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Application of Water-Soluble Titanium Complexes as Precursors for Synthesis of Titanium-Containing Oxides via Aqueous Solution Processes

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The growing significance of nanocrystalline inorganic functional materials in the fields of catalysis, electronics, and energy conversion together with the increasing demand of the society for safer, softer, and "greener" technologies has drawn considerable attention of the researchers toward water-based solution processes for synthesis of such materials. In this respect complex oxides, containing d^0-transition metals, such as Ti, Nb, Ta, or Si represent an outstanding challenge for materials chemists due to the extremely narrow range or almost complete absence of suitable precursor compounds compatible with aqueous systems. In the recent 10 years, a remarkable progress has been achieved in the development of new water-soluble complexes of titanium and considerable experience was accumulated in the application of these compounds for synthesis of nanocrystalline titanium-containing materials. The essential knowledge of coordination chemistry of such water-soluble titanium complexes is reviewed in this work, which succeeded to identify the key structural features responsible for stability of the compounds against hydrolysis and to provide guidelines for synthesis of these complexes. Finally, an extensive overview of highly selective aqueous solution based synthesis of TiO_2 polymorphs as well as complex oxide materials with the help of the novel water-soluble titanium complexes is provided.

1. Introduction

Sustainable development of society and conservation of the global environment are of increasing concern. Much emphasis has therefore been placed on the paradigm shift away from older and more conventional manufacturing processes, which tolerate utilization of toxic solvents and strongly corrosive acidic or alkaline media, toward alternative aqueous-based solution processes for manufacturing of modern functional inorganic materials. At the same time, water-soluble compounds are limited for elements in some Groups of the Periodic Table, including titanium and zirconium (Group 4), niobium and tantalum (Group 5), silicon (Group 14), and bismuth (Group 15). The limitations of water-incompatible compounds present a major challenge for production of materials comprising these elements by water-based synthesis techniques, significantly hindering development of synthetic routes for functional inorganic materials from aqueous solutions. At the same time, these elements are important as basic components of optoelectronic materials and inorganic photoceramics including photocatalysts and phosphors, which are manufactured on a large scale in industry. The current situation warrants development of a general approach for preparation of water-soluble complexes applicable to an array of water-incompatible elements (i.e., titanium, zirconium, niobium, tantalum, silicon, and bismuth), allowing synthesis of functional inorganic materials through environmentally benign aqueous solution processes.

In the present review, we focus on the water-incompatible element titanium and its compounds to address the current situation hindering the use of adequate titanium reagents for aqueous solution processes. Table 1 qualitatively shows the degree of solubility of representative titanium compounds in water as well as their stability in air or in aqueous solution. On the whole, titanium compounds are insoluble and unstable in water; titanium(III) trichloride, potassium hexafluorotitanate(IV), and ammonium bis(oxalato)oxotitanate(IV) are the few exceptions. Based on their characteristics, the titanium compounds in Table 1, excluding simple titanium compounds such as water-insoluble titanium dioxide and titanium carbide, can be classified into four groups.

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Table 1. Some Chemical Properties of Representative Titanium Compounds in Relation to Their Solubility in Water and Stability in Air or in Water

Group	Titanium compounds	Chemical formula	Their solubility in water and stability in air or in water
0	Titanium(II) oxide	TiO	It is unstable and readily oxidized in air.
	Titanium(III) oxide	Ti_2O_3	It is unstable and readily oxidized in air.
	Titanium(IV) oxide	TiO_2	It is stable, but is insoluble in water.
	Titanium(IV) carbide	TiC	It is stable, but is insoluble in water.
	Titanium(III) nitride	TiN	It is stable, but is insoluble in water.
	Titanium(IV) sulfide	TiS_2	It is readily decomposed under a humid air.
1	Titanium(III) trichloride	$TiCl_3$	It is soluble in neutral water, but is gradually oxidized to form a precipitate.
	Titanium(IV) tetrachloride	$TiCl_4$	It is soluble in a cold water, but is decomposed at room temperature in water to produce HCl fume accompanied with a precipitate.
	Titanium(III) sulfate	$Ti_2(SO_4)_3$	It is insoluble in water. It forms a precipitate resulting form its hydrolysis when it is treated with a boiling water.
	Titanium(IV) sulfate	$Ti(SO_4)_2$	Pure anhydride titanium(IV) sulfate, which is a colorless powder, is soluble in water accompanied with an exothermic reaction. It tends to be hydrolyzed, so usually it is used as a sulfuric acid solution.
	Titanium(IV) oxo–sulfate	$TiO(SO_4)$	It is readily hydrolyzed in the presence of water.
2	Potassium hexafluorotitanate(IV)	$K_2[TiF_6]$	It is soluble in water with a solubility of 1.28 g per 100 g of water at 20 °C. Its aqueous solution produces a precipitate when it is treated with alkaline reagents such as ammonia.
3	Titanium(IV) alkoxide	$Ti(OR)_4$	It is extremely sensitive to water and it is readily hydrolyzed in the presence of water to form a precipitate.
	Tris acetylacetonato titanium(IV) salt	$[Ti(C_5H_7O_2)_3]X$ (X denotes monovalent anion such as Cl^-)	It is readily decomposed in the presence of water, although it has a better stability for water than that of Ti alkoxides.
4	Ammonium oxo-oxalatotitanate(IV)	$(NH_4)_8[TiO(C_2O_4)_2]_4$	It is soluble in water. Since oxalic acid is toxic it should be handled with a greate care. The corresponding potassium salt is also known.

Group 1: *Titanium(IV) tetrachloride, titanium(IV) sulfate, and titanium(III) trichloride*. While titanium(IV) tetrachloride and titanium(IV) sulfate are most frequently used in industry, they are stable only in solutions containing excess acid. Titanium(IV) tetrachloride is soluble only in cold water; it vigorously reacts with water at room temperature, generating hydrogen chloride as a gas fume and producing an insoluble precipitate as shown in Figure 1a. For this reason, titanium(IV) tetrachloride is usually prepared in an aqueous solution of hydrochloric acid. Titanium(IV) sulfate is also utilized as an aqueous solution of sulfuric acid to avoid hydrolysis, but when neutralization is attempted by addition of an aqueous ammonia solution, a severe hydrolysis reaction takes place and produces a water-insoluble precipitate as shown in Figure 1b. Although these reagents are used in large quantities in industry, safety problems connected with corrosion by strong acids and possible danger to human health are major concerns. Thus such compounds cannot be easily used as raw materials for manufacturing titanium-containing ceramics. In contrast to titanium(IV) tetrachloride, titanium(III) trichloride is soluble in neutral water, but is gradually oxidized by air to yield insoluble titanium(IV) products. Moreover, when neutralization is attempted by an aqueous ammonia solution, a black precipitate forms as shown in Figure 1c. Titanium(III) sulfate and titanium(IV) oxo-sulfate, also categorized as **Group 1**, are almost insoluble in water.

Group 2: *Potassium hexafluorotitanate(IV)*. This compound dissolves into neutral water, but generates strongly toxic hydrogen fluoride in the presence of acids.

Group 3: *Titanium(IV) alkoxides*. Although titanium alkoxides are widely utilized as raw materials in the so-called sol–gel process, they are very unstable with respect to hydrolysis in water and produce water-insoluble precipitates as shown in Figure 1d, and thus they cannot be regarded as suitable titanium reagents for an aqueous solution process. In fact, this tendency to hydrolyze is the most important feature of titanium alkoxides and it allows for production of functional ceramic powders and thin films at low temperatures via careful control of hydrolysis and condensation reactions in the presence of small amounts of water. Such sol–gel technology is particularly important in ferroelectric thin film manufacturing, and practical research and development will continue to advance with technology for relatively small-scale production. Tris acetylacetonato titanium(IV) salts are not usually referred to as alkoxides, but they can be regarded as related compounds in which the alkoxy group OR in a given titanium alkoxide $Ti(OR)_4$ can be replaced by acetylacetonato (abbreviated as "acac") to form acac-derivatives. Although acac-derivatives are

Figure 1. Photographs demonstrating the reactivity of (a) $Ti^{IV}Cl_4$, (b) $Ti^{IV}(SO_4)_2$, (c) $Ti^{III}Cl_3$, and (d) $Ti(O\textit{i}\text{-}Pr)_4$ in either water or ammonia solution.

less water-sensitive than the original Ti–alkoxides, they readily decompose in the presence of water.

Group 4: *Ammonium bis(oxalato)oxotitanate(IV)*. Although this compound is soluble and reasonably stable in water, its usefulness as a reagent for synthesis of titanium-containing ceramics is limited because the oxalate itself is toxic, and the oxalate ions combine with many cations to form insoluble precipitates.

We introduce a series of original water-soluble titanium compounds as a new family of complexes belonging to **Group 4**. The ligands such as lactic and citric acids in these new chelate-type water-soluble titanium complexes are non-toxic and biodegradable organic compounds that are widely present in nature, and thus they resolve safety issues associated with the use of ammonium bis(oxalato)oxotitanate(IV). Moreover, the plain aqueous solutions containing these water-soluble titanium complexes have pH around 6 and the solutions remain stable over a wide range of pH including basic conditions. Chelate-type water-soluble titanium complexes therefore meet the requirements of prospective raw materials for synthesis of titanium-containing ceramics by aqueous solution processes. The remarkable retardation of hydrolysis of chelate-type titanium complexes is explained in terms of the so-called "Partial Charge Model (PCM)" theory developed by Livage's group.[1] This theory is based on the concepts of mean electronegativity of a given chemical species and partial charges of the elements. The theory predicts that hydrolysis continues until the mean electronegativity of the product becomes equal to the mean electronegativity of water ($\chi_r = 2.49$). The application of the PCM theory to Ti compounds is described below.

First, let us suppose a hypothetical hydrated species of titanium, $[Ti(H_2O)_6]^{4+}$, which must be highly reactive with water and tends to be stabilized via consecutive hydrolysis forming new species of $[Ti(H_2O)_{6-n}(OH)_n]^{4-n}$. The relative reactivity (or stability) of $[Ti(H_2O)_{6-n}(OH)_n]^{4-n}$ can be qualitatively understood in terms of the PCM theory. That is, an increase in the positive partial charge of Ti, denoted as "δ(Ti)," in $[Ti(H_2O)_{6-n}(OH)_n]^{4-n}$ leads to greater probability of hydrolysis due to increasing Coulombic interaction between the Ti in $[Ti(H_2O)_{6-n}(OH)_n]^{4-n}$ and the negative partial charge of the O in H_2O. Replacement of H_2O in $[Ti(H_2O)_{6-n}(OH)_n]^{4-n}$ by ligand X (eq 1) leads to a new precursor with modified chemical reactivity:

$$[Ti(H_2O)_{6-n}(OH)_n]^{4-n} + zX \\ \rightarrow [Ti(X)_z(H_2O)_{6-n-z}(OH)_n]^{4-n} + zH_2O \qquad (1)$$

As a typical example of this phenomenon, lactatotitanium complexes show outstanding stability toward water, where the lactate $[CH_3CH(O)COO]^{2-}$ (=la) coordinates to Ti to form $[Ti(la)_3]^{2-}$. On the way from $[Ti(H_2O)_6]^{4+}$ to $[Ti(la)_3]^{2-}$, δ(Ti), changes from +0.98 to +0.68. A smaller positive charge of δ(Ti) for $[Ti(la)_3]^{2-}$ indicates a greatly reduced interaction between Ti in $[Ti(la)_3]^{2-}$ and O in water. As a result, the mean electronegativity changes from $\chi_r = 2.85$ for the fully hydrated Ti ion to $\chi_r = 2.39$ for the Ti lactate complex. Therefore, hydrolysis should be remarkably depressed by the introduction of lactic acid. It can be anticipated that the la-modified Ti precursor solution does not form hydroxide precipitates even in the presence of excess water, as has indeed been confirmed by experiment.[2]

This review describes typical methods for the synthesis of water-soluble titanium complexes and introduces chemistry concepts required for understanding their solubility in water. Subsequently, it summarizes the current understanding of coordination chemistry and structures of water-soluble titanium complexes and clarifies the structural features essential for their solubility in water. Furthermore, we introduce relevant examples of syntheses of titanium-containing oxides by aqueous solution processes utilizing water-soluble titanium complexes. Finally, the "green" nature of their chemistry and potential application in synthesis of other water-soluble complexes via future aqueous solution processes is discussed.

2. Synthesis of Water-Soluble Titanium Complexes

In this section, methods for synthesis of water-soluble titanium complexes containing ligands such as hydroxycarboxylic acids are described. The essential chemistry of the processes is also briefly outlined. Two basic synthetic methods are known. The non-peroxo route is based on a direct reaction between either titanium tetrachloride or titanium alkoxide and almost exclusively citric acid (**Route A**). The peroxo route is based on a ligand-exchange reaction of a given hydroxo–peroxo titanium species such as $[Ti(O_2)(OH)_3]^-$ with a wide range of chelate-type ligands including ethylenediaminetetraacetic acid (H_4edta), citric acid and etc. (**Route B**).

2.1 Non-Peroxo Route: Route A. Until recently, Route A has been used exclusively for synthesis of mononuclear titanium citrato complexes, and a representative overall reaction can be written as follows:[3]

$$TiCl_4 + 3H_4cit^* + 10OH^- \\ \rightarrow [Ti(cit^*)(Hcit^*)_2]^{6-} + 4Cl^- + 10H_2O \qquad (2)$$

where H_4cit^* is an abbreviation for citric acid ($C_6H_8O_7$: $CH_2COOHC(OH)(COOH)CH_2COOH$) indicating four possible dissociative protons; thus cit^* stands for the fully deprotonated tetra-anionic form of citrate. Titanium tetrachloride is added slowly with continuous stirring to an aqueous solution of citric acid, followed by slow addition of an aqueous solution of either sodium hydroxide or ammonia for adjustment to the appropriate pH. The degree of deprotonation in H_4cit^* depends mainly on the pH of the solution, in addition to determining the final form of the titanium citrato complexes. As the pH of the solution is increased, more highly deprotonated citric acid species are coordinated to titanium. Indeed, crystallization of $[Ti(H_2cit^*)_3]^{2-}$, $[Ti(Hcit^*)_2(H_2cit^*)]^{4-}$, $[Ti(cit^*)(Hcit^*)_2]^{6-}$, and $[Ti(cit^*)_3]^{8-}$ with several different counter-ions was confirmed at pH 2,[4] 4,[5] 6,[3] and 7,[6] respectively.

Collins et al.[6] reported stability constants (β-values) and a species distribution diagram for titanium(IV) citrato complexes in aqueous solutions determined by potentiometric titration. The proposed model that best fit the potentiometric data was composed of the following equilibrium system:[6]

$$Ti^{4+} + Hcit^{*3-} \rightleftharpoons [Ti(Hcit^*)]^{+} \quad (3)$$

$$Ti^{4+} + 3H_2cit^{*2-} \rightleftharpoons [Ti(H_2cit^*)_3]^{2-} \quad (4)$$

$$Ti^{4+} + H_2cit^{*2-} + 2Hcit^{*3-} \rightleftharpoons [Ti(Hcit^*)_2(H_2cit^*)]^{4-} \quad (5)$$

$$Ti^{4+} + 3Hcit^{*3-} \rightleftharpoons [Ti(cit^*)(Hcit^*)_2]^{6-} + H^{+} \quad (6)$$

$$Ti^{4+} + 3Hcit^{*3-} \rightleftharpoons [Ti(cit^*)_3]^{8-} + 3H^{+} \quad (7)$$

$$Ti^{4+} + 2Hcit^{*3-} + 2H_2O \rightleftharpoons [Ti(cit^*)_2(OH)_2]^{6-} + 4H^{+} \quad (8)$$

The final optimized least-squares fit of the data based on these equilibriums generated the respective $\log\beta$ values of 9.18, 16.99, 20.41, 16.11, 4.07, and −7.94 for each individual citrate–Ti species produced on the right side of eqs 3–8. Importantly, based on the reported diagram of species distribution as a function of pH, the tris(citrato)titanate sepcies $[Ti(H_2cit^*)_3]^{2-}$, $[Ti(Hcit^*)_2(H_2cit^*)]^{4-}$, $[Ti(cit^*)(Hcit^*)_2]^{6-}$, and $[Ti(cit^*)_3]^{8-}$ account for more than 80% of the species at approximate pH 3.4, 4.5, 5.5, and 7.1, respectively. The amount of partially hydrolyzed species of $[Ti(cit^*)_2(OH)_2]^{6-}$ begins to increase sharply above pH 7, and is the dominant species (>80%) at pH 9. Given the likelihood that $[Ti(cit^*)_2(OH)_2]^{6-}$ species can readily undergo self-condensation to form polymeric species, we conclude that aqueous solutions involving a variety of titanium(IV) tris-citrato complexes with sufficient stability regarding hydrolysis/condensation may be constructed through adjusting the solution to within pH 2–7.

