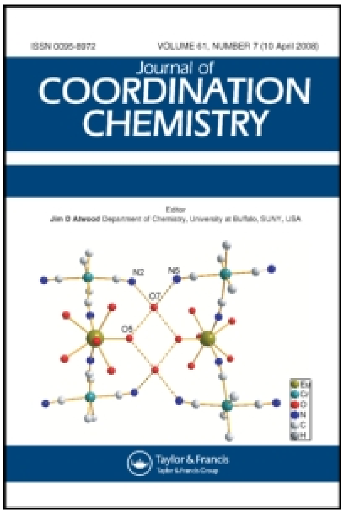

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Daqing Shi[abc]; Guolan Dou[b]; Huiyan Liu[b]; Haiying Wang[b]
[a] College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, P.R. China [b] Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, P.R. China [c] The Key Laboratory of Biotechnology on Medical Plant of Jiangsu Province, Xuzhou 221116, China

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Synthesis and crystal structure of a trinuclear titanium(IV) *β*-diketonate complex with a six-membered [Ti–(μ-O)]$_3$ ring

DAQING SHI*†‡§, GUOLAN DOU‡, HUIYAN LIU‡
and HAIYING WANG‡

†College of Chemistry and Chemical Engineering, Suzhou University,
Suzhou 215123, P.R. China
‡Department of Chemistry, Xuzhou Normal University,
Xuzhou 221116, P.R. China
§The Key Laboratory of Biotechnology on Medical Plant of
Jiangsu Province, Xuzhou 221116, China

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The trinuclear titanium(IV) β-diketonate complex, $[Ti_3(\mu\text{-}O)_3(dppd)_6]\cdot(DMF)(0.5EtOH)$ (**1**) (H-dppd = 1,3-diphenylpropane-1,3-dione) has been synthesized and its crystal structure and spectroscopic properties have been studied. Complex **1** crystallizes in monoclinic system with space group *C*2/*c* and $a = 20.954(5)$ Å, $b = 18.705(4)$ Å, $c = 24.617(6)$ Å, $\beta = 111.957(4)°$, $Z = 4$. The complex consists of a six-membered [Ti–(μ-O)]$_3$ ring, of which three titanium(IV) ions are linked together by bridging oxygen atoms. Each titanium(IV) possesses an octahedral geometry, with four oxygen atoms from the two β-diketonate ligands and two bridging oxygen atoms.

Keywords: Trinuclear titanium complex; Crystal structure; β-Diketone

1. Introduction

There is considerable current effort to develop the chemistry of titanium alkoxides for a variety of uses, including metal oxide ceramic precursors [1–4]. In order to tailor hydrolysis and condensation rates, these precursors are often modified through the addition of multidentate ligands such as acetic acid ($HOAc = HO_2CMe$) [5–7]. Other, sterically varied carboxylic acids have also been investigated [8–10]. Various forms of linked [Ti–O]$_4$ cubelike arrangements are favored for HORc-modified $Ti(OR)_4$ complexes [5]. Only two non-cubelike complexes are reported, which adopt the hexagon-prismatic structure of two offset [Ti–(μ-O)]$_3$ rings [5, 8]. In this article, we report the preparation, crystal structure and properties of a trinuclear titanium(IV) β-diketonate complex, $[Ti_3(\mu\text{-}O)_3(dppd)_6]\cdot(DMF)(0.5EtOH)$ (**1**). To our knowledge, this is the first titanium(IV) β-diketonate complex with a six-membered [Ti–(μ-O)]$_3$ ring.

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*Corresponding author. Email: dqshi@suda.edu.cn

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2. Experimental

2.1. *Synthesis*

THF was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under N_2. To a solution of 1,3-diphenylpropane-1,3-dione (3 mmol) in THF (10 mL) $TiCl_4$ (1.1 mL, 10 mmol) was added. The reaction mixture was then refluxed for 2 h. After this period, TLC analysis of the mixture showed the reaction to be complete. The reaction mixture was quenched with 5% HCl (50 mL) and extracted with $ClCH_2CH_2Cl$ (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude products were purified by recrystallization from DMF and H_2O. The solution was allowed to stand for several days, giving pale brown single crystals of complex **1**, yield ca 85%. m.p. >300°C; UV-vis (DMF) λ_{max}: 270, 352 nm; IR (KBr) 3057, 1593, 1518, 1452, 755, 718, 684 cm^{-1}. Anal. Calcd for $C_{94}H_{76}NO_{16.50}Ti_3$ (%): C 58.13, N 4.17, H 5.34; found C 58.09, N 4.22, H 5.29.

