Inorganic Chemistry Communications 93 (2018) 61–64

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

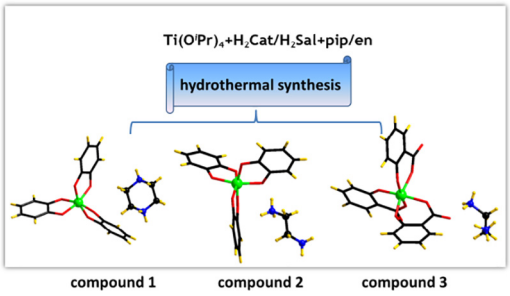
Hydrothermal synthesis, structures and visible light harvest of three titanium complexes

Guo-Liang Dong[a,b], Lei Wang[a,*], Wei-Hui Fang[b,*], Lei Zhang[b]

[a] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

GRAPHICAL ABSTRACT

Hydrothermal synthesis has been successfully used in the isolation of three crystalline titanium compounds.



ARTICLE INFO

Keywords:
Titanium complexes
Hydrothermal synthesis
Structures
Bandgaps

ABSTRACT

Hydrothermal syntheses have been extensively used in the area of polyoxometalates and metal organic frameworks. However, the hydrothermal synthesis of crystalline titanium(IV) complexes is a daunting challenge. The reason is that the high reactivity and spontaneous hydrolysis of titanium(IV) ions always leading to fast precipitation of corresponding oxide rather crystalline compounds. Herein, we reported an effective way towards crystalline titanium(IV) complexes. In the presence of organic amines, we successfully isolated three titanium (IV) compounds. It is worth noting that organic amines play a vital role in the synthesis process, while the introduction of chromophores largely enhanced the visible light harvest.

At present, the synthesis of crystalline titanium compounds has received extensive worldwide attention for their potential photo-related applications [1–4]. As a result, tremendous development in this area has been achieved, which is closely related to the revolution of preparation technologies and approaches. In early researches, titanium oxo clusters are normally synthesized under a dry, O_2-free atmosphere in terms of the easy hydrolysis of $Ti(OR)_4$ (R = alkyl) [5–7]. Such method puts forward high request for the equipment and manipulation. To a great extent, it hampers the rapid development of titanium oxo clusters. Nowadays, in addition to strict inert conditions, diverse synthetic strategies such as solvothermal, ionothermal, and even water phase synthesis have been reported [8].

As everyone knows, titanium compounds can be synthesized in a nucleophilic reaction with water. However, excessive water is likely to lead to rapid sol-gel formation of the bulk TiO_2 phases. Hence, the presence of water is essential but requires careful control. In practice, the source of water can be provided in three situations according to the literatures. Firstly, the trace of water is generated in the esterification reaction like acid and alcohol. Such method has been proven to be an effective way to obtain a broad range of titanium compounds from low nuclearity to high nuclearity ones [8]. Secondly is the directly dosage of water as raw material. Under the rational control of the stoichiometric

* Corresponding authors.
E-mail addresses: inorchemwl@126.com (L. Wang), fwh@fjirsm.ac.cn (W.-H. Fang).

https://doi.org/10.1016/j.inoche.2018.05.012
Received 3 April 2018; Received in revised form 2 May 2018; Accepted 8 May 2018
Available online 10 May 2018
1387-7003/