2.2 Peroxo Route: Route B. In Route B, the first step involves the preparation of peroxo–hydroxo titanium complexes such as $[Ti(O_2)(OH)_3]^-$ and $[Ti(O_2)(OH)_2]$, which can be achieved by either direct reaction between titanium tetrachloride and hydrogen peroxide under acidic conditions (e.g., eqs 9–11) or reaction of metallic titanium powder with hydrogen peroxide in the presence of ammonia (eq 12):

$$Ti^{4+} + H_2O_2 + H_2O \rightarrow [Ti(O_2)(OH)]^{+} + 3H^{+} \quad (9)$$

$$Ti^{4+} + H_2O_2 + 2H_2O \rightarrow [Ti(O_2)(OH)_2] + 4H^{+} \quad (10)$$

$$Ti^{4+} + H_2O_2 + 3H_2O \rightarrow [Ti(O_2)(OH)_3]^{-} + 5H^{+} \quad (11)$$

$$Ti + 3H_2O_2 + NH_3 \rightarrow [Ti(O_2)(OH)_3]^{-} + H_2O + NH_4^{+} \quad (12)$$

The peroxo–hydroxo titanium complexes in eqs 9–12, which have an orange-to-yellow color in aqueous solutions (depending on the pH of the solution), can be dimerized, leading to formation of various oxo–peroxo–hydroxo di-titanium complexes. Some examples are shown in eqs 13–15:

$$[Ti(O_2)(OH)_2] + [Ti(O_2)(OH)_2] \rightarrow [Ti_2(O)(O_2)_2(OH)_2] + H_2O \quad (13)$$

$$[Ti(O_2)(OH)_2] + [Ti(O_2)(OH)_3]^{-} \rightarrow [Ti_2(O)(O_2)_2(OH)_3]^{-} + H_2O \quad (14)$$

$$[Ti(O_2)(OH)_3]^{-} + [Ti(O_2)(OH)_3]^{-} \rightarrow [Ti_2(O)(O_2)_2(OH)_4]^{2-} + H_2O \quad (15)$$

These dimeric complexes can undergo further self-condensation or react with other dimers and monomers to form oligomers. As a result of the continuous condensation, a precipitate of polynuclear oxo–peroxo–hydroxo titanium $[Ti(O)(O_2)_2(OH)_2]_n$ is obtained. The detailed chemistry of aqueous solutions involving Ti^{IV} ions and hydrogen peroxide has been well documented in the literature.[7]

It should also be mentioned that the hydroxo–peroxo titanium(IV) complexes themselves are unstable and decompose (hydrolyze) to produce a precipitate of titanium hydroxide as represented by eq 16 or titanium oxide hydrates (titanic acid) $TiO_2 \cdot xH_2O$:

$$[Ti(O_2)(OH)_3]^{-} + H_2O \rightarrow Ti(OH)_4 + (1/2)O_2 + OH^{-} \quad (16)$$

In the presence of excess hydrogen peroxide, titanium hydroxide can be re-dissolved in accordance with the reaction in eq 17:

$$Ti(OH)_4 + H_2O_2 \rightarrow [Ti(O_2)(OH)_3]^{-} + H_3O^{+} \quad (17)$$

Similarly, excess hydrogen peroxide in the presence of ammonia helps in dissolving a variety of forms of titanic acid and polynuclear peroxo titanium(IV) hydrate. A large excess of hydrogen peroxide maintains the solubility of $[Ti(O_2)(OH)_3]^-$ in the solution and most likely retards its successive condensation, thus preserving a transparent aqueous solution without any precipitation.

The second step of Route B is to promote a ligand exchange reaction for $[Ti(O_2)(OH)_3]^-$ or similar types of peroxo–hydroxo titanium complexes with an appropriate ligand. Details of the reactions with traditional chelating reagents such as ethylenediaminetetraacetic acid (H_4edta) or hydroxycarboxylic acids such as citric acid (H_4cit^*) are given in Sections **2.2.1** and **2.2.2**, respectively.

2.2.1 Ligand-Exchange Reactions between Hydroxo–Peroxo Titanium Complexes and Traditional Chelating Reagents: History Overview: The choice of the ligand is crucial for forming a stable complex with titanium in aqueous solution before titanium hydroxide precipitation. The formulas of $[Ti(O_2)(OH)]^+$, $[Ti(O_2)(OH)_2]$, $[Ti(O_2)(OH)_3]^-$, and corresponding dimeric complexes, the products from the monomeric complexes described in eqs 13–15, suggest the feasibility of a replacement of the coordinated hydroxy and/or peroxo group by chelating agents. The first example of such a replacement was found for peroxo–titanium oxalates as early as 1907 by Mazzucchelli.[8] About half a century later, Sweetser and Bricker[9] suggested formation of peroxo titanium complex coordinated by edta with the Ti:H_2O_2:edta ratio of 1:1:1.

Mühlebach and Schwarzenbach[7] subsequently carried out a more extensive study of chelation in peroxo titanium complexes and they succeeded in preparing chelates of mononuclear $[Ti(O_2)(OH)]^+$ (eq 9) and binuclear $[Ti_2(O)(O_2)_2(OH)_2]$ (eq 13) complexes according to the following reactions:

$$[Ti(O_2)(OH)]^+ + H_2edta^{2-} \rightarrow [Ti(edta)(O_2)]^{2-} + H_3O^+ \tag{18}$$

$$[Ti(O_2)(OH)]^+ + Hnta^{2-} \rightarrow [Ti(nta)(O_2)(OH)]^{2-} + H^+ \tag{19}$$

$$[Ti_2(O)(O_2)_2(OH)_2] + 2H_2dipic \rightarrow [Ti_2(dipic)_2(O)(O_2)_2]^{2-} + 2H_3O^+ \tag{20}$$

$$[Ti_2(O)(O_2)_2(OH)_2] + 2H_2digl \rightarrow [Ti_2(digl)_2(O)(O_2)_2]^{2-} + 2H_3O^+ \tag{21}$$

$$[Ti_2(O)(O_2)_2(OH)_2] + 2H_2ida \rightarrow [Ti_2(ida)_2(O)(O_2)_2]^{2-} + 2H_3O^+ \tag{22}$$

where H_3nta, H_2dipic, H_2digl, and H_2ida are the respective abbreviations for nitrilotriacetic acid; $C_6H_9O_6N{=}N(CH_2COOH)_3$, dipicolinic acid; 2,6-dipyridinedicarboxylic acid, $C_7H_5O_4N$, diglycolic acid; $(O(CH_2COOH)_2)$, and iminodiacetic acid; $HN(CH_2COOH)_2$, indicating 3 or 2 possible dissociative protons; nta, dipic, digl, and ida represent the fully deprotonated anionic forms of each chelate compound.

These outstanding pioneering works in the field of pure "analytical chemistry" have stimulated the authors of this review to tailor new water-soluble titanium complexes as molecular precursors suitable for environmentally benign synthesis of functional ceramics. The first discovery of such a molecular precursor is the citratoperoxotitanate(IV) complex,[10] which has been successfully utilized in the synthesis of thin films of TiO_2 and barium titanate powders using water as a processing solvent.[11]

2.2.2 Ligand-Exchange Reactions between Hydroxo–Peroxo Titanium Complexes and Hydroxycarboxylic Acids: More Recent Works: Hydroxycarboxylic acids that can form stable complexes with titanium in aqueous solutions include glycolic acid (H_2ga); $CH_2(OH)COOH$, lactic acid (H_2la); $CH_3CH(OH)COOH$, malic acid (H_3mal); $CH_2COOHCH(OH)COOH$, tartaric acid (H_4tart); $CH(OH)COOHCH(OH)COOH$, and citric acid (H_4cit^*); $CH_2COOHC(OH)COOHCH_2COOH$. Figure 2 compares the structures of hydrocarboxylic acid with those of the corresponding non-hydroxy carboxylic acids (acetic acid, HOAc: CH_3COOH; propionic acid, Hpa: CH_3CH_2COOH; succinic acid, H_2sa: $CH_2COOHCH_2COOH$; and tricarballylic acid, H_3tca: $CH_2COOHCH(COOH)CH_2COOH$. These hydroxycarboxylic acids contain hydroxy (OH) and carboxylic acid (COOH) groups that can be deprotonated to form alkoxylato (CO^-) and carboxylato (COO^-) groups, respectively. The resulting alkoxylato and carboxylato groups may simultaneously coordinate titanium forming a chelate ring. This ring is responsible for the stability of the resulting complex in a given aqueous solution (detailed structures of these complexes are described in the next section). For example, as shown in eq 23, when citric acid is used as a chelating reagent, it reacts with the peroxo titanium complex formed in eq 12 to produce a stable peroxo–citrato titanium complex, $[Ti_4(cit^*)_4(O_2)_4]^{8-}$:[10]

$$4[Ti(O_2)(OH)_3]^- + 4H_4cit^* \rightarrow [Ti_4(cit^*)_4(O_2)_4]^{8-} + 4H_3O^+ + 8H_2O \tag{23}$$

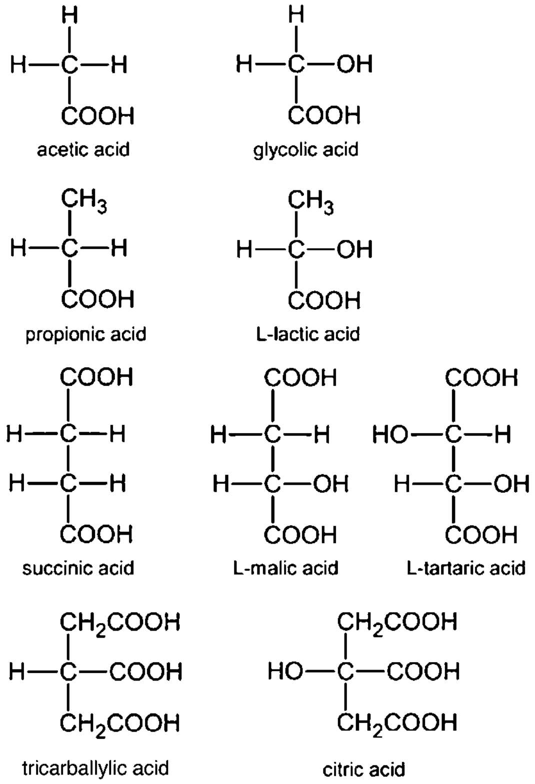


Figure 2. Structures of various hydroxy–carboxylic acids and the corresponding original non-hydroxy carboxylic acids.

This complex can exist in an aqueous solution as a stable form for more than a year.

Figure 3 compares transparent aqueous solutions containing various hydroxycarboxylato–peroxo titanium complexes prepared using chelating reagents, H_2ga, H_2la, H_3mal, and H_4cit^* with turbid titanium aqueous solutions prepared using corresponding non-hydroxy carboxylic acids (HOAc, Hpa, H_2sa, and H_3tca). Moreover, comparison of a titanium aqueous solution prepared using α-hydroxybutyric acid (α-H_2ba, $CH_3CH_2CH(OH)COOH$) with that prepared using 3-hydroxybutyric acid (β-H_2ba, $CH_3CH(OH)CH_2COOH$) (Figure 4) indicates that the hydroxy group in a given hydroxycarboxylic acid should be located at the α-position with respect to the carboxyl group to obtain a transparent titanium aqueous solution. The immediate conclusion from these observations is that stability of the corresponding titanium complex can be achieved with a carboxyl group and an α-hydroxy group as the minimum required structural unit of a given hydroxycarboxylic acid, and deprotonation of these groups yields a very stable five-membered chelate ring that incorporates a titanium atom (Figure 5).

2.2.3 Summary of Route B: Choice of Starting Titanium Sources: Figure 6 summarizes the method for preparing water-soluble titanium complexes according to Route B. Metallic titanium in the form of a fine powder is treated with hydrogen peroxide and ammonia to form the peroxo–hydroxo titanium complex $[Ti(O_2)(OH)_3]^-$, according to eq 12. As shown in Figure 6(1), this treatment should be carried out in an ice-cold solution because of the exothermic nature

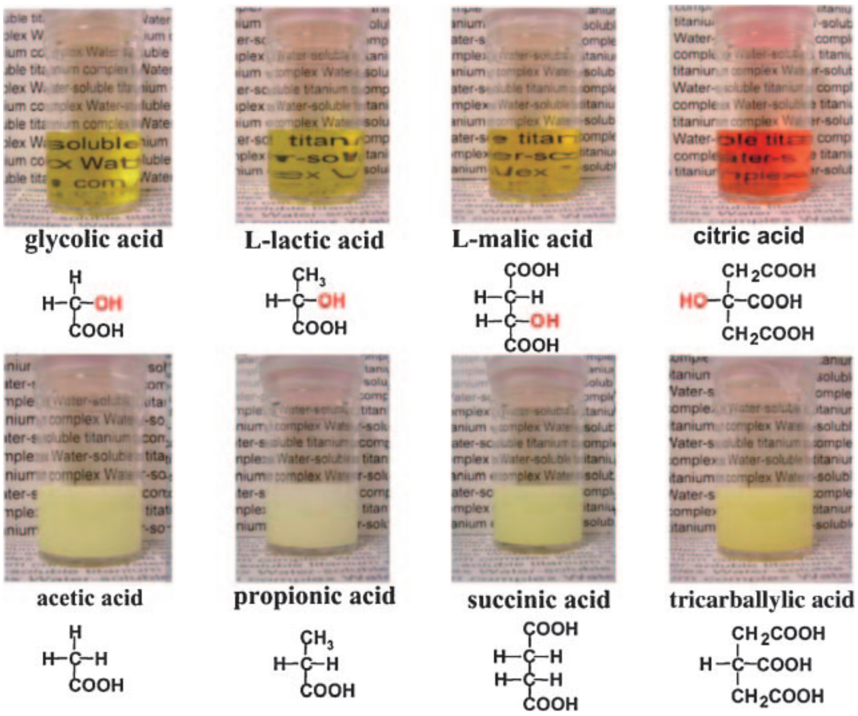


Figure 3. Comparison of aqueous solutions of various water-soluble titanium complexes prepared using glycolic acid, L-lactic acid, L-malic acid, and citric acid as complexants with turbid solutions prepared using acetic acid, propionic acid, succinic acid, and tricarballylic acid.

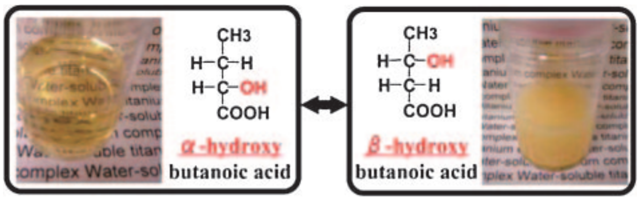


Figure 4. Comparison of an aqueous solution of a water-soluble titanium complex prepared using α-hydroxy butanoic acid as a complexant with a turbid solution prepared using β-hydroxy butanoic acid.

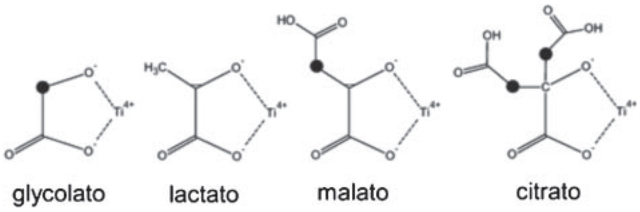


Figure 5. Schematic views of partial coordination structures of Ti-complexes with glycolato, lactato, malato, and citrato ligands showing formation of a stable five-membered chelate ring.