2.2. *Physical measurements*

C, N and H elemental analyses were carried out with a Perkin-Elmer 2400II instrument. An IR spectrum was recorded on a Bruker Tensor 27 spectrophotometer as KBr pellets. An electronic spectrum was recorded on a Shimadzu UV2501PC spectrophotometer. All starting materials and solvents were of analytical grade from commercial sources and used without further purification.

2.3. *Crystal structure determination*

A block single crystal with approximate dimensions of $0.35 \times 0.18 \times 0.14\,mm^3$ was placed on a Bruker Smart-1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were collected with the ω scan technique at 298(2) K in the range $1.51 \le \theta \le 25.01$ and data were corrected for absorption using the program SADABS [11]. A total of 23,167 reflections were collected, of which 7829 unique reflections were used for structure determination. The structure was solved by direct methods using the program SHELXS-97 [12], subsequent Fourier difference techniques, and anisotropically refined by full-matrix least-squares on F^2 using SHELXL-97 [13]. Hydrogen atoms were added theoretically and refined with the riding model and fixed isotropic thermal parameters. Crystal data and structural refinements are shown in table 1.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of **1** is illustrated in figure 1. Selected bond distances and angles are listed in table 2. Complex **1** is made up of trinuclear $[Ti_3(\mu_2\text{-}O)_3(dppd)_6]$ species, one DMF molecule and half EtOH molecule. Complex **1** consists of a $[Ti\text{–}(\mu\text{-}O)]_3$ ring, with

Table 1. Crystal data and structure refinement for **1**.

	1
Empirical formula	$C_{94}H_{76}NO_{16.50}Ti_3$
Formula weight	1627.26
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	20.954(5)
b (Å)	18.705(4)
c (Å)	24.617(6)
β (°)	111.957(4)
V (Å^3)	8949(3)
Z	4
D_{Calcd} (Mg m^{-3})	1.208
μ (mm^{-1})	0.325
Reflection collected	23,167
Independent reflection	7829 ($R_{\mathrm{int}} = 0.0786$)
Reflections with $[I > 2\sigma(I)]$	3579
Goodness-of-fit on F^2	1.033
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0749$, $wR_2 = 0.1863$
R indices (all data)	$R_1 = 0.1748$, $wR_2 = 0.2676$
Largest diff. peak and hole (e Å^{-3})	0.779 and −0.359

#1: $(1 - x, y, 1.5 - z)$.

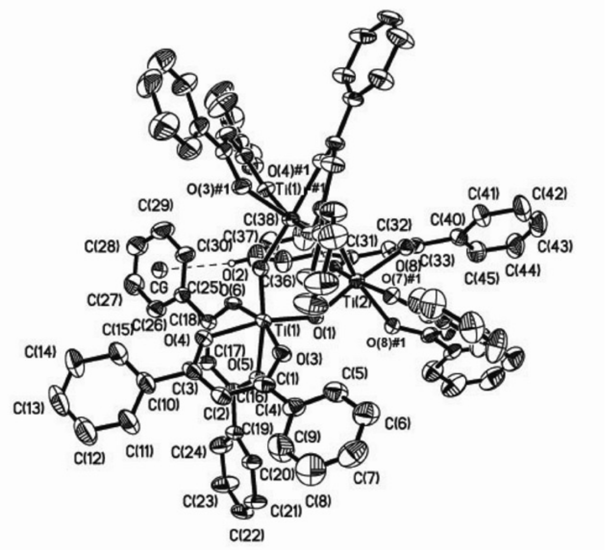

Figure 1. Molecular structure of **1**, showing 40% probability displacement ellipsoids. The dashed line represents the C–H $\cdots \pi$ interaction between the two neighboring β-diketonate ligands. Cg is the centroid of the C25–C30 ring. Symmetry transformation codes: #1$(1 - x, y, 1.5 - z)$.

three titanium(IV) ions linked by bridging oxygen atoms. The $[\mathrm{Ti}\text{–}(\mu\text{-O})]_3$ ring is a distorted hexagon, with alternating angles of 98 and 142°; the largest deviation from the least-squares plane is 0.0383 Å for O(1). Each titanium(IV) possesses an octahedral geometry, with four oxygen atoms from the two β-diketonate ligands and two bridging oxygen atoms (figure 2).

