Yu Youzhu*, Guo Yuhua, Niu Yongsheng, Liu Nana and Zhang Hongfei

Crystal structure of bis(μ_2 -2-oxido-2-phenylacetate- $\kappa^3 O:O,O'$)-bis(1-isopropoxy-2-oxo-2-phenylethan-1-olato- $\kappa^2 O,O'$)-bis(propan-2-olato- $\kappa^1 O$)dititanium(IV), $C_{44}H_{52}O_{14}Ti_2$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.23 × 0.21 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.43 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II
$\theta_{\max}$, completeness:	25.0°, 97%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	41,802, 3867, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3166
$N(\text{param})_{\text{refined}}$:	301
Programs:	Bruker [1, 2], SHELX [3], Diamond [4]

<https://doi.org/10.1515/ncrs-2020-0590>

Received November 10, 2020; accepted December 18, 2020;
published online January 13, 2021

Abstract

$C_{44}H_{52}O_{14}Ti_2$, orthorhombic, *Pbca* (no. 61), $a = 15.0005(7)$ Å, $b = 15.9478(8)$ Å, $c = 18.4438(10)$ Å, $V = 4412.2(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0372$, $wR_{\text{ref}}(F^2) = 0.1089$, $T = 296(2)$ K.

CCDC no.: 2051187

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.

*Corresponding author: Yu Youzhu, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P. R. China, E-mail: 119yyz@163.com. <https://orcid.org/0000-0001-8151-8239>

Guo Yuhua, Niu Yongsheng, Liu Nana and Zhang Hongfei, College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, Henan, P. R. China

A mixture of phenylphosphonic acid (0.5 mmol, 79 mg) and mandelic acid (3 mmol, 0.456 g) were added with stirring to acetonitrile (5 mL) and isopropanol (1 mL). After 5 min, $Ti(O^iPr)_4$ (3 mmol, 0.92 mL) was added to the above solution, and then the resulting mixture was sealed in a Teflon-lined stainless vessel (15 mL) and heated at 373 K for 3 d under autogenous pressure. After cooling to room temperature at a rate of $5 \text{ K} \cdot \text{h}^{-1}$, colorless block crystals were isolated, washed with acetonitrile and then dried in air.

Experimental details

H atoms were subsequently treated as riding atoms with distances C–H = 0.98 (CH₃), 0.99 (CH) and 0.95 (ArH) Å.

Comment

In the field of solar energy conversion and degradation of environmental pollutants, titanium dioxide (TiO_2) is one of the most promising photocatalysts because of its high efficiency, non-toxic nature and biocompatibility [5–7]. However, the imprecise and inhomogeneous characteristics of TiO_2 materials may greatly inhibit the theoretical calculations study and mechanistic research [8]. As the structure and reactivity model of TiO_2 , titanium-oxo clusters (TOCs) have garnered intense attraction in the very recent years