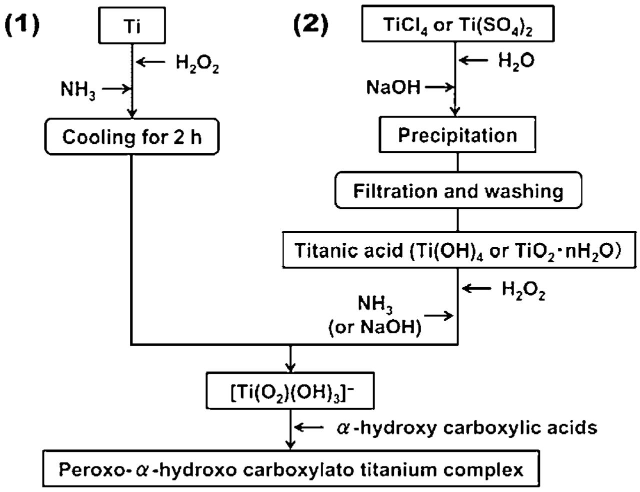


Figure 6. Flowchart for synthesis of a water-soluble peroxo–hydroxo carboxylato titanium complex starting from (1) titanium metal and (2) $TiCl_4$ or $Ti(SO_4)_2$.

of the reaction. Without proper cooling, a rapid increase in temperature may induce a vigorous decomposition of hydrogen peroxide and overflowing of the solution. Conversely, because of the low temperature, titanium does not dissolve completely. The peroxo–hydroxo titanium complex $[Ti(O_2)(OH)_3]^-$ can also be prepared by direct reaction between $TiCl_4$ and H_2O_2. However, the whole procedure is somewhat complicated and requires manipulations at precise low temperatures (between −25 and −30 °C). Great care must be taken to prevent possible explosion owing to improper temperature control. Moreover, solutions of $[Ti(O_2)(OH)_3]^-$ prepared in this manner contain a large amount of chloride ions, limiting their use as precursors for titanium-containing ceramics. Complete removal of chloride ions is a common problem, and residual chloride can degrade the electronic properties of the final material even at very low concentrations.[12]

For these reasons, an alternative synthetic route to $[Ti(O_2)(OH)_3]^-$ via titanic acid starting from either $TiCl_4$ or $Ti(SO_4)_2$ is strongly recommended (Figure 6(2)). Addition of

L-lactic acid Glycolic acid Citric acid

Figure 7. Single crystals of water-soluble titanium complex ammonium salts: (left) lactic acid complex, (middle) glycolic acid complex, and (right) citric acid complex.

water and NaOH to a solution of $TiCl_4$ (or $Ti(SO_4)_2$) yields a precipitate of titanic acid ($Ti(OH)_4$ or $TiO_2{\cdot}xH_2O$), which should be filtered and washed with water to remove NaOH and unnecessary anions such as chloride or sulfate. “Freshly” precipitated titanic acid (implying less polymerization) can be re-dissolved by addition of H_2O_2, but in many cases addition of base such as ammonia or NaOH is necessary to promote the solubility of titanic acid. The peroxo–hydroxo titanium complex $[Ti(O_2)(OH)_3]^-$ is then treated with an α-hydroxy carboxylic acid to obtain a water-soluble peroxo–α-hydroxy–carboxylato titanium complex. The minimum amount of chelating reagent to stabilize the complex is different for each chelating reagent; that is, 1–1.5, 2–3, 1, 1, 1, and 4 mol are needed per mole of titanium for H_2ga, H_2la, H_3mal, H_4tart, H_4cit*, and α-H_2ba, respectively. Kobayashi et al.[13] have recently reported that hydroxy amino acids such as serine ($CH_2(OH)CH(NH_2)COOH$) and threonine ($CH_3CH(OH)$-$CH(NH_2)COOH$) coordinate titanium, forming water-soluble titanium complexes. Details of this study are discussed in Section **3.3.5**.

During gradual evaporation of water, some of these titanium complexes form single crystals of the corresponding ammonium salts (Figure 7). They have been further purified by recrystallization from water and used for single-crystal X-ray diffraction studies. These studies are described in the next sections (**3.3.2.1**, **3.3.2.2**, and **3.3.4.2**).

3. Chemical Insight into the Structure of Water-Soluble Titanium Complexes

3.1 Titanium Peroxo Complexes with Traditional Chelating Reagents. To the best of our knowledge, the first water-soluble titanium complexes with organic ligands that have been crystallized in the form of single crystals suitable for detailed X-ray investigations are a series of oxo–peroxo titanium complexes with chelating reagents developed by Schwarzenbach. These include $K_2[Ti_2(dipic)_2O(O_2)_2]{\cdot}5H_2O$[14] (**1**), $[Ti(dipic)(H_2O)_2(O_2)]{\cdot}2H_2O$[15] (**2**), $K_2[Ti(dipic)F_2(O_2)]{\cdot}2H_2O$[15] (**3**), and $Na_4[Ti_2(nta)_2O(O_2)_2]{\cdot}11H_2O$[16] (**4**). After Schwarzenbach’s pioneering works, preparation and characterization of five complexes of titanium(IV) with the amine-based chelating ligands H_3nta,[17] H_4edta,[18] and H_3ed3a[18] have been reported: $Cs_4[Ti_4(nta)O_{44}]{\cdot}6H_2O$ (**5**), $(NH_4)_2[Ti(edta)(O_2)]{\cdot}2H_2O$ (**6**), $(NH_4)[Ti(Hedta)(O_2)]{\cdot}2H_2O$ (**6′**), Na[Ti(ed3a)-$(O_2)]{\cdot}H_2O$ (**7**), and $(NH_4)[Ti(Hed3a)(O_2)]$ (**7′**).

As expected, all of these complexes involve a common structural unit represented by Figure 8, where a nitrogen atom together with two oxygen atoms of each two adjacent carboxylato groups coordinate a titanium atom building up a fused double five-membered chelate ring. Except for compound **5**, the peroxo ion $(O_2)^{2-}$ binds to Ti in a side-on δ^2-fashion, occupying two coordination sites (for δ^2, $(O_2)^{2-}$ is bonded to a metal in a triangular bidentate manner). The remaining two sites (X and Y) bonded to Ti come from two oxygen atoms of the oxo group bridging two titanium atoms and a water molecule (**1**), two oxygen atoms of the two coordinated water molecules (**2**), the two fluorine atoms (**3**), two oxygen atoms of the oxo group and the third carboxylato group (**4**), and one nitrogen atom in the second amine group and one oxygen atom in the third carboxylato group (**6**, **6′**, **7**, and **7′**). As a result, the titanium is heptacoordinated with seven donor atoms (O, N, or F) for all of the peroxo-coordinated complexes. The coordination sphere around Ti in compound **5** is unusual. Each titanium(IV) center in the tetranuclear $[Ti_4(nta)_4O_4]^{4-}$ anion is six-coordinated with one nitrogen atom, three oxygen atoms from three carboxylato groups in nta and two cis μ-oxo bridging oxygen atoms, forming a puckered eight-member ring. The tetrameric structure of **5** is very similar to that reported for $(NH_4)_2[TiO(ox)_2]{\cdot}H_2O$ (**8**), as is discussed below.

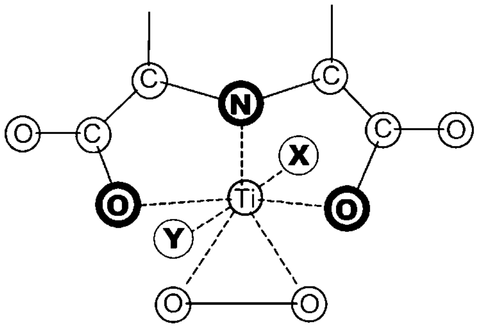


Figure 8. Schematic view of a partial coordination structure commonly observed in various Ti–peroxo complexes stabilized with traditional chelate reagents like ethylenediaminetetraacetic acid (H_4edta) showing formation of a fused double five-membered chelate ring.

3.2 Titanium Complexes with Oxalic Acid. The oxo–oxalato titanium complex, which is more popular in the field of materials chemistry due to its potential to form precipitates with other metals that have desired stoichiometry, has been crystallized in the form of ammonium or potassium salts. These crystal structures were solved by analyzing single-crystal X-ray diffraction data.[19–21] The structure contains tetranuclear anions of chemical composition $[TiO(ox)_2]_4{}^{8-}$, which form eight-membered rings of four Ti and four O atoms (μ-oxo bridging groups) as shown in Figure 9. Each Ti atom is coordinated by two oxalate ions, each forming a five-membered chelate ring. As a result, each Ti atom has a distorted octahedral environment. The tetranuclear anion $[TiO(ox)_2]_4{}^{8-}$ when dissolved in water reacts with Ba^{2+} ions, forming a precipitate containing barium and titanium having exactly 1:1 stoichiometry in accordance with the reaction in eq 24:[22,23]

$$4Ba^{2+} + [TiO(ox)_2]_4{}^{8-} \rightarrow Ba_4[TiO(ox)_2]_4 \qquad (24)$$

This precipitate can be completely converted to $BaTiO_3$ upon heating at temperatures above 800 °C.

3.3 Titanium Complexes with Hydroxy–Carboxylic Acids. Surprisingly, after the reports on the crystal structures

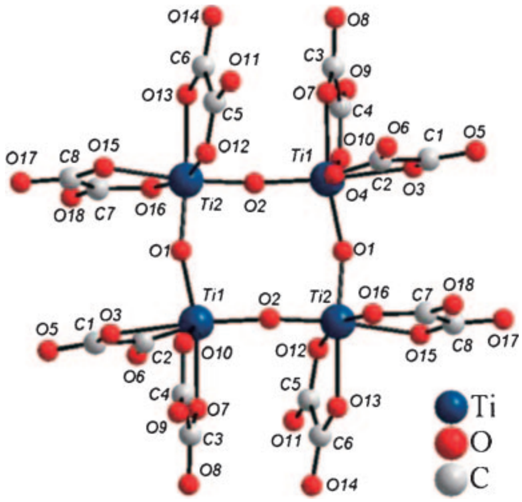


Figure 9. Structure and labeling of a tetra nuclear anion of oxo–oxalato titanium complex $[TiO(ox)_2]_4^{8-}$.

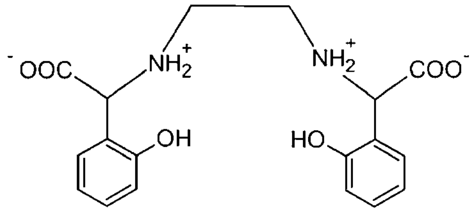


Figure 10. Structure of *N*,*N*′-ethylenebis(*o*-hydroxyphenylglycine).

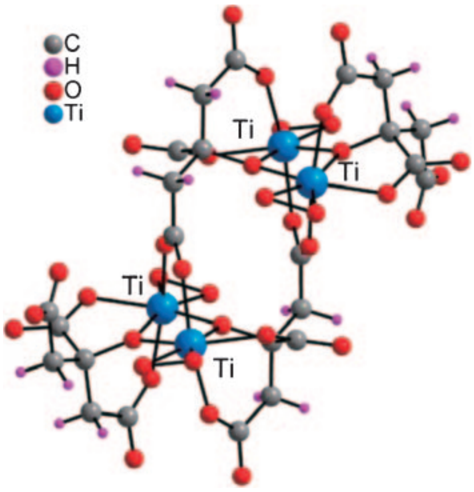


Figure 11. Structure of a tetra nuclear anion of citratoperoxotitanate(IV) complex $[Ti_4(cit^*)_4(O_2)_4]^{8-}$.

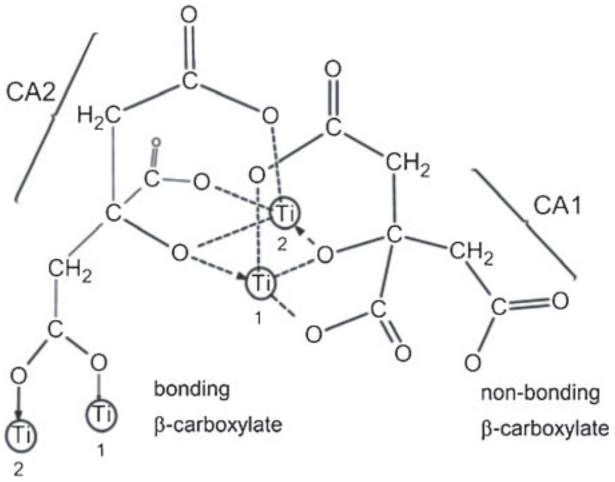


Figure 12. A schematic structural view of a binuclear fragment of the citratoperoxotitanate(IV) complex $[Ti_4(cit^*)_4(O_2)_4]^{8-}$.

of $Na_4[TiO(O_2)_2(nta)_2]\cdot 11H_2O$ (**4**) by Schwarzenbach et al. in 1975[16] and $Cs_4[Ti_4O_4(nta)_4]\cdot 6H_2O$ (**5**) by Wieghardt et al. in 1980,[17] no crystal structures of water-soluble titanium complexes were reported until 2000/2001.

3.3.1 Titanium Complexes with *o*-Hydroxyphenylglycine: The first examples reported in 2000 correspond to rather unusual titanium complexes with the hexadentate ligand *N*,*N*′-ethylenebis(*o*-hydroxyphenylglycine) (H_4ehpg; see Figure 10). Crystal structures of two novel Ti–ehpg complexes having the chemical formulas $[Ti(ehpg)(H_2O)]\cdot(11/3)H_2O$ (**9**) and $[\{Ti(Hehpg)(H_2O)\}_2O]\cdot 13H_2O$ (**10**) were described.[24] In view of the fact that the solubility of these complexes in neutral water is relatively low (typically below 5 mmol dm^{-3} at room temperature), they might find possible use as anticancer drugs in clinical applications rather than as a molecular precursors for titanium containing ceramics.

3.3.2 Tetranuclear Peroxo Titanium Complexes: 3.3.2.1 Tetranucler Peroxo–Citrato Complex; The second example reported in 2000/2001 by the present authors is the tetranuclear citratoperoxotitanate(IV) complex having the chemical formula $(NH_4)_8[Ti_4(cit^*)_4(O_2)_4]\cdot 8H_2O$ (**11**), which can be categorized as a new class of titanium complex.[10] Figure 11 shows the structure of the tetranuclear anion $[Ti_4(cit^*)_4(O_2)_4]^{8-}$ determined from single-crystal X-ray diffraction data. The structure is composed of two binuclear fragments interlinked through the bridging β-carboxylato group of one citrate ligand. The binuclear fragment is schematically drawn in Figure 12, where the peroxo group, $(O_2)^{2-}$, is omitted for clarity. There is a $[Ti_2O_2]$ core in the center of the dimer that is built in such a way that the deprotonated α-alkoxylato oxygen atoms from CA1 and CA2 (marked with a small arrow around Ti) simultaneously bond to two Ti atoms. Both CA1 and CA2 are fully deprotonated and thus have a negative charge of −4. The striking feature of the citrate ligand is its tridentate nature as a whole molecule. As a result, the α-alkoxylato oxygen atom and the oxygen atoms from the α-carboxylato and one of the two β-carboxylato groups build a fused five- and six-membered chelate ring, providing maximum stability for the complex. While the remaining β-carboxylato group remains free in CA1, the one in CA2 bridges two Ti atoms in another binuclear fragment, thus occupying one site of each Ti atom. At this stage, each Ti atom is coordinated by five oxygen atoms (one α-alkoxylato O from CA1, another α-alkoxylato O from CA2, one α-carboxylato O from CA1, one β-carboxylato O from CA1, and one β-carboxylato O from a CA2 ligand in the opposite binuclear fragment). The coordination sphere around each Ti atom is completed with the peroxo group. The $(O_2)^{2-}$ group binds to Ti in a side-on η^2-fashion, occupying two coordination sites in the equatorial plane as seen in Figures 11

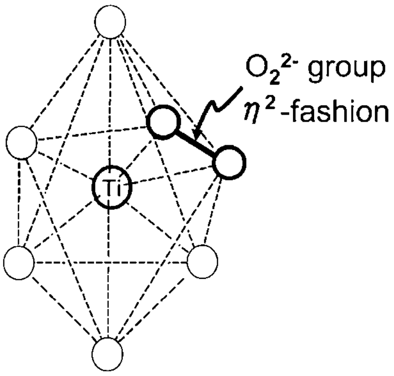


Figure 13. A distorted pentagonal bipyramidal coordination environment around Ti characterized by the presence of a peroxo (O_2^{2-}) group binding to the Ti atom in a side-on η^2-fashion.

and 13. In consequence, the coordination number around each Ti atom is seven, reflecting a distorted pentagonal bipyramidal coordination environment for each Ti, as is shown schematically in Figure 13.

The coordinated peroxo group of complex **11** may play two important roles.

