

## 단 신

### 티타늄 붕치 화합물의 합성과 분자 구조

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### Thio Sol-Gel Approach to An Octanuclear Titanium(IV) Cluster Compound

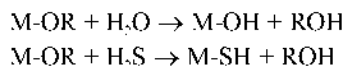
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**주제어:** 티타늄 알콕사이드 붕치화합물, 티오 졸-겔법, 이황화티타늄

**Keywords:** Titanium Alkoxide Cluster, Thio Sol-Gel Process, Titanium Disulfide

Since Vecht and Quddus have reported the preparation of alkaline earth sulfides by using the reaction between alkaline earth alkoxides and  $H_2S$  in 1976,<sup>1</sup> a thio sol-gel process has been reported for the synthesis of metal sulfides using alkoxides or thiolates.<sup>2-6</sup> The thio sol-gel process in which metal alkoxides act as the metal source uses  $H_2S$  for a thiolysis reaction similar to  $H_2O$  for the hydrolysis reaction in the conventional sol-gel process as follows:



In the case of titanium(IV) complexes, however, Bottomley has reported the different reactivity of  $H_2O$  and  $H_2S$  toward to  $Cp_2Ti(CO)_2$  that the reaction between  $Cp_2Ti(CO)_2$  and  $H_2S$  gives  $(CpTi)_3S_6$ , whereas the reaction between  $Cp_2Ti(CO)_2$  and  $H_2O$  produces  $(CpTi)_6O_8$ .<sup>7</sup> A black precipitate, which is speculated to be an alkoxy sulfide, is obtained by the treatment of titanium alkoxides with  $H_2S$  and can be converted to  $TiS_2$  by heating at 800 °C under the  $H_2S$  gas. Even though titanium thiolates are used as the metal source, the resulting precipitate

can only be transferred to the single phase  $TiS_2$  with the presence of  $H_2S$  gas at high temperatures such as 800 °C. Otherwise a small amount of  $TiO_2$  is also formed at the milder conditions or under nitrogen atmosphere. (see Fig. 1) The origin of trace of oxygen in the products has not disclosed in the thio sol-gel approach yet, even though titanium ions have been known to be very oxophilic. Here we describe the isolation and characterization of the intermediate species in the thio sol-gel process. The new cluster  $Ti_8O_4(S_2)_4S_4(OCH(CH_3)_2)_{12}C_6H_6$ , described here is the first example of an isolated thio sol-gel precursor of titanium disulfide from titanium alkoxides.

In our attempt to prepare the titanium alkoxy sulfide by reaction of titanium isopropoxide with hydrogen sulfide, we found that a red crystalline compound could be isolated in about 20% yield.<sup>8</sup> The X-ray crystal structure analysis of this molecule revealed a new structure type within octanuclear titanium (IV) isopropoxy sulfide clusters. (see Fig. 1)<sup>9</sup> It showed that the compound is made up of four oxygen atoms, four sulfur atoms, two disulfide ligands, twelve isopropoxide ligands and one solvated benzene. The structure resembles distorted octahe-

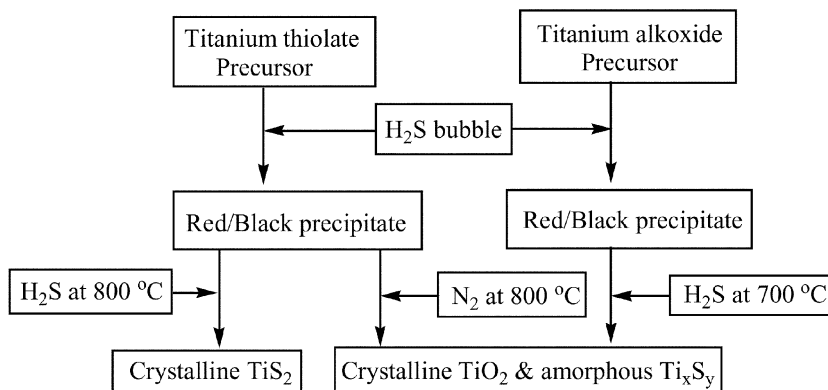


Fig. 1. Schematic flow chart showing thio sol-gel approach to  $TiS_2$ .