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Ti1	0.60658 (2)	0.49523 (2)	0.49017 (2)	0.03814 (14)
O1	0.63018 (10)	0.39918 (10)	0.44827 (9)	0.0528 (4)
O2	0.70255 (10)	0.49320 (8)	0.55300 (8)	0.0449 (4)
O3	0.65064 (9)	0.57004 (10)	0.41393 (8)	0.0503 (4)
O4	0.62187 (12)	0.68145 (12)	0.34494 (10)	0.0680 (5)
O5	0.49208 (8)	0.53860 (9)	0.44489 (7)	0.0391 (3)
O6	0.59783 (10)	0.61686 (9)	0.54934 (8)	0.0476 (4)
O7	0.66932 (11)	0.69279 (11)	0.63243 (9)	0.0622 (5)
C1	0.37725 (17)	0.63642 (18)	0.30520 (15)	0.0635 (7)
H1	0.3577	0.6813	0.3351	0.076*
C2	0.3327 (2)	0.6195 (2)	0.24039 (17)	0.0799 (9)
H2	0.2835	0.6532	0.2261	0.096*
C3	0.3592 (3)	0.5562 (3)	0.19874 (17)	0.0920 (10)
H3	0.3285	0.5444	0.1548	0.110*
C4	0.4293 (3)	0.5085 (3)	0.2184 (2)	0.1057 (12)
H4	0.4476	0.4634	0.1882	0.127*
C5	0.4751 (2)	0.5247 (2)	0.28271 (16)	0.0802 (8)
H5	0.5245	0.4908	0.2962	0.096*
C6	0.44895 (14)	0.58893 (14)	0.32602 (12)	0.0462 (5)
C7	0.49835 (14)	0.60732 (13)	0.39574 (11)	0.0418 (5)
H7	0.4717	0.6581	0.4189	0.050*
C8	0.59786 (15)	0.62327 (14)	0.38226 (12)	0.0465 (5)
C9	0.5296 (2)	0.7347 (2)	0.6818 (2)	0.1018 (11)
H9A	0.5051	0.6797	0.6688	0.153*
H9B	0.4817	0.7765	0.6815	0.153*
H9C	0.5561	0.7319	0.7303	0.153*
C10	0.59845 (17)	0.75868 (17)	0.62864 (16)	0.0669 (7)
H10	0.5721	0.7601	0.5788	0.080*
C11	0.6408 (3)	0.8404 (2)	0.6453 (2)	0.1007 (11)
H11A	0.6677	0.8382	0.6937	0.151*
H11B	0.5957	0.8848	0.6440	0.151*
H11C	0.6871	0.8523	0.6092	0.151*
C12	0.65871 (15)	0.62608 (14)	0.59184 (12)	0.0466 (5)
C13	0.72830 (14)	0.55672 (13)	0.60012 (12)	0.0462 (5)
H13	0.7257	0.5348	0.6509	0.055*
C14	0.82233 (15)	0.58741 (14)	0.58502 (12)	0.0476 (5)
C15	0.86174 (19)	0.5710 (2)	0.51958 (16)	0.0758 (8)
H15	0.8306	0.5397	0.4838	0.091*
C16	0.9470 (2)	0.6000 (3)	0.5054 (2)	0.0959 (11)
H16	0.9740	0.5882	0.4600	0.115*
C17	0.99248 (19)	0.6450 (2)	0.5554 (2)	0.0846 (9)
H17	1.0506	0.6653	0.5449	0.101*
C18	0.9547 (2)	0.66092 (19)	0.62019 (19)	0.0777 (8)
H18	0.9866	0.6921	0.6556	0.093*
C19	0.86944 (18)	0.63214 (17)	0.63556 (15)	0.0651 (7)
H19	0.8435	0.6435	0.6815	0.078*
C20 ^a	0.7372 (6)	0.2940 (6)	0.4768 (4)	0.083 (2)
H20A ^a	0.7693	0.2451	0.4581	0.125*
H20B ^a	0.7020	0.2777	0.5193	0.125*
H20C ^a	0.7801	0.3375	0.4906	0.125*
C21 ^a	0.6770 (5)	0.3271 (5)	0.4198 (3)	0.0649 (17)
H21 ^a	0.6346	0.2831	0.4023	0.078*
C22 ^b	0.7359 (8)	0.3598 (10)	0.3584 (5)	0.086 (3)
H22A ^b	0.7693	0.3131	0.3370	0.129*
H22B ^b	0.7777	0.4015	0.3776	0.129*

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H22C ^b	0.6985	0.3859	0.3211	0.129*
C20A ^b	0.6959 (6)	0.2649 (4)	0.4558 (5)	0.0780 (19)
H20D ^b	0.6971	0.2647	0.5089	0.117*
H20E ^b	0.7427	0.2278	0.4372	0.117*
H20F ^b	0.6376	0.2451	0.4389	0.117*
C21A ^b	0.7116 (5)	0.3530 (4)	0.4285 (4)	0.0682 (18)
H21A ^b	0.7215	0.4013	0.4576	0.082*
C22A ^a	0.7087 (8)	0.3502 (10)	0.3448 (5)	0.078 (2)
H22D ^a	0.7184	0.4067	0.3254	0.117*
H22E ^a	0.6503	0.3296	0.3289	0.117*
H22F ^a	0.7554	0.3126	0.3269	0.117*

^aOccupancy: 0.491(8), ^bOccupancy: 0.509(8).

and a great number of TOCs have been reported [9–11]. To be noted most of the reported TOCs exhibited high photocatalytic properties due to their coordinated ligands. However, it is still challenging to rationally design and synthesize TOCs with desired properties. As is known, Ti⁴⁺ ions belong to hard Lewis acids and are easily coordinated with oxygen atoms. Mandelic acid are endowed with hydroxyl and carboxyl groups which is an ideal ligand for Ti⁴⁺. However, to the best of our knowledge, only a few TOCs based on mandelic acid have been reported [12, 13].