1. It retards further oligomerization or polymerization of the tetranuclear anion by occupying the free sites in the equatorial pentagonal plane that can be active sites for nucleophilic attack by water molecules or hydroxy ions (**OH**$^-$), inducing hydrolysis.

2. It provides an additional negative charge to the complex, thus allowing for the formation of an ammonium (or potassium or other metal) salt that is soluble in water. This principle may hold for the other peroxo titanium complexes with dipic (**1** and **3**), nta (**4**), edta (**6**) and ed3a (**7**).

Another tetranuclear peroxo titanium citrato complex in the form of the barium/ammonium salt, $Ba_2(NH_4)_2[Ti_4(cit^*)_2(Hcit^*)_2(O_2)_4]\cdot 10H_2O$ (**11′**), was reported.[25] The structure of the tetranuclear anion $[Ti_4(cit^*)_2(Hcit^*)_2(O_2)_4]^{6-}$ is essentially the same as that of $[Ti_4(cit^*)_4(O_2)_4]^{8-}$ (Figure 11). An important application of this compound is its use as a molecular precursor for $BaTi_2O_5$, which is one of the important ferroelectric barium titanates. The same type of barium salt with the formula $Ba_4[Ti_4(cit^*)_2(Hcit^*)_2(O_2)_4]\cdot 8H_2O$ has been obtained from an aqueous solution containing the $[Ti_4(cit^*)_4(O_2)_4]^{8-}$ anion and barium ion.[26] Again, this compound has been demonstrated to be a convenient precursor for synthesis of $BaTiO_3$ by calcination in air at a reduced temperature of 700 °C.

3.3.2.2 Tetranuclear Peroxo–Glycolato Complex; Tetranuclear titanium complexes seem to be quite rare, and just one other example of such a complex in addition to $(NH_4)_8[Ti_4(cit^*)_4(O_2)_4]\cdot 8H_2O$ (**11**) has been reported to date. The ammonium salt of a tetranuclear species with glycolic acid[27] has the chemical formula $(NH_4)_6[Ti_4(ga)_4(Hga)_2(\mu\text{-}O)_2(O_2)_4]\cdot 4H_2O$ (**12**). The structure of the tetranuclear anion $[Ti_4(ga)_4(Hga)_2(\mu\text{-}O)_2(O_2)_4]^{6-}$ was determined from single-crystal X-ray diffraction data as shown in Figure 14. It is composed of two binuclear fragments that are connected to each other through the bridging μ-oxo groups (O12 and O13) with relatively short Ti–O distances (Ti1–O12 1.830 Å and Ti2–O13 1.815 Å) compared with other Ti–O bonds (for instance, Ti1–O3 2.055 Å and Ti2–O3 2.026 Å).

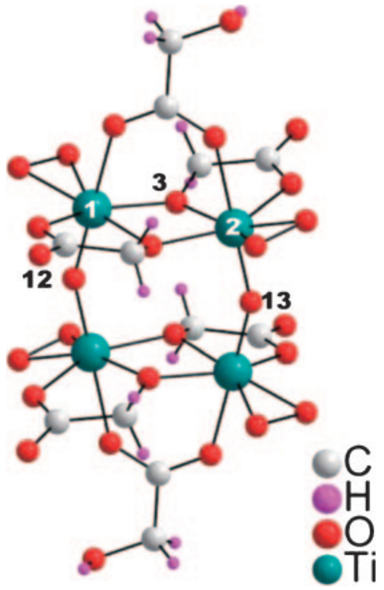


Figure 14. Structure and labeling of a tetra nuclear anion of oxo–peroxo–glycolato titanium complex $[Ti_4(ga)_4(Hga)_2(\mu\text{-}O)_2(O_2)_4]^{6-}$.

The coordination environment for each Ti atom is nearly equivalent, and it is schematically shown in Figure 15. One fully deprotonated glycolic acid (GA1) binds to Ti through the α-carboxylato and α-alkoxylato oxygen atoms, leading to formation of a five-membered ring. The α-alkoxylato oxygen in another fully deprotonated glycolic acid (GA2) participates in bonding Ti. These two α-alkoxylato oxygen atoms in GA1 and GA2 act as bridging groups to the neighboring Ti atom to give a $[Ti_2O_2]$ core similar to that of the citratoperoxotitanate(IV) complex shown in Figure 12. One more singly deprotonated glycolic acid (Hga) coordinates Ti through one of the two oxygen atoms in the α-carboxylato group of Hga (another oxygen atom in the same α-carboxylato group binds to the neighboring Ti atom, so that Hga, acting as a binding molecule, may help to stabilize the binuclear fragment in conjunction with GA1 and GA2). The coordination sphere around Ti is completed with oxygen atoms belonging to the oxo group and one η^2-$(O_2)^{2-}$ peroxide group. Titanium exhibits, therefore, a seven-fold coordination, yielding a distorted pentagonal bipyramid similar to that seen in the structure of the tetranuclear citratoperoxotitanate(IV) complex (Figure 13).

3.3.3 Binuclear Peroxo Titanium Complexes with Citric Acid: A binuclear citratoperoxotitanate(IV) complex can be obtained by adjusting a given aqueous solution containing $TiCl_4$, citric acid (H_4cit^*), and H_2O_2 to pH ≈4.5 by addition of ammonia,[28] in accordance with the reaction in eq 25:

$$2TiCl_4 + 2H_4cit^* + 2H_2O_2 + 12NH_4OH \rightarrow [Ti_2(cit^*)_2(O_2)_2]^{4-} + 12NH_4^+ + 8Cl^- + 12H_2O \quad (25)$$

Single crystals are then obtained by treating the resulting red aqueous solution containing the citratoperoxotitanate(IV) com-

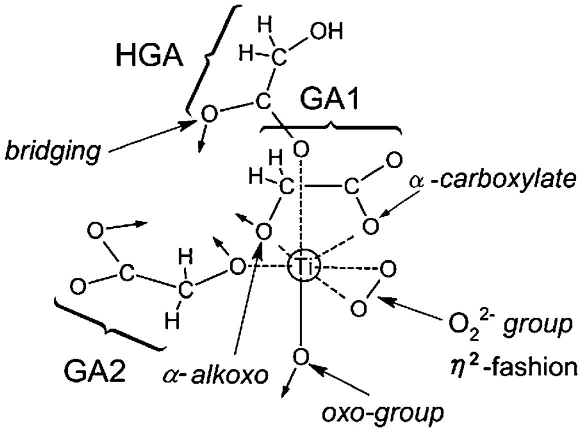


Figure 15. A schematic structural view of a binuclear fragment of the oxo–peroxo–glycolato titanium complex $[Ti_4(ga)_4(Hga)_2(\mu\text{-}O)_2(O_2)_4]^{6-}$.

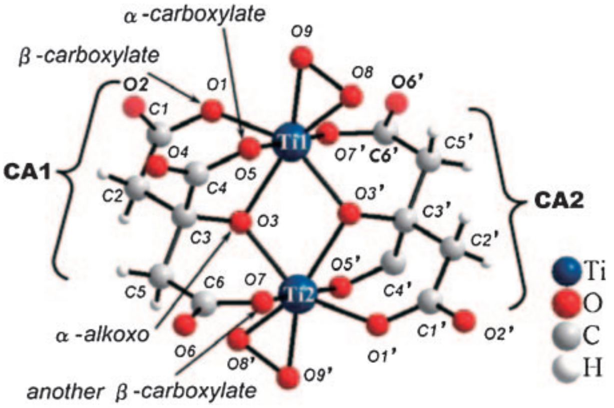


Figure 16. Structure and labeling of a binuclear anion of citratoperoxotitanate(IV) complex $[Ti_2(cit^*)_2(O_2)_2]^{4-}$.

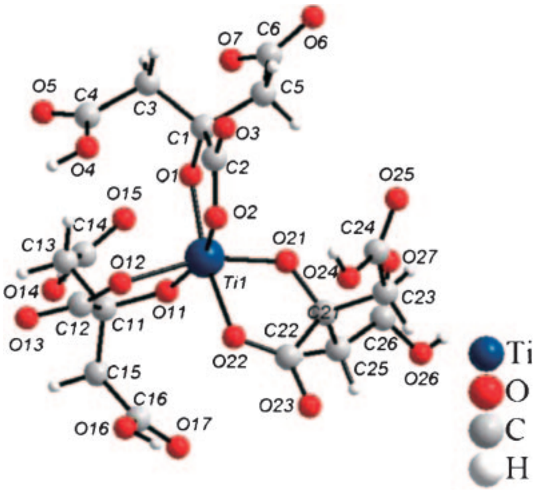


Figure 17. Structure and labeling of a mononuclear anion of citrato titanium complex $[Ti(Hcit^*)_3]^{5-}$.

plex with ethanol at 4 °C. The chemical formula of an isolated single crystal was reported to be $(NH_4)_4[Ti_2(cit^*)_2(O_2)_2]\cdot 2H_2O$ (**13**). The structure of the anion $[Ti_2(cit^*)_2(O_2)_2]^{4-}$ in **13** is shown in Figure 16. The anion **13** is a dimer of two titanium atoms coordinated by two citrate ligands. The bonding fashion of each citrate ligand to Ti is similar to that of the dimeric fragment in $[Ti_4(cit^*)_4(O_2)_4]^{8-}$ (Figure 12) in that: 1. one β-carboxylato oxygen (O1), one α-carboxylato oxygen (O5), and one α-alkoxylato oxygen (O3) in the first citrate ligand (CA1) coordinate jointly one titanium (Ti1) forming a fused five- and six-membered ring (Ti1–O3–C3–C4–O5–Ti1 and Ti1–O3–C3–C2–C1–O1–Ti1), and another fused five- and six-membered ring coordinating the second titanium (Ti2) is created through the second citrate ligand (CA2); and 2. the deprotonated α-alkoxylato oxygen (O3) simultaneously bonds to the two titanium atoms (Ti1 and Ti2), leading to formation of a nearly planar $[Ti_2O_2]$ core.

The main difference between the structure of $[Ti_2(cit^*)_2(O_2)_2]^{4-}$ and the dimeric fragment in $[Ti_4(cit^*)_4(O_2)_4]^{8-}$ is that while the β-carboxylato oxygen (O7) in the first citrate ligand (CA1) in the former complex coordinates to the second titanium (Ti2) to form another six-membered ring with the help of the α-alkoxylato oxygen (O3) (Ti2–O7–C6–C5–C3–O3–Ti2), the corresponding β-carboxylato oxygen atoms in the latter complex either bridge the two titanium atoms in another binuclear fragment or remain free from any coordination to Ti (Figure 12). As a result, the citrate ion acts as a tetradentate ligand in **13**. The $(O_2)^{2-}$ group binds to Ti in a side-on η^2-fashion, which is the same as that seen in the other peroxo–citrato and peroxo–glycolato complexes shown in Figures 11 and 14. The coordination sphere around each Ti atom is summarized as follows: Ti is coordinated by seven oxygen atoms belonging to the peroxo group $(O_2)^{2-}$ (O8–O9), one β-carboxylato oxygen (O1) and one α-carboxylato oxygen (O5) from the first citrate, two α-alkoxylato oxygens (O3 and O3′) from both citrates, and one β-carboxylato oxygen (O7′) from the second citrate. Finally, this coordination environment leads to formation of a planar $[Ti_2O_2]$ core by virtue of a center of inversion.

3.3.4 Mononuclear Titanium Complexes: 3.3.4.1 Mononuclear Titanium Complexes with Citric Acid; To date, no mononuclear citratoperoxotitanate(IV) complex has been reported, although a series of mononuclear tris-citrato titanium complexes are known. The first structural examples of such complexes were reported by Zhou et al.,[4] who solved the crystal structures of mixed-cation compounds having chemical formulas of $KMg_{1/2}[Ti(H_2cit^*)_3]\cdot 6H_2O$ and $(NH_4)Mg_{1/2}[Ti(H_2cit^*)_3]\cdot 6H_2O$. Similar types of mononuclear tris-citrato titanium complexes were crystallized in the form of different metal salts, which include $Na_3[Ti(Hcit^*)(H_2cit^*)_2]\cdot 9H_2O$,[5] $K_4[Ti(Hcit^*)_2(H_2cit^*)]$,[5] $K_5[Ti(Hcit^*)_3]\cdot 4H_2O$,[6] $Ba_2[Ti(Hcit^*)_2(H_2cit^*)]\cdot 8H_2O$,[29] $Na_3(NH_4)_3[Ti(cit^*)(Hcit^*)_2]\cdot 9H_2O$,[3] $Na_6[Ti(cit^*)(Hcit^*)_2]\cdot 16H_2O$,[3] and $Na_8[Ti(cit^*)_3]\cdot 7H_2O$.[6] Figure 17 shows the structure of the anion of $K_5[Ti(Hcit^*)_3]\cdot 4H_2O$ (**14**) reported by Deng et al.[5] The structure of the anion in **14** is a mononuclear complex of Ti coordinated by three citrate ligands, where each of the citrates acts as a bidentate ligand, chelating titanium through the α-alkoxylato and α-carboxylato oxygens, leading to the formation of a stable five-membered ring. As a result, the central titanium atom is six-coordinated in an octahedral environment. The non-coordinated protonated β-carboxy groups are strongly hydrogen-bonded to the deprotonated β-carboxylato groups of an adjacent molecule, resulting in a polymeric anionic structure of the complex **14**. The strong

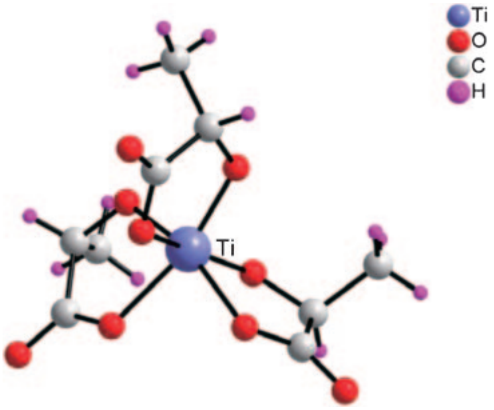


Figure 18. Structure of a mononuclear anion of lactate titanium complex $[Ti(la)_3]^{2-}$.

hydrogen bonding nature in **14** can be deduced from the intramolecular distances of O···O bonds, which range from 2.483 to 2.512 Å and are shorter than the typical hydrogen-bonding distance of 2.636 Å observed in the molecule with strong hydrogen-bonding such as salicylic acid. The series of mononuclear tris-citrato titanium complexes in the form of Na-, K-, and Ba-salts contain almost identical Ti–citrate parts to those shown in Figure 17. The difference is related only to the arrangements of the β-carboxylato groups connected to the alkaline or barium ions.

3.3.4.2 Mononuclear Titanium Complexes with Lactic Acid; Aqueous reactions of the peroxo–hydroxo titanium complex with lactic acid (H_2la) under basic conditions adjusted by ammonia followed by slow evaporation of water afforded a new water-soluble titanium complex having the chemical formula $(NH_4)_2[Ti(la)_3]$ (**15**).[2] Figure 18 shows the structure of the anion **15**. The titanium atom is coordinated by six oxygen atoms from three fully deprotonated lactic acid molecules, la, forming the stable five-membered rings. The TiO_6 octahedron thus formed is slightly distorted with the O–Ti–O angle of 162.7° and has the titanium atom shifted from the center, giving two sets of Ti–O interatomic distances of 2.071 and 1.848 Å; the oxygen atom contributing to the longer bond distance comes from the deprotonated α-alkoxylato group, and the one contributing to the shorter bond distance comes from the α-carboxylato group.

3.3.5 Titanium Complexes with Hydroxy–Amino Acids: Coordination structures of water-soluble titanium complexes with L-serine and L-threonine,[13] known as β-hydroxy-α-amino acids (Figures 19a and 19b), remain unclear, since no single crystals are yet available. In view of the fact that both L-serine and L-threonine contain three donor atoms coming from β-hydroxy, α-amino, and carboxy groups that in principle can coordinate Ti, at least two possible coordination modes of β-hydroxy-α-amino acids to Ti can be proposed as shown in Figure 19.

Mode 1: Formation of a five-membered ring resulting from joint coordination of the α-amino nitrogen and the carboxylato oxygen to Ti.

Mode 2: Formation of a six-membered ring resulting from joint coordination of the deprotonated β-hydroxy (β-hydroxy alkoxylato) and carboxylato oxygens to Ti.

