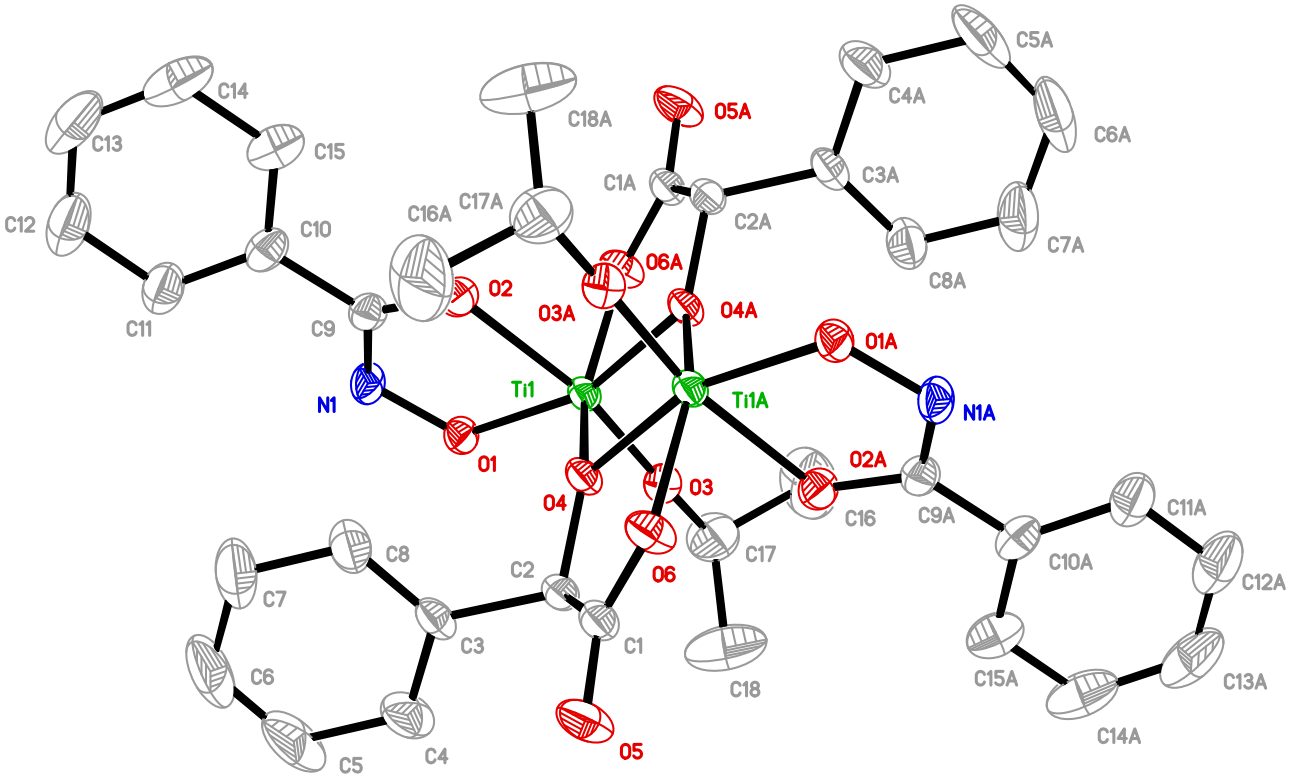
Crystal structure of bis(μ_2-2-oxido-2-phenylacetato-$\kappa^3O,O':O'$)-bis(*N*-oxido-benzamide-κ^2O,O')-bis(propan-2-olato-κ^1O)dititanium(IV), $C_{36}H_{38}N_2O_{12}Ti_2$



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Abstract

$C_{36}H_{38}N_2O_{12}Ti_2$, monoclinic, $P2_1/n$ (no. 14), a = 10.3151(7) Å, b = 15.8747(11) Å, c = 11.5020(8) Å, β = 98.471(3)°, V = 1862.9(2) Å^3, Z = 2, $R_{gt}(F)$ = 0.0386, w$R_{ref}(F^2)$ = 0.1075, T = 296(2) 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.

Source of material

All reagents and solvents employed in this work were commercially available and used without further purification.

Table 1: Data collection and handling.

Crystal:	Yellowish block
Size:	0.22 × 0.21 × 0.17 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.49 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20724, 4653, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3841
$N(param)_{refined}$:	241
Programs:	Bruker [1, 2], SHELX [3], Diamond [4]

Firstly, a mixture of mandelic acid (5 mmol, 0.761 g) and benzohydroxamic acid (1 mmol, 0.137 g) were placed in a Teflon-lined stainless vessel (15 mL), in which isopropanol (1 mL) and acetonitrile (5 mL) were added. After stirring for 5 min, $Ti(O^iPr)_4$ (1.63 mmol, 0.5 mL) was added. The resulting mixture was sealed and heated at 373 K for 72 h under autogenous pressure. After cooling to room temperature at a rate of 5 K h^{-1}, yellowish block crystals were obtained and washed with acetonitrile. The yield was 0.106 g (27%, based on mandelic acid).

Experimental details

H atoms were subsequently treated as riding atoms with distances C—H = 0.98 (CH_3), 0.99 (CH) and 0.95 (ArH) Å.

