

## Part I. Chemical Processing of Barium Titanates

## Part II. The Chemistry of Sulfotitanic Acids, Molecular Analogues of Sulfated Metal Oxide Superacids

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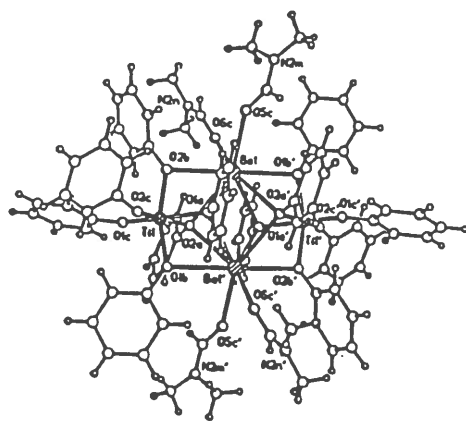
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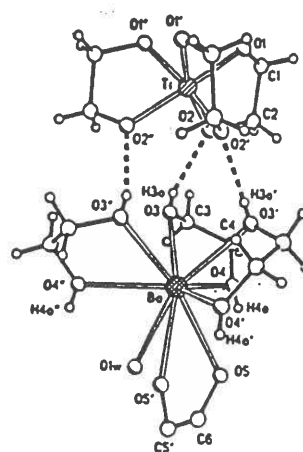
## Part I

Barium titanates are scientifically and technologically important dielectric materials [1]. Barium titanate ( $\text{BaTiO}_3$ ) is a ferroelectric material widely used in the fabrication of ceramic capacitors [2] and thermistors [3], and barium polytitanates such as  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  exhibit microwave dielectric properties which have found applications in microwave communications [4]. The synthesis and processing of these materials have been subjects of extensive research; many recent investigations focus on solution chemical approaches, which offer advantages in terms of processibility and phase purity over the conventional powder process [5].

Several new barium titanium alkoxides,  $\text{BaTi}(\text{OPh})_6 \cdot 2\text{DMF}$  (a),  $[\text{Ba}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{H}_2\text{O})][\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_3]$  (b),  $\text{BaTi}_2\text{O}(\text{OBz})_8 \cdot \text{BzOH}$  (Bz = benzyl) (c), and  $\text{BaTi}_4(\text{OR})_{18}$  (R = Et,  $^n\text{Pr}$ ) (d), have been synthesized and structurally characterized [6].



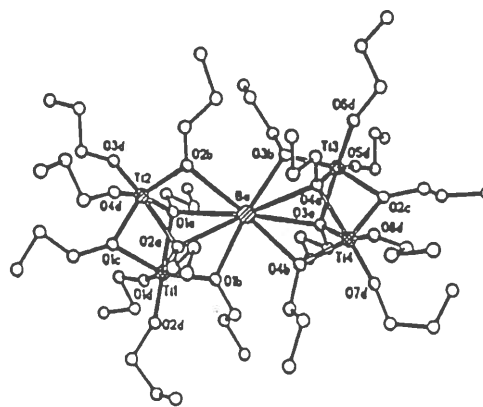
a



b



c



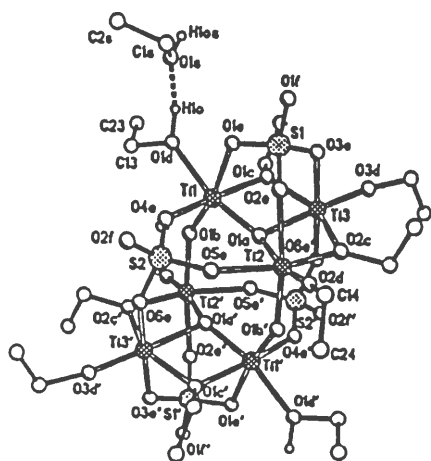
d

Complex **a**, as a single-source precursor, is well-suited for the sol-gel processing of  $\text{BaTiO}_3$  in the form of gels, powders, and thin films [7]. Complex **b** is a viable precursor for the processing of  $\text{BaTiO}_3$  powders by thermal decomposition [8]. Calcination of **b** at  $600\text{ }^\circ\text{C}$  yields submicron  $\text{BaTiO}_3$  powders, which can be sintered into  $\text{BaTiO}_3$  ceramics at  $1300\text{ }^\circ\text{C}$ . Gels and xerogels have been prepared from the complexes **c** and **d**. Heat treatment of the xerogels derived from **c** up to  $1100\text{ }^\circ\text{C}$  yields  $\text{BaTi}_2\text{O}_5$  and a small amount of  $\text{BaTiO}_3$ . Phase pure  $\text{BaTi}_4\text{O}_9$  is obtained after firing the xerogels derived from **d** at temperatures above  $1200\text{ }^\circ\text{C}$ .

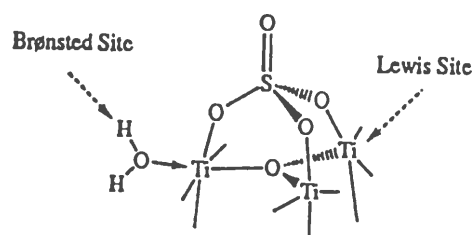
## Part II

Sulfated metal oxides such as  $\text{TiO}_2/\text{SO}_4^{2-}$  and  $\text{ZrO}_2/\text{SO}_4^{2-}$  are solid superacids which have potential applications as catalysts for hydrocarbon isomerization and alkylation [9]. Despite extensive investigation, fundamental questions regarding the surface structure and acid sites of these catalysts still remain unanswered and are open to debate [9]. The purpose of the present research is to attempt to answer these questions by the synthesis and characterization of molecular analogues of these superacid catalysts.

The sulfotitanic acids  $\text{H}_2[\text{Ti}_6\text{O}_4(\text{SO}_4)_4(\text{OR})_{10}]$  ( $\text{R} = \text{Et}, \text{Pr}^n$ ), the first titanium heteropolyacids, are prepared by reaction of  $\text{Ti}(\text{OR})_4$  with aqueous sulfuric acid in alcohol solution. Their conjugate bases,  $(\text{Et}_3\text{NH})_2[\text{Ti}_6\text{O}_4(\text{SO}_4)_4(\text{OR})_{10}]$ , are obtained by reaction of the acids with  $\text{Et}_3\text{N}$ . According to single crystal X-ray diffraction studies of the ethoxide acid and its triethylamine salt, both compounds have the same anion structure containing tridentate sulfate ligands, each bonded to three Ti(IV) centers. The proton in the ethoxide acid (**e**) is bonded to a terminal ethoxide oxygen. The sulfate stretching vibrations in **e** have been identified by infrared spectroscopy using  $^{18}\text{O}$ -labeled sulfate. Comparison of these sulfate vibrational spectra with data reported for sulfated titania [10] reveals several common features, implicating tridentate sulfate coordination in sulfated titania. Accordingly, a structural model (**f**) is proposed for sulfated titania in which sulfate ions adopt a tridentate coordination mode, five-coordinate Ti(IV) centers are Lewis acid sites, and water molecules coordinated to the Ti(IV) centers are Brønsted acid sites.



e



f

## References

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