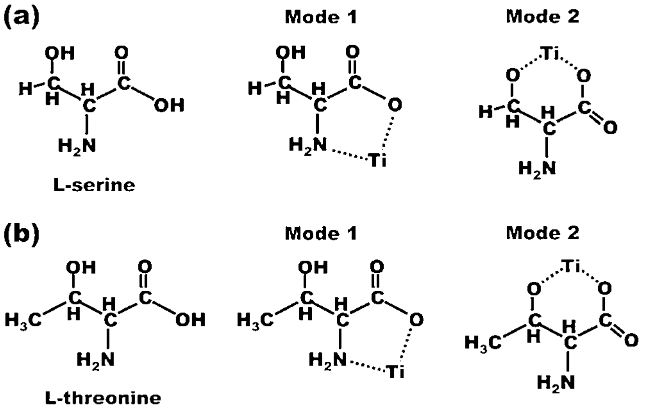


Figure 19. Structures of L-serine and L-threonine and their possible coordination modes to Ti: Mode 1 and Mode 2 are characterized by formation of five-membered and six-membered chelate rings, respectively.

Considering the usual coordination mode of α-amino carboxylatos to transition metal centers, Mode 1 would be the most probable one due to formation of a thermodynamically favored five-membered ring.[30] The presence of Mode 1 is also supported by the observed strong coloration (deep orange to brown) in Ti–L-serine and Ti–L-threonine complexes. The intensive coloring indicates possible Ti···N donor–acceptor bond formation, resulting in partial reduction of Ti^{IV} to Ti^{III}. This observation in turn suggests that Mode 2 would be less probable. The minimum amount of L-serine or L-threonine to solubilize Ti into water is 3 mol, which may indicate formation of $[Ti\{CH_2(\boldsymbol{OH})CH(NH_2)COO\}_3]^+$ or $[Ti\{CH_3CH(\boldsymbol{OH})\text{-}CH(NH_2)COO\}_3]^+$. The presence of the free hydroxy (***OH***) groups (not attached to Ti) in these complexes appears to be crucial to their solubility in water. L-Alanine, which would be expected to form the complex $[Ti\{CH_3CH(NH_2)COO\}_3]^+$ with a structure similar to the Ti–L-serine complex and involving a similar five-membered ring (Ti–O–C–C–N), does not have such a free hydroxy group and cannot solubilize Ti in water.

The above discussion regarding the coordination structures of L-serine and L-threonine to Ti must be oversimplified given the complexity of the chemistry of titanium with β-hydroxy-α-amino acids in aqueous solution. Either isolation of single crystals for structure determination or a thorough spectroscopic investigation in solution is necessary for clarifying their true structures.

3.3.6 Titanium Complexes with Porphyrin: As an exceptional case, a peroxo–titanium porphyrin-derived complex[31] that is practically insoluble in water involves stabilization of the titanium atom by six-membered rings, rather than five-membered rings. As shown in Figure 20, the structure of the reported peroxo titanium octaethylporphyrin (H_2oep) complex is characterized by the pseudo tetragonal pyramidal coordination with four nitrogen atoms of the macro-cyclic dianionic H_2oep ligand in the equatorial plane and the peroxo $(O_2)^{2-}$ ligand in the axial position. Thus, four six-membered rings (Ti–N–C–C–C–N–Ti) are formed and fused with each other.

3.4 Summary of Water-Soluble Titanium Complexes. 3.4.1 Minimum Required Structural Unit for Stabilization of Titanium Complexes: Figure 21 displays schematically

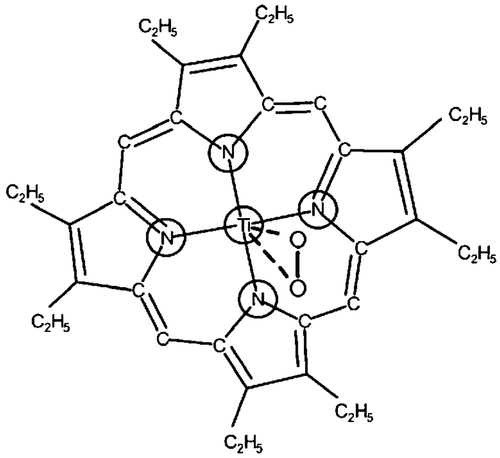


Figure 20. Structure of a peroxo–titanium octaethylporphyrin complex characterized by a pseudo tetragonal coordination with four nitrogen atoms and a peroxo (O_2^{2-}) ligand.

the formation of five- or six-membered rings by the bidentate coordination of various ligands to each individual titanium atom in the complexes **1–15**, including values of some relevant bond distances (Å) and angles.

The compounds **1–7**, **9**, and **10** involve five-membered rings formed by donor nitrogen atoms strongly bonded to Ti and oxygen atoms from α-carboxy groups. Values of O–Ti=N bond angles exhibit a large variation from 71.2 to 90.4° depending upon the ligand used, whereas the corresponding bond angles of O–Ti–O* in each individual five-membered ring composed of Ti–O(α-carboxylato)–C–C–O*(α-alkoxylato) exhibit less variation, ranging between 75.2 and 79.7°. The bond distances of Ti–O(α-carboxylato) in the titanium complexes with α-hydroxy carboxylic acids (**11**, **13**, **14**, and **15**) range from 2.049 to 2.071 Å, which are somewhat shorter than those of Ti–O(α-carboxylato) (2.061 to 2.095 Å) in the titanium complexes with N-donor chelate ligands (**1–4**, **9**, and **10**). The only exceptions refer to the tetrameric glycolatoperoxotitanate(IV) complex **12** and the tetrameric (μ-oxo)nitrilotriacetatotitanate(IV) complex **5**, for which the bond distances of Ti–O(α-carboxylato) in **12** and **5** are reported to be 2.103 and

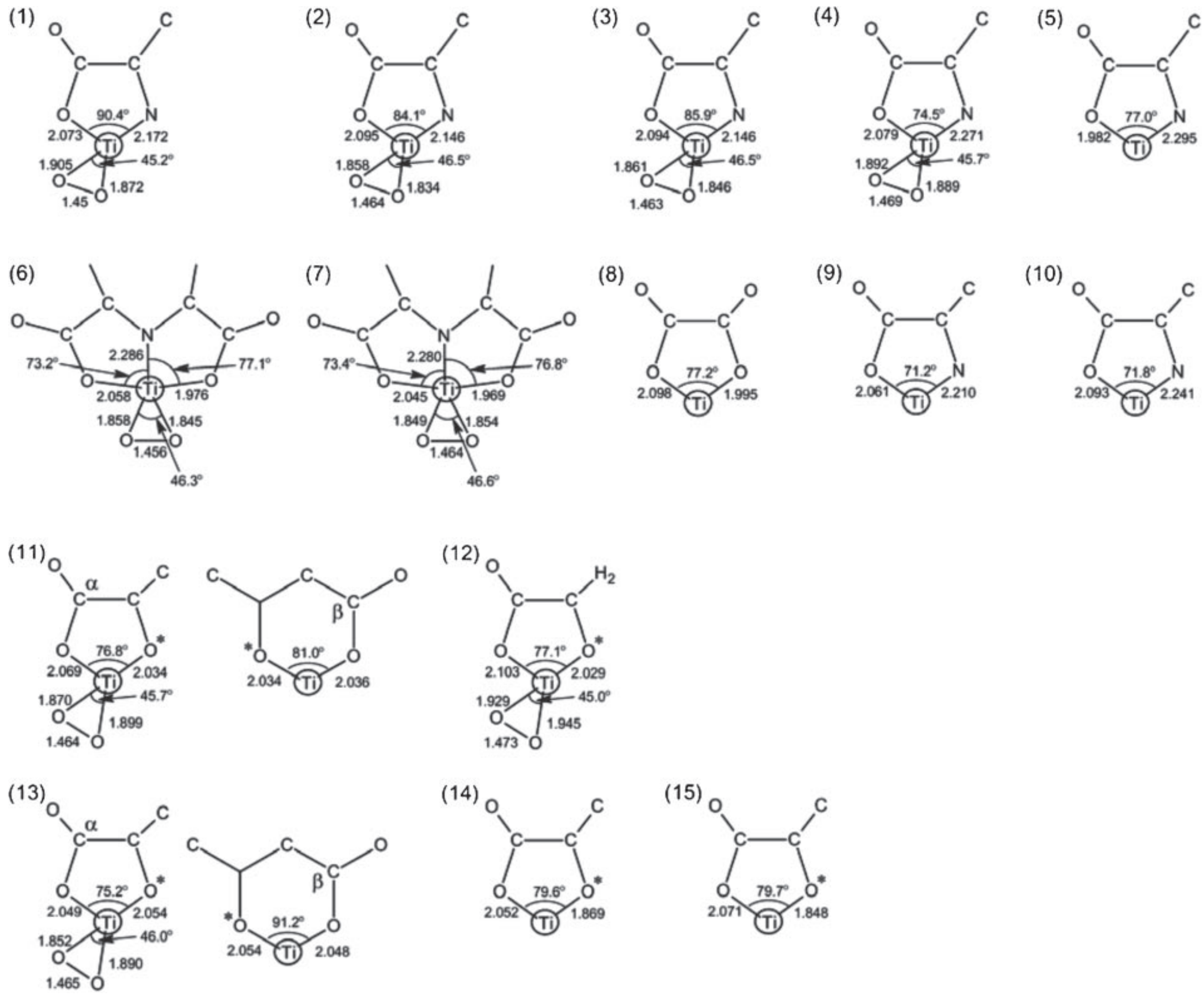


Figure 21. Schematic views of the formation of five- or six-membered rings by the bidentate coordination of various ligands to Ti atoms in the complexes **1–15** with values of some relevant bond distances (Å) and angles.

1.982 Å, respectively, which significantly deviate from the normal range of Ti–O(α-carboxylato) distances. The peculiar features of these bond distances could be accounted for in terms of the unusual coordination environments around the Ti atoms in **12** and **5**. In **12**, two unique oxygen atoms, one α-alkoxylato oxygen bonded to a primary carbon atom and one μ-oxo bridging oxygen, participate in the coordination, while in **5** each Ti is coordinated by two μ-oxo bridging oxygen atoms forming an unusual puckered eight-membered ring of Ti–O–Ti–O–Ti–O–Ti–O (similar to that of **8** shown in Figure 9).

The bond distances of Ti–N in **1**–**4**, **9**, and **10** are in the range of 2.146–2.271 Å, which, as expected, are considerably larger than those of Ti–O(α-carboxylato) bonds (2.061–2.095 Å) in the same complexes. Again, the bond distance of Ti–N in **5** (2.295 Å) is exceptionally long and the Ti–O(α-carboxylato) is exceptionally short (1.982 Å). The bond distances of Ti–O*(alkoxylato) in **11**–**13** range from 2.029 to 2.054 Å, which are similar to those of Ti–O(α-carboxylato) bonds (2.049–2.103 Å). On the contrary, the bond distances of Ti–O*(alkoxylato) in **14** and **15** are 1.869 and 1.848 Å, respectively, and are considerably shorter than the Ti–O(α-carboxylato) distances (2.052–2.071 Å). The large inequality of bond distances between Ti–O*(alkoxylato) and Ti–O(α-carboxylato) in **14** and **15** leads to the formation of largely distorted five-membered rings. Notably, both **14** and **15** are monomeric titanium complexes with the titanium atoms bound to three citrates and lactates, respectively, where each of the carboxylatos is acting as a bidentate ligand, chelating through the alkoxylato and α-carboxylato oxygens, thus yielding three sets of almost equally arranged five-membered chelate rings. No such inequality was observed for bond distances between Ti–O*(alkoxylato) and Ti–O(β-carboxylato) in **11** and **13** (2.034 Å/2.036 Å and 2.054 Å/2.048 Å, respectively), which results in minimized distortions of the six-membered chelate rings.

The geometry of peroxo $(O_2)^{2-}$ groups bonded to Ti, shown also in Figure 21, is quite similar among various peroxo–titanium complexes with different ligands, again except for the peroxo–glycolato titanium complex **12**. The average bond distance of each two Ti–O(peroxo) bonds is 1.866 Å for **1**–**4**, **6**, **7**, **11**, and **13**, whereas the corresponding average bond distance of Ti–O(peroxo) in **12** is 1.937 Å, which seems to be outside the normal range for Ti–O(peroxo). The bond distances of O(peroxo)–O(peroxo) and angles of O(peroxo)–Ti–O(peroxo) remain almost constant in the range of 1.45–1.47 Å and 45.0–46.6°, respectively, for all of the complexes **1**–**4**, **6**, **7**, and **11**–**13**. A striking feature that is commonly observed in the peroxo-containing titanium complexes of **1**–**4**, **6**, **7**, and **11**–**13**, is that both the nitrogen atoms of pyridine-derived or amino–carboxylato ligands in **1**–**4**, **6**, and **7**, and the α-alkoxylato oxygen atoms of hydroxy–carboxylic acid ligands in **11**–**13** are always trans to the peroxo $(O_2)^{2-}$ ligand. This arrangement also appears to be a common rule in other peroxo–titanium complexes less soluble or even insoluble in water, which include $[Ti(O_2)(pic)_2(hmpt)]$,[32] $[Ti(O_2)\{2,3\text{-py(COO)(COOH)}(acac)(hmpt)\}]$,[33] $[Ti(O_2)\{PhC(NSiMe_3)_2\}_2(py)]$,[34] and $[Ti(O_2)(tacMe_3)(NCO)_2]$[35] (hmpt; hexamethylphosphoric triamide, py; pyrazine, tacMe$_3$; 1,4,7-trimethyl-1,4,7-triazacyclononane).

Noteworthy, all of the complexes discussed here exhibit at least one common structural feature characterized by a five-membered ring composed of either Ti–O–C–C–N or Ti–O–C–C–O*–Ti. This observation implies that the minimum required structural unit for stabilization of a given titanium complex is the five-membered ring. Six-member rings, however, may exist only as a constituent of a fused five- and six-membered ring, as is seen in **11** and **13**. Attempts to synthesize water-soluble titanium complexes with 3-hydroxybutyric acid, which would give a six-member ring, have been unsuccessful as has been mentioned in Section **2** (Figure 4).

3.4.2 Reason for the Solubility of Water-Soluble Titanium Complexes in Water: In all of the water-soluble titanium complexes known to date and considered in the present review whose crystal structures have been solved by single-crystal XRD analyses, Ti possesses a coordination number of six or seven. In the six non-peroxo titanium complexes **5**, **8**–**10**, **14**, and **15**, the coordination number of each Ti atom is six, whereas in the other nine peroxo–titanium complexes **1**–**4**, **6**, **7**, and **11**–**13** each Ti atom is heptacoordinated with seven donor atoms (oxygen and nitrogen).

Of crucial importance is that in all of the complexes **1**–**15** there are no potential free groups for oligomerization. At the same time, tight coordination of six or seven donor atoms to Ti creates spatial difficulties for nucleophilic attack, which is the first step in hydrolysis. This argument explains why the bis(hydroxo–lactato) titanium complex $[Ti(la)_2(OH)_2]^{2-}$, which was first patented by DuPont, readily undergoes oligomerization, most notably in basic solutions in accordance with the condensation reaction of eq 26:

$$n[\mathrm{Ti(la)_2(OH)_2}]^{2-} \rightarrow \mathrm{HO{-}Ti(la)_2{-}[O{-}Ti(la)_2]_{n-1}}^{(2-2n)}\mathrm{{-}OH} \qquad (26)$$

In contrast, the anionic form of the titanium–tris-lactato complex $[Ti(la)_3]^{2-}$ undergoes neither hydrolysis nor oligomerization even after one year in a basic solution of pH 8. In this case, the coordination sites of Ti in $[Ti(la)_3]^{2-}$ are completely occupied by six oxygen atoms from three sets of fully deprotonated lactato ligands.

The solubility of each individual complex in water depends on several factors such as the temperature and pH of the solution in addition to its dissociation ability, which is the most crucial factor. As a general rule, titanium compounds in the form of alkaline or ammonium salts that can dissociate in water have much higher solubilities than those of neutral titanium compounds. Thus complex **3**, $K_2[Ti(O_2)(dipic)F_2]\cdot 2H_2O$, which involves a coordination sphere of Ti quite similar to that in complex **2**, $[Ti(O_2)(dipic)(H_2O)_2]\cdot 2H_2O$, may have a higher solubility in water compared with that of **2**. Non-dissociation neutral complexes **9** and **10** have solubilities in water at room temperature of only 5 mmol dm^{-3} and less than 1 mmol dm^{-3}, respectively. As expected, the solubility of **9** in water increased up to 50 mmol dm^{-3} at close to boiling temperature. Although no data on the solubility limits in water have been reported for a series of water-soluble complexes, our experience indicates that the anionic forms of titanium complexes with α-hydroxy carboxylic acids can be dissolved in water at a titanium concentration greater than 1 mol dm^{-3}.