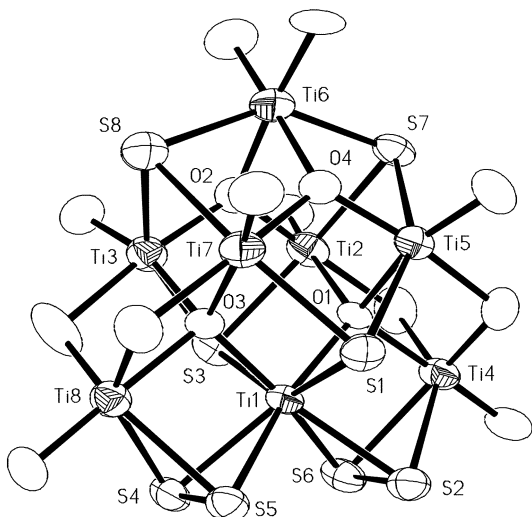


Fig. 2. ORTEP drawing of  $[Ti_8(\mu_4-O)_2(\mu_4-O)(S_7)_4(S_4)(O)_2]$  core of  $Ti_8O_4(S_7)S_4(OCH(CH_3)_2)_{17} \cdot C_6H_6$  (**1**).

dral  $Ti_8O_4S_7$  moieties attached with two Ti ions (Ti4 and Ti8) and two disulfide ions. Within the octahedral framework four oxo oxygen atoms (O1, O2, O3 and O4) and four sulfides (S1, S3, S7 and S8) tetrahedrally coordinate to titanium ions with triply-bridging forms, respectively. But as two Ti atoms (Ti4 and Ti8) are added, two (O1 and O3) of triply-bridging oxo oxygens in the octahedron bond to Ti ions with quadruply-bridging forms. To the best of our knowledge, no titanium sulfoxo alkoxy complexes derived from the thio sol-gel process have been reported in the literature, even though compound  $CsTi_4S_2$  has been reported to consist of infi-

nite 1-dimensional  $[Ti_3(S_2)_2(S)^{-2}]$  chains.<sup>10</sup>

The molecular formation  $Ti_8O_4(S_7)S_4(OCH(CH_3)_2)_{17} \cdot C_6H_6$  (**1**) has been confirmed by elemental analysis and spectroscopy.<sup>8</sup> In the  $^1H$  NMR four sets of isopropyl groups attribute to 4 bridging isopropyl groups and 8 terminal isopropyl groups which contain three different environments with a ratio of 2:2:4, respectively. In the FT-IR bands at 1169, 1123 and 1011  $cm^{-1}$  is also characteristic of the isopropyl groups bonded to titanium (IV) ions.<sup>2</sup>

The differential thermal analysis (DTA) data of **1** under the nitrogen atmosphere show that the compound is decomposed with increasing temperatures; ~120, 196, 260, ~530 and 610  $^{\circ}C$  as shown in Fig. 3. First three temperatures can impute to the liberation of solvated benzene and decomposition of isopropoxide ligands, whereas later two temperatures may attribute to decomposition of bridging disulfides and sulfides. The black precipitates can be obtained from reaction between **1** and  $H_2S$  in THF. The X-ray diffraction patterns of powders obtained after conducting calcinations of the precipitate for 1 h under the  $H_2S$  atmosphere are shown in Fig. 4. At 600  $^{\circ}C$ , both of crystalline  $TiO_2$  and  $TiS_2$  phases were observed, whereas  $TiS_2$  phase was observed with trace of  $TiO_2$  at 700  $^{\circ}C$ . In Fig. 2 tetrahedrally bonded oxo oxygen atoms are located inside the Ti cluster rather than on the surface of the cluster, which means that it is difficult to change from O to S in the thio sol-gel process. However, alkoxy oxygen atoms on the surface of the cluster

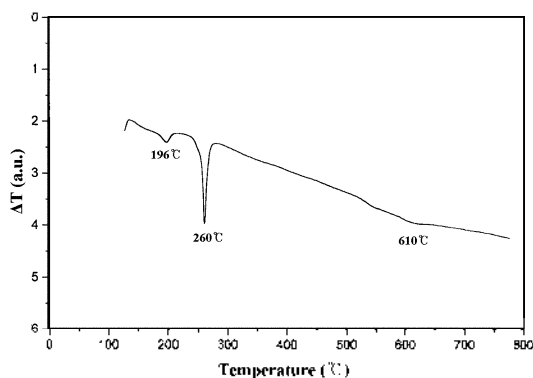


Fig. 3. Differential Thermal Analysis of  $\text{Ti}_6\text{O}_4(\text{S}_2)_2\text{S}_4(\text{OCH}(\text{CH}_3)_2)_{12} \cdot \text{C}_6\text{H}_6$  (1).