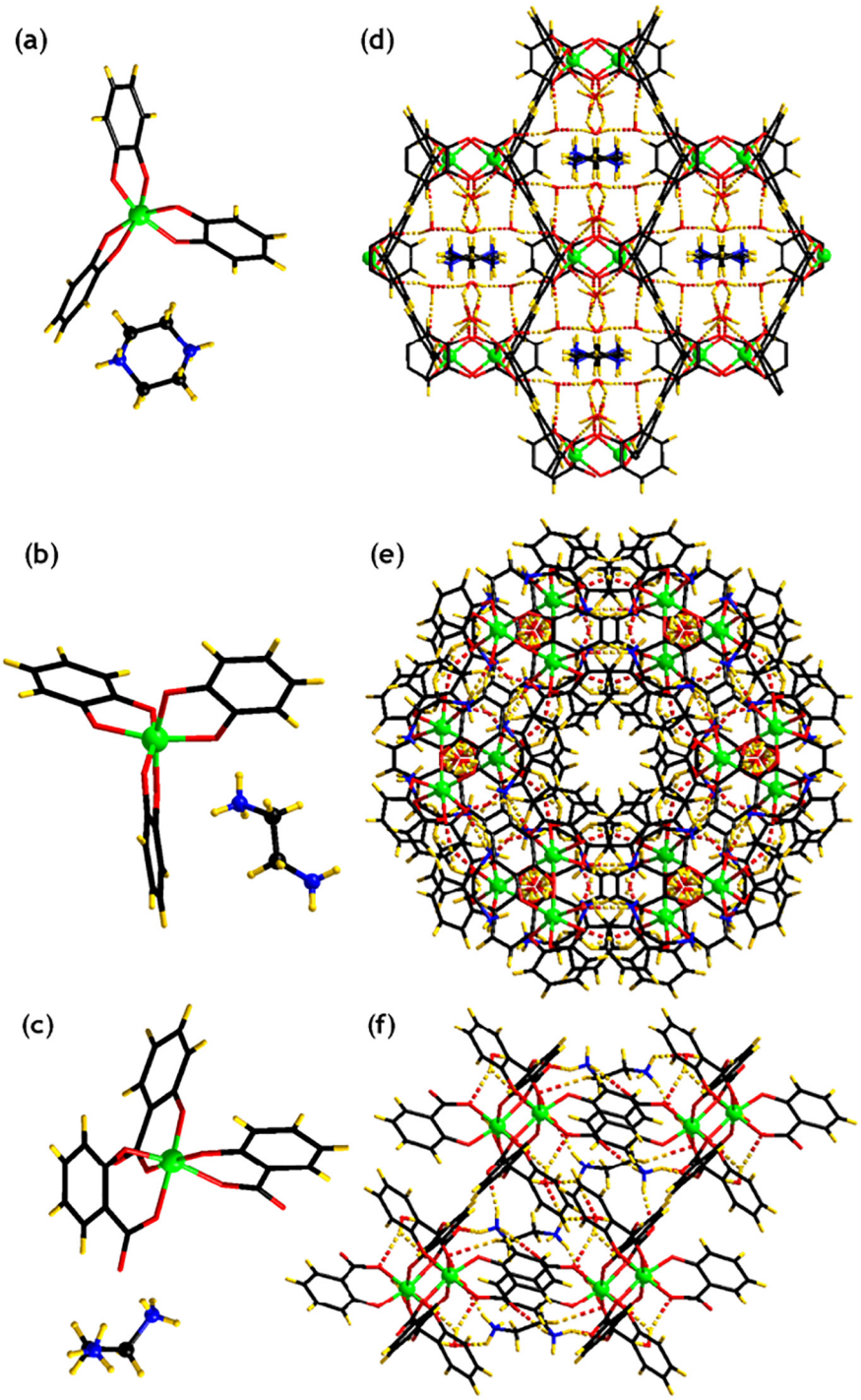


Fig. 1. (a–c) Molecular structure of the three tris compounds. Lattice water molecules are omitted for clarity. (d–f) Stack mode of the three compounds showing the hydrogen bonds. Atom code: Ti green; O red; N blue; C black; H yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ratio of $H_2O/Ti(OR)_4$, Klemperer and coworkers have successfully isolated a series of titanium compounds, like trinuclear Ti_3 [9], Ti_{12} cage [10] and Keggin like Ti_{18} cluster [11]. Moreover, they demonstrate the bridged oxo comes from water molecular by using ^{17}O nuclear magnetic resonance spectroscopy [12]. Thirdly, water can be used as a solvent [13,14]. Compared with the source of organic $Ti(OR)_4$ in organic solvent, inorganic $TiCl_4$ and $TiOSO_4$ can be readily dissolve in water and generate isolation of titanium compounds. Recently, Wang and coworkers have contributed a lot in this aspect and report a number of titanium compounds with pentagonal-prismatic geometry as a representation [15–19].

Recent years, our group makes a significant amount of effort in the isolation of crystalline titanium compounds [20–24]. Fortunately, we have achieved some progress especially in the synthetic approaches. For example, ionothermal synthesis is initially adopted in this system [25]. In fact, hydrothermal synthesis is a green and convenient route often employed in polyoxometalates and metal organic framework field [26,27]. Based on our previous research and to explore the less studied challenge hydrothermal synthesis [28], we herein report three titanium compounds, namely $Ti(Cat)_3{\cdot}H_2pip{\cdot}8H_2O$ (**1**; H_2Cat = Catechol;