In conclusion, to obtain a stable water-soluble titanium complex having a sufficient solubility in neutral water, the following four factors should be considered.

(1) The ligand should contain either a hydroxy or amino group in addition to a carboxy group.

(2) The ligand should coordinate titanium in such a way that it forms a five-membered ring or a fused five- and six-membered ring.

(3) The coordination number of titanium must be six or seven.

(4) The complex should be anionic.

With these factors, the attack of Ti by H_2O or OH^- in an aqueous solution is hindered by steric factors with no precipitation of titanium hydroxide, leading to a stable titanium aqueous solution. Environmentally benign synthesis of titanium-based ceramics using these aqueous solutions is described in the next section.

4. Synthesis of Titanium-Containing Oxides Using Water-Soluble Titanium Complexes

As described in the preceding sections, it is difficult to obtain a stable aqueous solution containing titanium species except for in a strongly acidic solution. Therefore, organic solvents are most commonly used for the synthesis of titanium-containing oxides by solution methods. Utilizing water as a processing solvent in the synthesis of titanium-containing oxides has now become possible, however, with the advent of water-soluble titanium complexes. In this section, we describe several representative examples of synthesis of titanium-containing oxides from aqueous solutions using water-soluble titanium complexes, including synthesis of complex oxides such as $BaTiO_3$, $Ba_{1-x}Sr_xTiO_3$, and $Bi_4Ti_3O_{12}$ (Section **4.1**), synthesis of a variety of barium titanates with different stoichiometry by the "compound" precipitation method (Section **4.2**), and the hydrothermal synthesis of four representative polymorphs of titanium oxides (TiO_2): TiO_2 (*rutile* type), TiO_2 (*anatase* type), TiO_2 (*brookite* type), and monoclinic $TiO_2(mC)$ (Section **4.3**), with a special focus on their selective syntheses.

4.1 Synthesis of $BaTiO_3$, $Ba_{1-x}Sr_xTiO_3$, and $Bi_4Ti_3O_{12}$ by the Amorphous Metal-Complex Method Using Water as a Processing Solvent. The method described here is called the "amorphous metal-complex (AMC)" method.[36] It provides a very convenient and simple way to synthesize at a reduced temperature multi-component oxides with the following important characteristics.[37]

(i) Water is used as a processing solvent.

(ii) A "gel"-like matter rather than a simple precipitate is to be formed.

(iii) A chelate-type ligand, most preferably citric acid, is used as a stabilizer for the constituent metal ions present in a given aqueous solution.

(iv) A precursor material, obtained after a thermal decomposition of the "gel"-like matter, is XRD amorphous, ensuring in most cases the compositional homogeneity of the target oxide material.

The present authors have already reported the use of water-soluble titanium complexes as precursors for the aqueous solution-based synthesis of various titanates by the AMC method.[11,38] The AMC synthesis of $BaTiO_3$ using a citratoperoxotitanate(IV) complex is described below.

A flowchart for the synthesis of $BaTiO_3$ is shown in Figure 22. Metallic titanium powder is dissolved into a mixture of hydrogen peroxide and ammonia under ice-cold conditions, followed by addition of citric acid to obtain a stable aqueous solution containing the citratoperoxotitanate(IV) complex. An excess of citric acid should be used, considering the coordination of barium. Next, a barium salt is added, maintaining the proper stoichiometry. Among the numerous barium compounds, $Ba(CH_3COO)_2$ and $BaCO_3$ are preferable because of their solubility in citric acid solution. After evaporation of the solvent, a yellowish "gel" is obtained and $BaTiO_3$ is synthesized by heating the gel at 500–800 °C. The XRD patterns of the samples heated at 500 to 800 °C for 5 h are shown in Figure 23. In the samples heated up to 500 °C, carbonates remain as evidenced by reflections around 25° (2θ) and lack of peaks of $BaTiO_3$. A single-phase $BaTiO_3$ is obtained at temperatures higher than 600 °C.

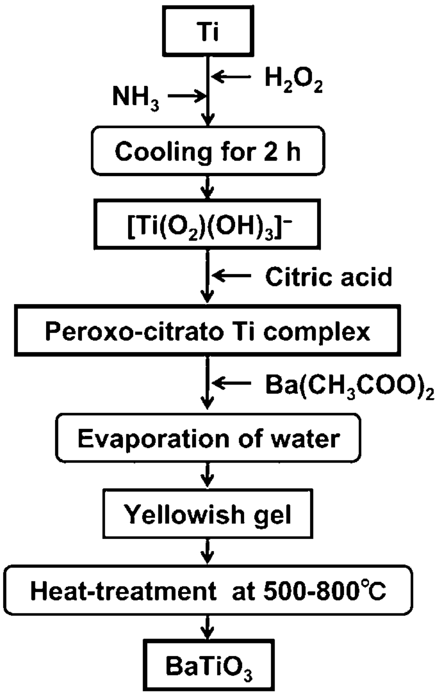


Figure 22. Flowchart for the synthesis of $BaTiO_3$ by the amorphous metal complex method using citric acid as a complexant.

In the synthesis of Sr-substituted barium titanate, $Ba_{1-x}Sr_xTiO_3$, the use of the citratoperoxotitanate(IV) complex is difficult since strontium forms a precipitate with citric acid that is barely soluble in water. In this case, the complexing agent should be changed. Use of lactic acid is one of the ways to stabilize all of the metal ions present in a given aqueous solution. Lactate ions do not form precipitates with strontium or barium ions. Therefore all of the titanium, barium, and strontium ions can be retained in the aqueous solution with use of lactic acid, making synthesis of $Ba_{1-x}Sr_xTiO_3$ possible. Figure 24 shows XRD patterns for $Ba_{0.5}Sr_{0.5}TiO_3$ prepared using citric acid or lactic acid as a complexing agent and with heat treatment at 700 °C. There are no secondary phases in the sample obtained with lactic acid, but in the case where citric acid was used, impurities that seem to be due to carbonate were clearly detected. It appears that, in the case of citric acid, sufficient miscibility is not obtained due to the precipitation

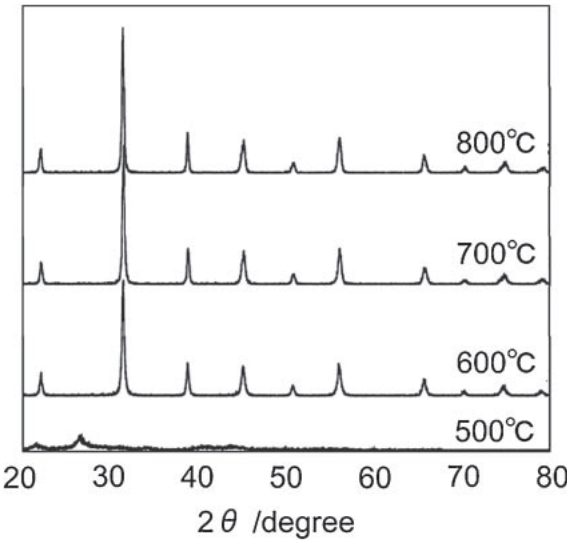


Figure 23. X-ray diffraction patterns of $BaTiO_3$ synthesized by the amorphous metal complex method using citric acid as a complexant.

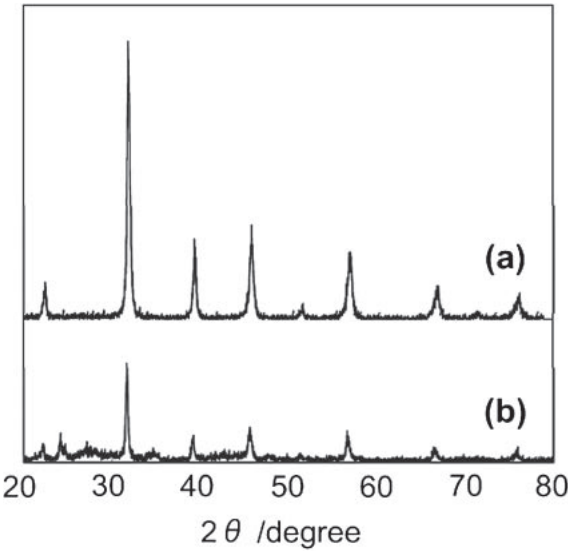


Figure 24. X-ray diffraction patterns of $Ba_{0.5}Sr_{0.5}TiO_3$ synthesized by the amorphous metal complex method using (a) lactato titanium complex and (b) citratoperoxotitanate(IV) complex.

of strontium and citric acid. In contrast, high miscibility is retained in the case of lactic acid, yielding a single phase $Ba_{0.5}Sr_{0.5}TiO_3$.

$Bi_4Ti_3O_{12}$ with a layered perovskite structure (Aurivillius phase), which is a well known ferroelectric material, can also be prepared by the AMC method using lactic acid as a complexing agent. Bi–lactic acid aqueous solution and lactato titanium complex aqueous solution were stoichiometrically mixed (Bi:Ti = 4:3) with an excess of lactic acid. After evaporation of the mixed solution, heat treatment was carried out for 5 h at 600, 800, and 1000 °C. XRD patterns of the heated samples at each temperature are shown in Figure 25. Although $Bi_4Ti_3O_{12}$ formed as the main phase, the presence of

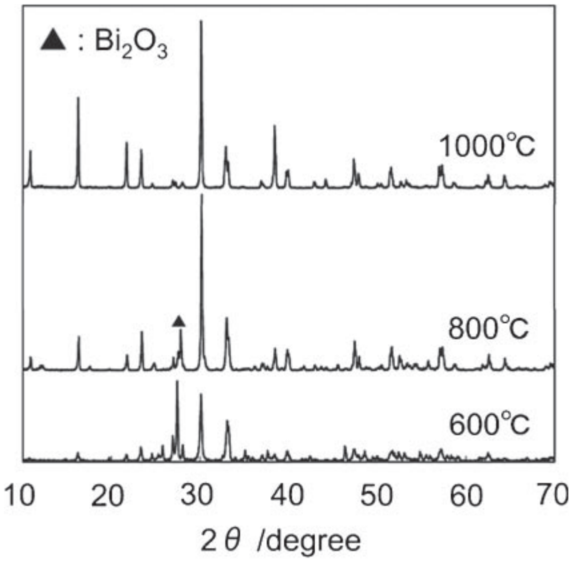


Figure 25. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ synthesized by the amorphous metal complex method using lactic acid as a complexant.

Bi_2O_3 was observed as an impurity, and its amount decreased as the heat treatment temperature increased. In this case, however, a Bi-deficient phase, which often forms when the conventional solid-state reaction method is employed, is not detected in the sample heat treated at 1000 °C. Therefore, loss of bismuth is negligible in the synthesis of $Bi_4Ti_3O_{12}$ powder by the AMC method.

4.2 Synthesis of Barium Titanates by the "Compound Precipitation" Method. Another important application of new water-soluble titanium complexes includes their use as counter anions for forming "compound precipitations" containing two metal ions in the ratio required by the stoichiometry of the target oxide material, such as $Ba[Ti(C_6H_4O_7)O_2]\cdot 2H_2O$,[26] $Ba_2[Ti(C_6H_5O_7)_2(C_6H_6O_7)]\cdot 8H_2O$,[25] and $Ba_2(NH_4)_2[Ti_4(C_6H_4O_7)_2(C_6H_5O_7)_2(O_2)_4]\cdot 10H_2O$,[29] which in turn may be used for the preparation of $BaTiO_3$, Ba_2TiO_4, and $BaTi_2O_5$ in a single step similar to molecular precursors. Here we describe the synthesis of $BaTiO_3$ using $Ba[Ti(C_6H_4O_7)O_2]\cdot 2H_2O$ as the precursor.[26]

By controlling the pH, temperature, and concentration of the reaction solution, citratoperoxotitanate(IV) ion, $[Ti(C_6H_4O_7)O_2]^{2-}$, can form a "compound precipitate" with barium and/or strontium. The ratios of metallic elements of both precipitates are 1:1, therefore $BaTiO_3$ and $SrTiO_3$ can be synthesized by thermal decomposition of the corresponding "compound." The color of both precipitates is orange. The XRD pattern of the "compound" precipitate with barium, shown in Figure 26a, indicates that this precipitate is not amorphous but crystalline. The composition of the precipitate was found to be $Ba[Ti(C_6H_4O_7)O_2]\cdot 2H_2O$ according to the results of TG/DTA and elemental analysis. The precipitate was heat treated for 5 h at 700 °C to obtain $BaTiO_3$. The XRD pattern of the heat-treated sample is shown in Figure 26b. Virtually single-phase $BaTiO_3$ is obtained, indicating that this precipitate can be used as a molecular precursor for synthesis of $BaTiO_3$. Further details of this synthesis are reported elsewhere.[26]

4.3 Solution-Based Synthesis of Four Polymorphs of TiO_2: TiO_2 (*Rutile* Type), TiO_2 (*Anatase* Type), TiO_2 (*Brookite* Type), and TiO_2(*mC*). TiO_2 (*anatase* type) and TiO_2 (*rutile* type) are widely used in technological applications. Their crystal structures are shown in Figures 27a and 27b, respectively. TiO_2 (*brookite* type) and the so-called TiO_2(B) are the other important but less known polymorphs of TiO_2, and since their crystal structures (Figures 27c and 27d) differ from those of TiO_2 (*anatase* type) and TiO_2 (*rutile* type), it is of vital importance to elucidate their functional properties compared with those of TiO_2 (*anatase* type) and TiO_2 (*rutile* type). Since TiO_2(B) conforms to a base-centered cell with monoclinic symmetry, it is also called "monoclinic TiO_2." Therefore, we will use TiO_2(*mC*) notation for this unusual polymorph instead of TiO_2(B) in order to avoid a possible confusion between "brookite" and TiO_2(B). While TiO_2 (*brookite* type) has been successfully used as an excellent photocatalyst for both dehydrogenation of 2-propanol and silver deposition,[39] TiO_2(*mC*) has recently found application as a Li intercalation host material for lithium ion batteries owing to its unique tunnel structure.[40] Among these four polymorphs of TiO_2, TiO_2 (*anatase* type) and TiO_2 (*rutile* type) are easy to synthesize in their pure form, and a variety of solution methods have been applied for their preparation, which include either sol–gel methods[1,41] based upon hydrolysis of titanium tetraalkoxides, e.g., tetraisopropoxides $Ti(OCHMe_2)_4$ in alcohol solutions in the presence of small amounts of water[42–45] or hydrothermal methods[46,47] using either titanium tetrachloride ($TiCl_4$)[48] or titanium tetraisopropoxide[49] in aqueous solutions. An exceptional approach for the synthesis of TiO_2 (*anatase* type) was reported by Möckel et al.,[50] who succeeded in forming uniform size TiO_2 (*anatase* type) nanocrystals by hydrothermal decomposition of bis(ammonium–hydroxo–lactato) titanium, $(NH_4)_2[Ti(la)_2(OH)_2]$, in neutral aqueous solutions at temperatures above 100 °C. It is also worthy to refer to some relevant publications reporting on selective synthesis of TiO_2(*anatase* type) and TiO_2(*rutile* type), their phase stability and transformation between them.[51–55] Contrary to the ease of synthesis of TiO_2 (*anatase* type) and TiO_2 (*rutile* type), synthesis of TiO_2 (*brookite* type) and TiO_2(*mC*) in their pure form is still challenging.