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Ti(1)–O(1)	0.1813(4)	Ti(2)–O(1)	0.1804(4)
Ti(1)–O(2)	0.1816(2)	Ti(2)–O(1)#1	0.1804(4)
Ti(1)–O(6)	0.1953(4)	Ti(2)–O(7)#1	0.1967(4)
Ti(1)–O(3)	0.1974(4)	Ti(2)–O(7)	0.1967(4)
Ti(1)–O(4)	0.2082(4)	Ti(2)–O(8)#1	0.2081(4)
Ti(1)–O(5)	0.2089(4)	Ti(2)–O(8)	0.2081(4)
O(1)–Ti(1)–O(2)	97.46(19)	O(1)–Ti(2)–O(1)#1	98.2(2)
O(1)–Ti(1)–O(6)	99.04(16)	O(1)–Ti(2)–O(7)#1	96.94(16)
O(2)–Ti(1)–O(6)	91.66(11)	O(1)#1–Ti(2)–O(7)#1	90.93(16)
O(1)–Ti(1)–O(3)	93.54(16)	O(1)–Ti(2)–O(7)	90.93(16)
O(2)–Ti(1)–O(3)	99.16(12)	O(1)#1–Ti(2)–O(7)	96.94(16)
O(6)–Ti(1)–O(3)	162.21(16)	O(7)#1–Ti(2)–O(7)	168.0(2)
O(1)–Ti(1)–O(4)	168.71(16)	O(1)–Ti(2)–O(8)#1	92.10(16)
O(2)–Ti(1)–O(4)	93.30(19)	O(1)#1–Ti(2)–O(8)#1	168.13(16)
O(6)–Ti(1)–O(4)	83.98(16)	O(7)#1–Ti(2)–O(8)#1	81.92(15)
O(3)–Ti(1)–O(4)	81.35(16)	O(7)–Ti(2)–O(8)#1	88.76(15)
O(1)–Ti(1)–O(5)	89.12(16)	O(1)–Ti(2)–O(8)	168.13(16)
O(2)–Ti(1)–O(5)	171.56(16)	O(1)#1–Ti(2)–O(8)	92.10(16)
O(6)–Ti(1)–O(5)	82.05(15)	O(7)#1–Ti(2)–O(8)	88.76(15)
O(3)–Ti(1)–O(5)	85.64(16)	O(7)–Ti(2)–O(8)	81.92(15)
O(4)–Ti(1)–O(5)	80.50(16)	O(8)#1–Ti(2)–O(8)	78.4(2)

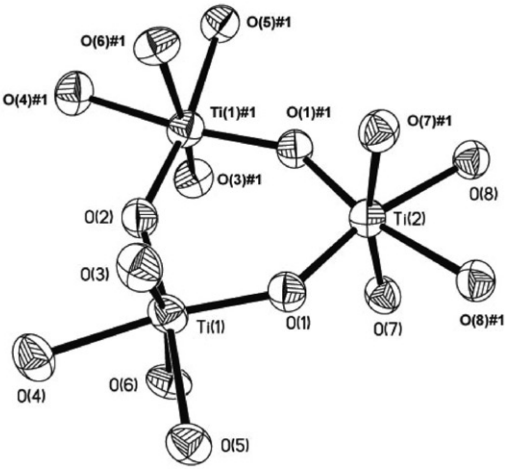

Figure 2. Central core of **1**. Symmetry transformation codes: #1($1-x$, y, $1.5-z$).

The average Ti–(μ-O)–Ti angle of 97.7° is close to the value of 96.6° observed in $Ti_3(O)(Cl)(ONp)_9 \cdot C_7H_8$, in which three titanium metal centers are linked together by briding ONp ligands [5]. However, the average Ti–(μ-O) and Ti $\cdots$ Ti distances of 1.81 and 3.43 Å, respectively, are shorter and longer than those of 2.03 and 3.04 Å in $Ti_3(O)(Cl)(ONp)_9 \cdot C_7H_8$ [5]. The dppd ligands in **1** are symmetrically chelated to titanium. The Ti–O distances and O–Ti–O chelate angles lie in the range of 1.953–2.089 Å and 81.35–82.05°, respectively, comparable with those observed in titanium and zirconium complexes with chelating β-diketonate ligands [14–16].

Figure 1 reveals a C–H$\cdots\pi$ interaction between two neighboring β-diketonate ligands, which are separated by a distance of 3.026(7) Å.

3.2. *IR spectra and electronic spectra*

The electronic spectrum of **1** in DMF shows two bands at 270 and 352 nm which are assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic ring and a $n \rightarrow \pi^*$ transition of the C=O group, respectively [17, 18].

The IR spectrum of **1** shows a strong ν(C=O) at 1518 cm^{-1}, which is shifted to lower frequency compared to that of the free β-diketonate ligand [17]. The band at 3057 cm^{-1}, ν(Ar–H), and bands in the 1452–1593 and 684–755 cm^{-1} regions are assigned to ν(C=C) and δ(C–H) of the phenyl ring, respectively.

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