The crystal structure of the title compound shows that the basic dinuclear complex consists of two Ti⁴⁺ ions, two 2-oxido-2-phenylacetate (mandalate) ligands two esterified mandelate and two propan-2-olate groups (the figure). Notably, the hydroxyl groups of mandelic acid which do not participate in coordination tend to be esterified. The two Ti⁴⁺ ions show octahedral TiO₆ coordination environments and are linked by two μ₂-O atoms to generate the Ti₂ core. The distance of the two Ti⁴⁺ ions is 3.222 Å which is longer than the reported 2.961 Å of the TOC based on another mandalate [13]. In addition, the average bond length of Ti–O is 1.963 Å, to be consistent with the literature [13–15].

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Foundation of Anyang Institute of Technology (YPY2019003).

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

References

1. Bruker. *APEX2*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2005.
2. Bruker. *SAINT-Plus*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2001.

3. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Version 3.2j*; Crystal Impact: Bonn, Germany, 2012.
5. Chen X., Mao S. S. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. *Chem. Rev.* 2007, *107*, 2891–2959.
6. Fujishima A., Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972, *238*, 37–38.
7. Kongkanand A., Tvrđy K., Takechi K., Kuno M., Kamat P. V. Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture. *J. Am. Chem. Soc.* 2008, *130*, 4007–4015.
8. Sokolow J. D., Trzop E., Chen Y., Tang J., Allen L. J., Crabtree R. H., Benedict J. B., Coppens P. Binding modes of carboxylate- and acetylacetonate-linked chromophores to homodisperse polyoxotitanate nanoclusters. *J. Am. Chem. Soc.* 2012, *134*, 11695–11700.
9. Yu Y.-Z., Zhang Y.-R., Geng C.-H., Sun L., Guo Y., Feng Y.-R., Wang Y.-X., Zhang X.-M. Precise and wide-ranged band-gap tuning of Ti₆-core-based titanium oxo clusters by the type and number of chromophore ligands. *Inorg. Chem.* 2019, *58*, 16785–16791.
10. Yu Y. Z., Guo Y., Zhang Y. R., Liu M. M., Feng Y. R., Geng C. H., Zhang X. M. A series of silver doped butterfly-like Ti₈Ag₂ clusters with two Ag ions panelled on a Ti₈ surface. *Dalton Trans* 2019, *48*, 13423–13429.
11. Fang W. H., Zhang L., Zhang J. Synthetic strategies, diverse structures and tuneable properties of polyoxo-titanium clusters. *Chem. Soc. Rev.* 2018, *47*, 404–421.
12. Schetter B., Stosiek C., Ziemer B., Mahrwald R. Multinuclear enantiopure titanium self-assembly complexes-synthesis, characterization and application to organic synthesis. *Appl. Organomet. Chem.* 2007, *21*, 139–145.
13. Mahrwald R., Ziemer B. Insight into the mechanism of direct catalytic aldol addition mediated by ambifunctional titanium complexes. *Tetrahedron Lett.* 2002, *43*, 4459–4461.
14. Fang W. H., Zhang L., Zhang J. A 3.6 nm Ti₅₂-oxo nanocluster with precise atomic structure. *J. Am. Chem. Soc.* 2016, *138*, 7480–7483.
15. Hou J. L., Huo P., Tang Z. Z., Cui L. N., Zhu Q. Y., Dai J. A titanium oxo cluster model study of synergistic effect of co-coordinated dye ligands on photocurrent responses. *Inorg. Chem.* 2018, *57*, 7420–7427.