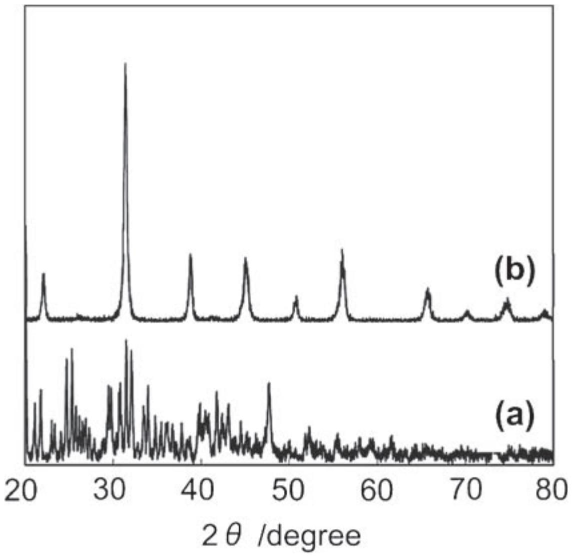
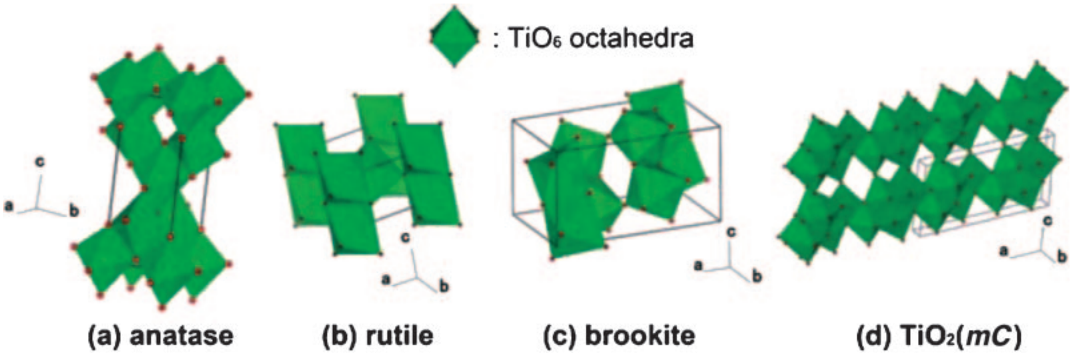


Figure 26. X-ray diffraction patterns of (a) "compound" precipitation of a citratoperoxotitanate(IV) complex with barium ion and (b) $BaTiO_3$ synthesized by "compound" precipitation.

In this section, we therefore briefly review the current status of solution-based synthesis of TiO_2 (*brookite* type) and TiO_2(*mC*) polymorphs (Section **4.3.1**) and introduce a novel approach for one-step and selective synthesis of the four polymorphs based on hydrothermal decomposition of a series of water-soluble titanium complexes developed by the present authors' group (Section **4.3.2**).

4.3.1 Synthesis of TiO_2 (*Brookite* Type) and Monoclinic TiO_2(*mC*): 4.3.1.1 TiO_2 (*Brookite* Type); Among the TiO_2 (*anatase* type), TiO_2 (*rutile* type), and TiO_2 (*brookite* type) polymorphs, TiO_2 (*brookite* type) is the most difficult to obtain as nanocrystals in a phase-pure form. In a series of previous reports focusing on TiO_2 (*brookite* type) formation, this phase was usually obtained together with other polymorphs of TiO_2.[56] Nevertheless, successful synthesis of pure TiO_2 (*brookite* type) practically free from other polymorphs of TiO_2 was achieved by several groups.

As seen in Table 2, the hydrothermal method is the most promising approach for obtaining pure TiO_2 (*brookite* type) (Entries **1**–**4** and **6**–**8**) except for Entry **5**, where a simple homogeneous precipitation method using urea as an in situ pH regulator was employed. The methodology may be divided into four categories depending upon the source of Ti used.



(a) anatase (b) rutile (c) brookite (d) TiO_2(*mC*)

Figure 27. Structures of various polymorphs of TiO_2: (a) TiO_2 (*anatase* type), (b) TiO_2 (*rutile* type), (c) TiO_2 (*brookite* type), and (d) TiO_2(*mC*).

Table 2. Summary of Methods to Achieve Single-Phase Synthesis of Brookite-Type of TiO_2: B, A, R, and TiO_2(*mC*) Stand for TiO_2 (*Brookite* Type), TiO_2 (*Anatase* Type), TiO_2 (*Rutile* Type), and Monoclinic TiO_2, Respectively

Entry	Source of Ti	Method	Brief description of procedures for obtaining pure brookite	Controlled parameters		Phase constituents	Ref.
				Source of Na	pH		
1	Amorphous TiO_2	Hydrothermal	Amorphous $TiO_2/NaOH/H_2O$ with Ti/Na = 1 and pH 12.9 was hydrothermally treated at 200 °C for 24 h.	NaOH	12.9	**B (100%)**	57
				Na_2CO_3	11.3	A ≒ B	
				$Na_2B_4O_7$	9.3	A > B	
				CH_3COONa	8.1	A ≫ B	
				pH in ②			
2	Anatase TiO_2	Hydrothermal	① Anatase $TiO_2/NaOH/H_2O$ with Ti/Na = 0.156 was hydrothermally treated at 120 °C for 24 h. ② Precipitates from ① was hydrothermally treated at 200 °C with pH 10.9 for 20 h.	6		A (100%)	58
				7.6		A ≫ B	
				8.8		A > B	
				9.6		A ≒ B	
				10.9		**B (100%)**	
				pH			
3	$Ti^{IV}Cl_4$	Hydrothermal	$Ti^{IV}Cl_4/NaOH/H_2O$ with Ti/Na = 0.25 and pH 8 was hydrothermally treated at 245 °C for 12 h.	1		A ≫ R, B	59
				3		A ≫ R, B	
				6		A (100%)	
				8–10		**B (100%)**	
				Solvent	pH		
4	$Ti^{III}Cl_3$	Homogeneous precipitation followed by hydrothermal	① Amorphous titania was obtained via homogeneous precipitation from $Ti^{III}Cl_3$/hexamethylenetetramine/H_2O at 90 for 1 h. ② The solution containing the amorphous titania in ① with pH 7 was hydrothermally treated at 190 °C for 2 h.	H_2O	7	**B (100%)**	60
				H_2O	9	R (100%)	
				H_2O/CH_3OH (50 vol %)	9	A (100%)	
5	$Ti^{III}Cl_3$	Homogeneous precipitation	① Crystalline brookite was obtaind via homogeneous precipitation from $Ti^{III}Cl_3$ (0.015 mol dm^{-3})/urea (0.5 mol dm^{-3})/H_2O at 70 °C for 2 h. ② The precipitate in ① was dried at 100 °C for 24 h.	Not described		**B (100%)**	61

Continued on next page.

Category 1: Either amorphous TiO_2 or TiO_2 (*anatase* type) is used as the Ti source in Entries **1** and **2**.

Category 2: Either $Ti^{IV}Cl_4$ or $Ti^{IV}(SO_4)_2$ are used as a Ti source in Entry **3**.

Category 3: $Ti^{III}Cl_3$ is used as a Ti source in Entries **4**–**6**.

Category 4: Complexes of Ti are used as Ti sources in Entries **7** and **8**.

In category 1, Nagase et al. (Entry **1**)[57] synthesized nearly single-phase TiO_2 (*brookite* type) by hydrothermal treatment of amorphous TiO_2 at 200 °C for 24 h in the presence of NaOH as the mineralizer with a TiO_2/NaOH mole ratio close to 1. They concluded that brookite is formed from intermediate hydrated sodium titanates by releasing Na^+ and H^+ from the surface accompanied by oxidation of Ti in the structure. Very recently, Deng et al. (Entry **2**)[58] have synthesized for the first time TiO_2 (*brookite* type) nanotubes with crystalline multilayer walls by a simple two-step hydrothermal process. First, titanate nanotubes with the chemical formula $Na_2H_{2-x}Ti_3O_7$ were prepared and used as a precursor. Second, the titanate nanotubes were transformed into pure TiO_2 (*brookite* type) nanotubes with a ≈5-nm inner diameter and a ≈0.78-nm interlayer space under hydrothermal conditions. A transformation scheme from titanate to TiO_2 (*brookite* type) similar to that proposed by Nagase et al.[57] was postulated: Na^+ and H^+ located in the interlayer spaces of titanate can be released and consequently the TiO_2 (*brookite* type) forms.

In category 2, pure TiO_2 (*brookite* type) was synthesized by the hydrothermal process starting from either $Ti^{IV}Cl_4$ or $Ti^{IV}(SO_4)_2$ under strongly basic conditions using NaOH (Entry **3**).[59] While the higher pH of the solution adjusted by NaOH is indispensable for formation of pure TiO_2 (*brookite* type), the lower pH of the initial solution favors formation of TiO_2

Continued.

Entry	Source of Ti	Method	Brief description of procedures for obtaining pure brookite	Controlled parameters		Phase constituents	Ref.
				$[TiCl_3]$ /mol dm^{-3}	pH		
6	$Ti^{III}Cl_3$	Hydrothermal	$Ti^{III}Cl_3$ (0.0625–0.075 mol dm^{-3})/H_2O_2/H_2O with $Ti/H_2O_2 = 1$ and pH 1.1–1.32 was hydrothermally treated at 180 °C for 3 h.	0.9	<0	R (100%)	62
				0.6	0.25	R (100%)	
				0.45	0.4	A (51%) + B (5%) + R (44%)	
				0.3	0.58	A (63%) + B (26%) + R (11%)	
				0.15	0.75	A (56%) + B (44%)	
				0.1	0.9	A (32%) + B (68%)	
				0.075	1.1	**B (100%)**	
				0.0625	1.32	**B (100%)**	
				0.05	1.68	A (39%) + B (61%)	
				Na/Ti			
7	$TiO(acac)_2$	Glycothermal /hydrothermal	$[TiO(acac)_2]$/sodium laurate (SL)/ethylene glycol (EG) with Na/Ti = 2 was glycothermally treated at 300 °C for 2 h in the presence of small amounts of water. The water was initially separated from EG solution in the autoclave but during the glycothermal treatment at 300 °C, H_2O was first vaporized and then dissolved in EG.	0		A (75%) + B (25%)	63
				0.5		[A + R] (81%) + B (19%)	
				1		[A + R] (32%) + B (68%)	
				1.5		A (27%) + B (73%)	
				2		**B (100%)**	
				Additive	pH		
8	Peroxo–oxo–glycolato–Ti	Hydrothermal	Peroxo–oxo–glycolato–Ti (0.25 mol dm^{-3})/H_2O/ammonia with pH 10 was hydrothermally treated at 200 °C for 24 h.	NH_3	10	**B (100%)**	27
				none	6	R (100%)	
				H_2SO_4	1	TiO_2(*mC*) (100%)	69

(*anatase* type) and may indicate that the TiO_2 (*brookite* type) forms via release of Na^+ and H^+ from possible intermediate sodium titanates produced under the hydrothermal conditions in the presence of large amounts of NaOH.

In category 3, $Ti^{III}Cl_3$ instead of $Ti^{IV}Cl_4$ was employed as a starting Ti source (Entries **4**–**6**). Sato et al. (Entry **4**)[60] obtained pure TiO_2 (*brookite* type) nanoparticles by homogeneous precipitation in aqueous mixed solutions of hexamethylenetetramine and titanium(III) chloride followed by an hydrothermal treatment of the resulting amorphous titania at pH 7 and 190 °C for 2 h. Interestingly, when the solution is adjusted to pH 9, pure TiO_2 (*rutile* type) forms, while a mixed solution of H_2O and CH_3OH (50–50 vol %) at pH 9 leads to formation of pure TiO_2 (*anatase* type). Li et al. (Entry **5**)[61] have claimed that monodispersed spherical particles of TiO_2 (*brookite* type) can be obtained under ambient pressure at 70 °C via reaction in a solution of urea and $Ti^{III}Cl_3$ followed by drying the obtained homogeneous precipitate in air at 100 °C for 24 h. The same authors have succeeded in selective synthesis of pure TiO_2 (*brookite* type) as well as pure TiO_2 (*anatase* type) and TiO_2 (*rutile* type) starting from $Ti^{III}Cl_3$ via one single redox route under mild hydrothermal conditions (180 °C, 3 h) in the presence of H_2O_2 as the oxidizer for Ti^{III} ions (Entry **6**).[62] As can be seen in Entry **6** in Table 2, the window for formation of pure TiO_2 (*brookite* type) is rather narrow; high pH favors TiO_2 (*anatase* type), low pH favors TiO_2 (*rutile* type), while intermediate pH stabilizes the TiO_2 (*brookite* type) phase.

In category 4, Kominami et al. (Entry **7**)[63] reported that thermal treatment of bis(acetylacetonato)oxotitanium(IV), $[TiO(acac)_2]$, in ethylene glycol (EG) in the presence of sodium laurate with a Na/Ti ratio of 2 and a small amount of water at 300 °C yielded pure TiO_2 (*brookite* type) nanoparticles having an average particle size of 14 × 67 nm. It was concluded that excess amounts of sodium ions with respect to titanium ions, water and $[TiO(acac)_2]$ as the Ti source were indispensable for the formation of TiO_2 (*brookite* type) crystals and the use of EG as the reaction medium was essential to avoid contamination by the TiO_2 (*anatase* type) and TiO_2 (*rutile* type) phases. While the absence of sodium ions resulted in the formation of a mixture of TiO_2 (*anatase* type) (75%) and TiO_2 (*rutile* type) (25%), TiO_2 (*anatase* type) predominantly formed when water was not present in the system, i.e., under glycothermal conditions. Tomita et al. (Entry **8**)[27] have reported that hydrothermal treatments of $[Ti_4(ga)_4(Hga)_2(\mu\text{-}O)_2(O_2)_4]^{6-}$ aqueous solutions at pH 6 and 10 at 200 °C for 24 h allowed the selective preparation of nanopowders of pure TiO_2 (*rutile* type) and TiO_2 (*brookite* type), respectively. Details are given in Section **4.3.2**.

4.3.1.2 Monoclinic TiO_2(*mC*); The pioneering work on the preparation of metastable TiO_2(*mC*) was reported by

Tournoux's group,[64–66] who treated a sample of a layered potassium titanate $K_2Ti_4O_9$ in 3 mol dm^{-3} HNO_3, yielding $H_2Ti_4O_9 \cdot xH_2O$, which transformed into $TiO_2(mC)$ upon heating at 500 °C. Subsequent research by Davies' group[67,68] has shown that $TiO_2(mC)$ can be prepared almost universally from proton exchange and subsequent dehydration of a series of layered titanates with the general formula of $A_2Ti_nO_{2n+1}$ ($A = Na$, K, and Cs; $3 \leq n \leq 6$). Except for recent works by Kobayashi et al.[69] and Yamamoto et al.,[70,71] where one-step synthesis of $TiO_2(mC)$ was successfully achieved by a hydrothermal method employing a water-soluble peroxo–oxo–glycolato Ti-complex, many recent reports of the synthesis of $TiO_2(mC)$[40,72–77] basically rely upon the three-step procedure established by Tournoux and Davies, a representative of which is described as follows in the case of sodium titanates.

Step 1: $Na_2Ti_3O_7$, $Na_2Ti_4O_9$, or $Na_2Ti_5O_{11}$ are synthesized by hydrothermal treatment of amorphous $TiO_2 \cdot xH_2O$, TiO_2 (*anatase* type) or TiO_2 (*rutile* type) in a 10 M NaOH solution.

Step 2: The sodium titanates thus obtained are washed with HCl or HNO_3 yielding $H_2Ti_3O_7 \cdot xH_2O$, $H_2Ti_4O_9 \cdot xH_2O$, or $H_2Ti_5O_{11} \cdot xH_2O$ hydrogen titanates through proton exchange reactions between the sodium titanates and the acids.

Step 3: The hydrogen titanates thus prepared are calcined at 400–600 °C to obtain the target material $TiO_2(mC)$.

Feist and Davies[68] have revealed how $TiO_2(mC)$ forms from a series of different starting layered titanates with different values of n by investigating each of the dehydration stages (the third step) using thermal analysis and crystallographic techniques, including collection of neutron diffraction data. They demonstrated that the dehydration proceeds through three distinct steps: an initial topotactic structural condensation step followed by a nucleation and growth step resulting in the formation of a $TiO_2(mC)$-like intermediate, and a final transformation step yielding $TiO_2(mC)$.