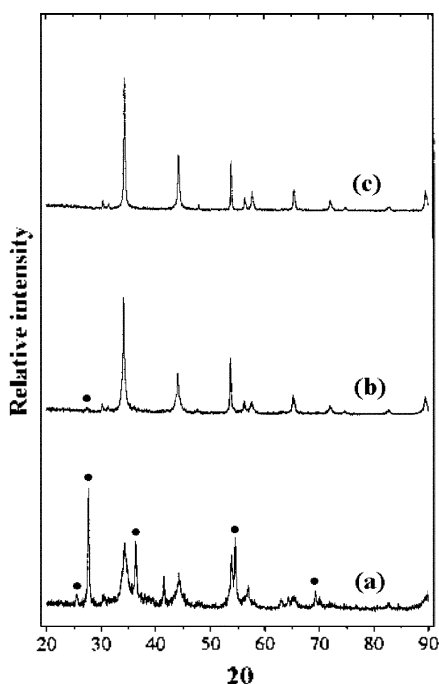


Fig. 4. X-ray diffractograms of powders prepared from calcinations of  $\text{Ti}_6\text{O}_4(\text{S}_2)_2\text{S}_4(\text{OCH}(\text{CH}_3)_2)_{12} \cdot \text{C}_6\text{H}_6$  (1) under  $\text{H}_2\text{S}$  at (a) 600 °C (b) 700 °C and (c) 800 °C. Peaks of  $\text{TiO}_2$  are marked by ●.

may easily be transformed to S or SII through thiolysis. This result is coincident with DTA data, which shows that oxo oxygens may be decomposed at higher temperatures than 610 °C.

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8.  $\text{Ti}_6\text{O}_4(\text{S}_2)_2\text{S}_4(\text{OCH}(\text{CH}_3)_2)_{12} \cdot \text{C}_6\text{H}_6$  (1): All manipulations were performed under argon atmosphere using standard Schlenk techniques. In a typical experiment, titanium isopropoxide (15 g, 52.8 mmol) was dissolved in 20 mL of benzene and  $\text{H}_2\text{S}$  gas was bubbled through it with flowing rate of 5 cc/min at room temperature. The colorless titanium mixture turned immediately red. The  $\text{H}_2\text{S}$  gas was allowed to bubble through it until a black precipitate formed. The resulting solution was isolated for 2 w, and the dark red liquid was decanted and then concentrated to half of its original volume. The resulting black solution was placed at 4 °C for 7 d to collect red cubic crystals. Yield 1.87g (20%)  $\text{C}_{30}\text{H}_{36}\text{Ti}_6\text{S}_8\text{O}_{16}$ : Calcd. C 32.81, H 4.45, S, 17.97; Found C 32.64, H 4.34, S, 17.64. FT-IR( $\text{cm}^{-1}$ , KBr): 3435(br), 2917(m), 2926(w), 2865(w), 1388(w), 1368(w), 1169(m), 1123(vs), 1011(vs), 940(w), 863(w), 832(w), 655(w), 609(vs), 538(s), 522(s).  $^1\text{H}$  NMR( $\text{CDCl}_3$ -d<sub>1</sub>): 1.236(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 1.387(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 1.412(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 1.529(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 4.876(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 5.152(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 5.226(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 5.479(m, OCH( $\text{CH}_3$ )<sub>2</sub>), 7.363(s,  $\text{C}_6\text{H}_6$ ).
9. A crystal suitable for X-ray crystallography was isolated from a benzene solution of 1. Stoe IPDS diffractometer, Mo-K $\alpha$  radiation ( $\lambda=0.7107$  Å), 150(1) K, crystal size 0.2×0.2×0.1 mm, *triclinic*, space group *P1*(bar) with  $a=12.011(2)$  Å,  $b=13.839(3)$  Å,  $c=21.434(4)$  Å,  $\alpha=78.633(16)^\circ$ ,  $\beta=84.676(16)^\circ$ ,  $\gamma=68.479(16)^\circ$ ,  $V=32.485(11)$  Å<sup>3</sup>,  $Z=2$ ,  $R_1=0.0648$ ,  $wR_2=0.1718$ .
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