Comment

In recent years, titanium oxo clusters (TOCs) have attracted much attention because their atomically precise molecular structures are ideal models for titanium dioxide (TiO_2) [5–7]. Moreover, most reported TOCs exhibit photocatalytic activities, such as photocatalytic degradation, hydrogen production, and water oxidation [8–10]. The solvothermal synthetic approach using $Ti(OR)_4$ as the titanium source have proven to be effective for construction TOCs, and a lot of TOCs with various nuclearities and diverse structures have been reported [11, 12]. Introduction of dye-functional ligands can enlarge the light-absorption range and reduce band gap values of TOCs, which is of great importance for photocatalytic applications. Generally, the dye-functional ligands for TOCs are characterized with $C(sp^2)$–O or $N(sp^2)$–O atoms as coordinative sites [13]. For example, catechol is a prevalent dye-functional ligand featuring $C(sp^2)$–O as coordinative sites for construction TOCs with narrow band gap values [14]. To be noted, only a few TOCs protected by ligand with type of $N(sp^2)$–O atom as coordinative site have been reported [15]. Herein, benzohydroxamic acid with $N(sp^2)$–O atom was selected as dye-functional ligand to construct the title TOC.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.45626 (18)	0.69315 (10)	0.39588 (14)	0.0392 (4)
C2	0.36042 (17)	0.61868 (10)	0.39164 (14)	0.0360 (3)
H2	0.2960	0.6304	0.4442	0.043*
C3	0.28918 (18)	0.60399 (11)	0.26875 (15)	0.0416 (4)
C4	0.1622 (2)	0.63159 (15)	0.2392 (2)	0.0677 (6)
H4	0.1182	0.6562	0.2955	0.081*
C5	0.0997 (3)	0.6221 (2)	0.1228 (3)	0.0995 (11)
H5	0.0150	0.6423	0.1012	0.119*
C6	0.1626 (4)	0.5835 (2)	0.0419 (3)	0.1034 (12)
H6	0.1202	0.5765	−0.0346	0.124*
C7	0.2873 (4)	0.55510 (19)	0.0719 (2)	0.0895 (10)
H7	0.3296	0.5285	0.0160	0.107*
C8	0.3516 (3)	0.56565 (15)	0.18523 (18)	0.0605 (6)
H8	0.4373	0.5467	0.2050	0.073*
C9	0.40037 (17)	0.35817 (10)	0.25850 (15)	0.0381 (4)
C10	0.4490 (2)	0.32279 (11)	0.15463 (17)	0.0464 (4)
C11	0.3691 (3)	0.31484 (14)	0.04697 (18)	0.0609 (6)
H11	0.2827	0.3335	0.0378	0.073*
C12	0.4191 (4)	0.27905 (17)	−0.0464 (2)	0.0811 (8)
H12	0.3654	0.2731	−0.1183	0.097*
C13	0.5444 (4)	0.25259 (18)	−0.0349 (3)	0.0914 (10)
H13	0.5763	0.2285	−0.0988	0.110*
C14	0.6253 (3)	0.26097 (17)	0.0704 (3)	0.0873 (9)
H14	0.7119	0.2428	0.0779	0.105*
C15	0.5772 (2)	0.29670 (15)	0.1659 (2)	0.0640 (6)
H15	0.6318	0.3029	0.2373	0.077*
C16	0.2324 (5)	0.4475 (3)	0.7661 (3)	0.1440 (19)
H16A	0.2677	0.3915	0.7648	0.216*
H16B	0.1661	0.4487	0.8164	0.216*
H16C	0.3013	0.4861	0.7951	0.216*
C17	0.1744 (3)	0.47213 (19)	0.6457 (2)	0.0745 (7)
H17	0.1064	0.4308	0.6174	0.089*
C18	0.1134 (4)	0.5562 (2)	0.6367 (5)	0.1316 (16)
H18A	0.1711	0.5959	0.6808	0.197*
H18B	0.0320	0.5542	0.6677	0.197*
H18C	0.0973	0.5731	0.5557	0.197*
H1	0.217 (2)	0.3328 (13)	0.2246 (18)	0.044(5)*
N1	0.27581 (15)	0.35972 (10)	0.26548 (13)	0.0411 (3)
O1	0.24168 (11)	0.39634 (8)	0.36442 (10)	0.0379 (3)
O2	0.47699 (12)	0.38863 (8)	0.34421 (11)	0.0419 (3)
O3	0.27218 (13)	0.46692 (9)	0.57341 (10)	0.0463 (3)
O4	0.43525 (12)	0.54754 (7)	0.43393 (9)	0.0358 (3)
O5	0.42037 (14)	0.76294 (8)	0.36059 (14)	0.0578 (4)
O6	0.57385 (12)	0.67569 (8)	0.44142 (11)	0.0452 (3)
Ti1	0.38148 (3)	0.43352 (2)	0.48073 (2)	0.03263 (10)

The X-ray crystal diffraction revealed that the title compound crystallizes in the monoclinic system. There is one six-coordinated Ti^{4+} ion, two one deprotonated benzohydroxamate, one mandelate and one isopropoxide groups in the asymmetric unit. The dinuclear title complex is furnished by an inversion center (see the figure). Thus the two Ti^{4+} present the same coordination environments featuring the octahedral TiO_6 mode. The six coordinated oxygen atoms belong to two mandelate ligands, one deprotonated benzohydroxamate and one isopropoxide groups respectively. Two μ_2–O-type atoms link the two Ti^{4+} ions together wtith the distance of 3.211 Å which is very close to the reported 3.222 Å of the TOC based on mandelic acid, and the average bond length of Ti–O is 1.956, almost the same as 1.963 Å of the reported structure [16].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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