Among many recent studies focusing on synthesis of $TiO_2(mC)$, improvement of crystallinity[70,71] and more importantly shape control have been key issues for rendering $TiO_2(mC)$ that can be feasibly used as a material in a variety of applications such as photocatalysts and intercalation electrodes in rechargeable lithium batteries or super capacitors. The first important issue is related to the crystallinity of $TiO_2(mC)$, which was reported to be strongly dependent on the initial titanate structures as well as the temperature at which dehydration of hydrogen titanates obtained in the second step is carried out. In the direction from $n = 5$ to $n = 3$ in $H_2Ti_nO_{2n+1} \cdot xH_2O$, the crystallinity of $TiO_2(mC)$ after the dehydration of these hydrogen titanates was increased significantly.[68]

The second important issue, which is more beneficial to materials chemists, is related to the shape control of $TiO_2(mC)$. It has been reported in recent publications that both nanotubes and nanowires with the $TiO_2(mC)$ structure can be selectively obtained. According to Armstrong and Bruce,[73] $TiO_2(mC)$ nanotubes were synthesized by the three-step method with a careful tuning of experimental conditions: (1) the first step is to obtain sodium titanate, which is synthesized by adding 6 g of TiO_2 (*anatase* type) to 28 cm^3 of an NaOH aqueous solution at a concentration of 15 mol dm^{-3}, followed by hydrothermal treatment at 150 °C for 72 h in an autoclave (40 cm^3); (2) the second step is to obtain hydrogen titanate, which is prepared by washing the product after the hydrothermal reaction with 0.05 mol dm^{-3} HCl for proton exchange; and (3) the third step is to obtain $TiO_2(mC)$ nanotubes, which are synthesized by heating the dried hydrogen titanates at 400 °C for 5 h.

$TiO_2(mC)$ nanowires can also be obtained in a way similar to the synthesis conditions for the $TiO_2(mC)$ nanotubes; the main differences are the temperature used in the second step and the volume of solution used in the first step, which were respectively 170 °C and 33 cm^3 in the case of the nanowire. The $TiO_2(mC)$ nanotubes thus obtained were multi-walled with external diameters in the range of 10–20 nm and internal diameters in the range of 5–8 nm. The external diameters of the nanotubes were less than those of typical nanowires, which have diameters in the range of 20–50 nm.[72]

It is generally accepted that the shape of $TiO_2(mC)$ in the form of nanowires is inherited directly from the preceding nanowired form of a given hydrogen titanate like $H_2Ti_3O_7 \cdot xH_2O$, whose morphology is a reflection of the original shape of nanowires (nanorods) of the corresponding sodium titanate $Na_2Ti_3O_7$, which is used as a starting compound. In other words, the original shape of $Na_2Ti_3O_7$ is retained during the entire process that includes transformation from $Na_2Ti_3O_7$ to $H_2Ti_3O_7 \cdot xH_2O$ and from $H_2Ti_3O_7 \cdot xH_2O$ to $TiO_2(mC)$. Therefore, it is concluded that from a morphological viewpoint, a hydrothermal treatment of different TiO_2 precursors in a highly alkaline medium, which can produce nanowires of sodium titanates, is an indispensable way to prepare nanowires of $TiO_2(mC)$ as well as hydrogen titanates. On the other hand, the mechanism for formation of $TiO_2(mC)$ nanotubes remains unclear, but it may be described in conjunction with the formation mechanism of $H_2Ti_3O_7$ nanotubes on the assumption that the transformation of the $H_2Ti_3O_7$ nanotube to $TiO_2(mC)$ proceeds without a significant change in its tubular structure. The proposed formation mechanism of $H_2Ti_3O_7$ nanotubes begins with $H_2Ti_3O_7$-type plates. Individual trititanate layers are peeled off from the plates and scroll up into nanotubes.[78–80] In other words, the peculiar shape of the final $TiO_2(mC)$ can be referred to as nanoscrolls. Extensive ab initio calculations of the surface tension, elastic strain energy, interlayer coupling energy and Coulomb force indicate that surface tension due to an asymmetry related to H deficiency in the surface layers of the plates is the principal driving force of the cleavage. The dimension of the nanotubes is controlled by this surface tension together with the interlayer coupling energy and Coulomb force.

The characteristic structure of $TiO_2(mC)$, which is composed of corrugated sheets of edge- and corner-sharing TiO_6 octahedra linked together by bridging oxygen atoms to form a three-dimensional framework with open channels (Figure 27d), renders $TiO_2(mC)$ of an excellent material for lithium rechargeable batteries.[40,72,73]

4.3.2 Selective Synthesis of Four Representative Polymorphs of TiO_2 by Hydrothermal Decomposition of Water-Soluble Titanium Complexes:

The present authors have reported that the hydrothermal treatment of aqueous solutions containing water-soluble titanium complexes at 200 °C for 24 h induced decomposition of the complexes resulting in formation of nanocrystalline TiO_2, and more importantly that the four polymorphs of TiO_2 (*anatase*, *rutile*, *brookite* type and $TiO_2(mC)$) were selectively synthesized by choosing an appropriate titanium complex and by adjusting the pH of the solution.[27,69–71] This development allowed us to investigate the photocatalytic properties of different polymorphs of TiO_2. It has been demonstrated that a pure TiO_2 (*brookite* type) has higher photocatalytic activity with respect to NO decomposition than those of the widely used TiO_2 (*anatase* type) photocatalysts with similar specific surface areas.[81,82]

Figure 28 shows XRD patterns of TiO_2 powders obtained after the hydrothermal treatment at 200 °C for 24 h of aqueous solutions containing either the citratoperoxotitanate(IV) complex (abbreviated Ti–cit) at pH 6 or the peroxo–oxo–glycolato titanium complex (abbreviated Ti–ga) at pH 1, 6, and 10. The TiO_2 (*anatase* type) can be obtained from a plain aqueous solution of the Ti–cit at pH 6, while TiO_2 with the rutile structure can be prepared from another plain aqueous solution of the Ti–ga at pH 6. It is of particular importance that TiO_2 (*brookite* type) formed as the only phase from an aqueous solution of the same Ti–ga when the solution is adjusted to pH 10 by adding an ammonia solution, while the TiO_2(*mC*) polymorph formed from an acidic aqueous solution containing the same Ti–ga at pH 1 adjusted by an addition of H_2SO_4. This approach represents the first example of the highly selective synthesis of the four TiO_2 polymorphs by a one-step procedure starting from the same type of solution. Aqueous solutions of water-soluble titanium complexes were employed as precursors for hydrothermal preparation of single-phase TiO_2 (*anatase* type), TiO_2 (*rutile* type), TiO_2 (*brookite* type), and TiO_2(*mC*).

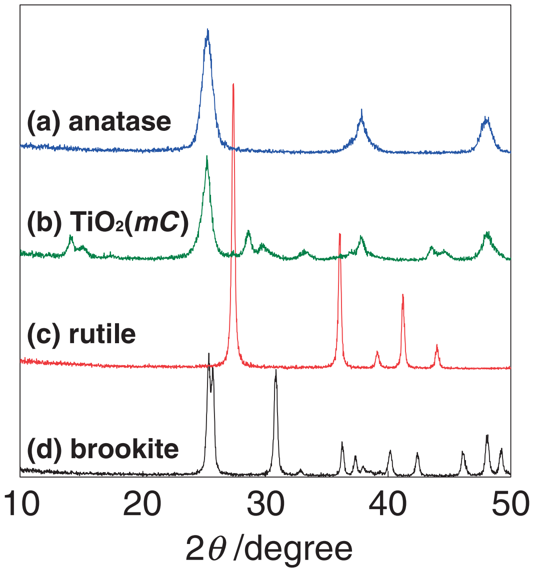


Figure 28. X-ray diffraction patterns of various polymorphs of titanium oxide prepared by the hydrothermal treatment of aqueous solutions of water-soluble titanium complexes at 200 °C for 24 h. (a) The TiO_2 (*anatase* type) is obtained starting from a titanium–peroxo–citrato complex at pH 6; the TiO_2 (*rutile* type), TiO_2 (*brookite* type), and TiO_2(*mC*) polymorphs are obtained starting from a titanium–peroxo–glycolato complex by adjusting the pH of the solution to (b) 1; (c) 6; and (d) 10, respectively.

It is interesting to discuss the reason why the three polymorphs of TiO_2 (*brookite*, *rutile* type and TiO_2(*mC*)) formed from aqueous solutions containing the same Ti–ga complex just by adjusting the solution to pH 10, 6, and 1, respectively. The formation of TiO_2 (*brookite* type) from Ti–ga was related to the inherent structure of the complex anion and its similarity to the brookite architecture,[27] which is shown in Figure 29. Figure 30 presents a possible scheme for TiO_2 (*brookite* type) formation from Ti–ga (complex **12**, Figure 14) under hydrothermal conditions. During heating, the anion **12** loses a "leaving" peroxo group to yield free oxygen. As shown in Figure 30a, the empty site in the coordination environment is then filled by the oxygen of a bridging oxo group and the oxygen atoms of an axial carboxy group to yield a dimer (Figure 30b) which can grow further as hydrolysis and decomposition of peroxo groups occur to produce stripes of $Ti_{4n}O_{14n+4}$ (Figure 30c). During the next step, the stripes are arranged into the brookite structure (Figure 30d) as a result of oxolation and, possibly, further hydrolysis. In contrast, at pH 6, while the peroxo group in **12** can be stabilized, the bridging oxo group would be protonated in this slightly acidic condition (Figure 31a), leading to formation of dimeric complex anions as shown in Figure 31b. These dimeric species cannot effectively build a brookite lattice, but they are suitable building blocks for the rutile lattice (Figures 31c and 31d). Although the explicit reason for the formation of TiO_2(*mC*) at pH 1 remains unclear, we[69] have argued that its synthesis is related to the possible appearance under relatively strong acidic conditions of intermediate protonated species such as $H_2Ti_3O_7$ and $H_2Ti_4O_9$ that subsequently lose water to yield TiO_2(*mC*) in a way similar to what has been discussed in Section **4.3.1.2**. It has been reported that the titania surface tends to adsorb

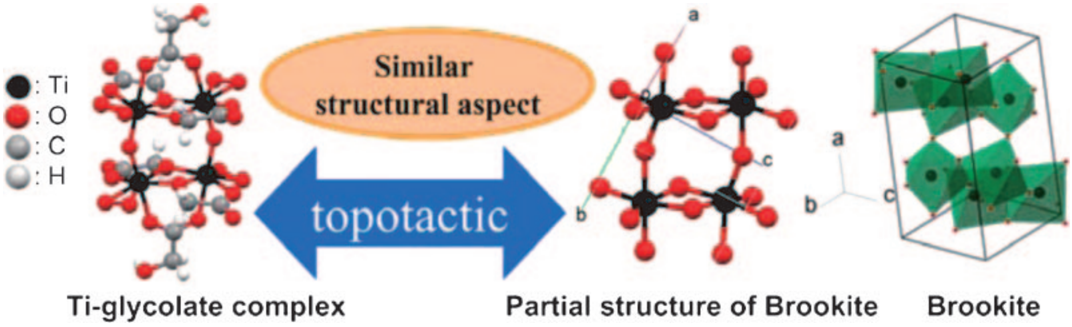


Figure 29. Resemblance between the structure of a titanium–peroxo–glycolato complex and that of TiO_2 (*brookite* type): (left) The structure of the complex, (right) the structure of TiO_2 (*brookite* type), and (middle) a partial view of Ti–O arrangements in TiO_2 (*brookite* type).

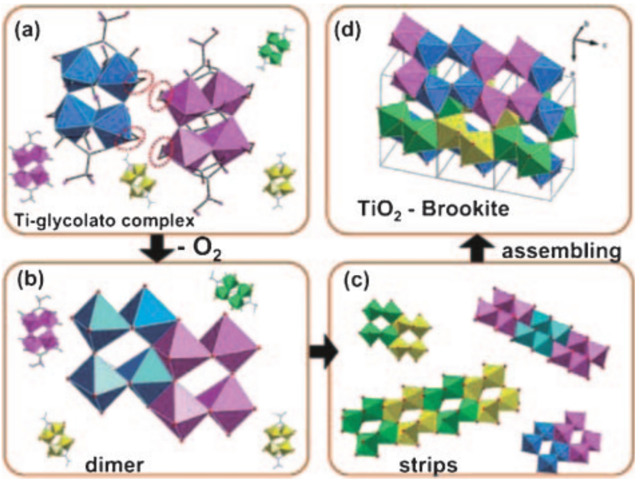


Figure 30. Possible mechanism of formation of TiO_2 (*brookite* type) under the hydrothermal treatment of a basic aqueous solution containing a titanium–peroxo–glycolato complex. (a → b) Removal of peroxo groups leading to formation of a "dimer," (b → c) consecutive oligomerization of "dimers," and (c → d) "self-assembling" of "oligomers" leading to formation of TiO_2 (*brookite* type).

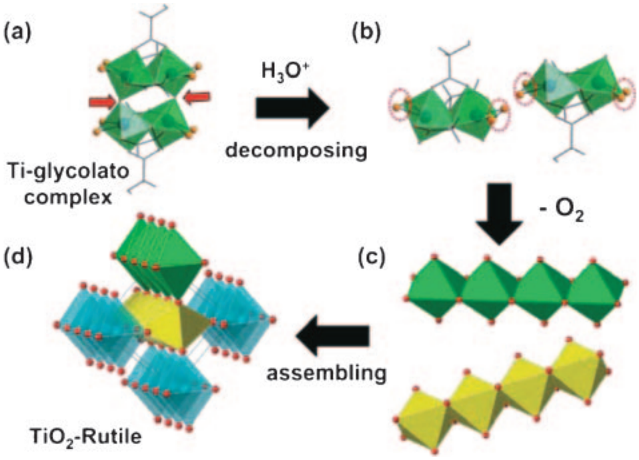


Figure 31. Possible mechanism of formation of TiO_2 (*rutile* type) under the hydrothermal treatment of an acidic aqueous solution containing titanium–peroxo–glycolato complex. (a → b) Decomposition of the complex resulting from attacks of hydrogen ions on the oxo group leading to the decomposed "dimer" fragments, (b → c) consecutive oligomerization of the "dimer-fragments," and (c → d) "self-assembling" of "oligomers" leading to formation of TiO_2 (*rutile* type).

protons below pH 3.5,[83,84] which in turn indicates that under the present hydrothermal conditions at pH 1, the nucleation process is presumably driven toward protonated species such as $H_2Ti_3O_7$ and $H_2Ti_4O_9$.

5. Summary and Concluding Remarks

Environmental concerns and the increasing significance of "green chemistry" synthetic strategies require utilization of new non-toxic precursors compatible with neutral water as a processing solvent. This objective was especially difficult to achieve for transition-metal ions in their highest oxidation state such as titanium, niobium, and tantalum due to the high susceptibility of these cations to hydrolysis.

In this review, a panel of known water-soluble titanium compounds was presented and their syntheses and structures were described to elucidate the underlying chemistry required for understanding their solubility in water. Typically such water-soluble titanium compounds include a central Ti atom chelated by a readily available hydroxy–carboxylic acid such as citric acid or amino–carboxylic acid such as H_4edta, which provide tight coordination forming a very stable five-membered ring composed of either Ti–O–C–C–O–Ti or Ti–O–C–C–N–Ti, respectively. Introduction of a peroxo group (O_2^{2-}) as an extra ligand into a given non-peroxo titanium complex is even more effective at increasing its solubility and stability in water, since the resulting overall negative charge of the complex molecule, induced by the introduction of $(O_2)^{2-}$, hinders subsequent hydrolysis and allows formation of a highly water-soluble salt (such as an ammonium salt).

Another important topic in this review is related to the environmentally benign synthesis of various titanium-containing oxides using water-soluble titanium compounds and water as a solvent. The new class of water-soluble titanium compounds proved to be handy precursors for highly selective synthesis of four polymorphs of nanocrystalline TiO_2, as well as for synthesis of a variety of titanium containing oxide materials including $BaTiO_3$, $Ba_{1-x}Sr_xO_3$, and $Bi_4Ti_3O_{12}$ using aqueous solution-based technologies.

The principles and underlying chemistry for solubilization of titanium in water described in this review can be applied to the design of other water-soluble compounds containing niobium and tantalum, which conventionally have been water incompatible.[85–100] The new generation of stable and water-soluble titanium, niobium, and tantalum precursors opens up multiple possibilities for environmentally benign synthesis of functional oxide materials containing these elements, in addition to development of new materials with superior functional properties using pure water as a process solvent.

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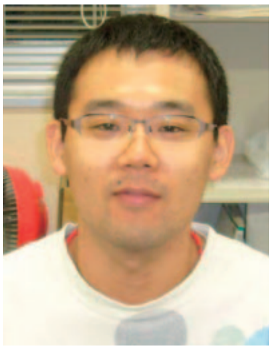

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