Inorg. Chem. **2004**, *43*, 6266–6273

Inorganic Chemistry

Article

pH-Dependent Isolations and Spectroscopic, Structural, and Thermal Studies of Titanium Citrate Complexes

Yuan-Fu Deng, Zhao-Hui Zhou,* and Hui-Lin Wan

Department of Chemistry and State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

Received March 25, 2004

Titanium(IV) citrate complexes $(NH_4)_2[Ti(H_2cit)_3]\cdot 3H_2O$ (**1**), $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti]\cdot 3H_2O$ (**2**), $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**), and $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti]\cdot 15H_2O$ (**4**) (H_4cit = citric acid) were isolated in pure form from the solutions of titanium(IV) citrate with various countercations. The isolated complexes were characterized by elemental analyses, IR spectra, and ^1H NMR and ^{13}C NMR spectra. The formation of titanium(IV) citrate complexes depends mainly on the pH of the solutions, that is, pH 1.0–2.8 for the formation of ammonium titanium(IV) citrate **1**, pH 2.5–3.5 for ammonium iron titanium(IV) citrate **2**, pH 2.8–4.0 for dibarium titanium(IV) citrate **3**, and pH 5.0–6.0 for ammonium barium titanium(IV) citrate **4**. X-ray structural analyses revealed that complexes **2**–**4** featured three different protonated forms of bidentate citrate anions that chelate to the titanium(IV) atom through their negatively charged α-alkoxyl and α-carboxyl oxygen atoms. This is consistent with the large downfield shifts of the ^{13}C NMR spectra for the carbon atoms bearing the α-alkoxyl and α-carboxyl groups. The typical coordination modes of the barium atoms in complexes **3** and **4** are six-coordinated, with three α-alkoxyl groups and three β-carboxyl groups of citrate ions. The strong hydrogen bonding between the β-carboxylic acid and the β-carboxyl groups [2.634(8) Å for complex **2**, 2.464(7) Å for complex **3**, and 2.467(7) Å for complex **4**] may be the key factor for the stabilization of the citrate complexes. The decomposition of complex **3** results in the formation of a pure dibarium titanate phase and **4** for the mixed phases of dibarium titanate and barium titanate at 1000 °C.

Introduction

The development of modern technologies with their appeal for miniaturization and increased performance of the applied materials has encouraged for more than several decades the search for techniques permitting much better and more versatile control over the composition, structure, and morphology of the produced inorganic materials than could be provided by the traditional reactions of solid-state synthesis.[1] This search gave rise to a broad variety of synthetic procedures, such as MOCVD,[2] sol−gel,[3] and molecular precursors,[4−7] permitting scientists to obtain the desired products under mild conditions.

Titanate-containing materials have an extremely broad range of industrial applications because of their characteristic ferroelectric, piezoelectric, and pyroelectric properties.[8] To prepare low grain size and chemical homogeneity powders of titanate materials, conscious efforts have been made and various molecular precursors have been used.[4,5] The titanium(IV) citrate route, also known as the Pechini process,[9] for preparing titanate materials with the general formulas $MTiO_3$ (M = Mg,[10] Ca,[11] Sr,[12] Ba,[13] or Pb[14]), $M_2Ti_2O_7$ (M = La or

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* Author to whom correspondence should be addressed. Tel: +86-592-2184531. Fax: +86-592-2183047. E-mail: zhzhou@xmu.edu.cn.

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10.1021/ic0496018 CCC: $27.50

Y),[15] and $BaTi_nO_{2n+1}$ ($n = 2-5$),[16] has received considerable interest because it circumvents the problem of preferential precipitation of titanium(IV) citrate complexes from aqueous media and leads to highly homogeneous and well-crystallized products. A detailed understanding of the speciation and the structure information by means of species isolation and structural characterization would be a quite useful approach for the subsequent establishment of solution species and the optimum preparative conditions. This could allow for better control of the purity and the properties of the resulting materials.[4] However, despite a wealth of available literature concerning the molecular constitution of titanium(IV) citrate precursors, aided by a wide range of physical techniques such as IR, NMR, and Raman spectroscopy,[12−26] a systematic understanding of the speciation behavior is lacking and the structure information related to the precursors is quite limited.[27]

We have reported the structural features of the acidic titanium(IV) citrate species in a previous communication.[27] As part of ongoing research, herein, the results of the pH-dependent species formation and transformation of the Ti(IV) $H_4cit \cdot H_2O$ system are presented. The isolations, spectroscopic and structural characterizations, and the thermal studies of titanium(IV) citrate complexes, $(NH_4)_2[Ti(H_2cit)_3] \cdot 3H_2O$ (**1**), $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti] \cdot 3H_2O$ (**2**), $Ba_2[Ti(H_2cit)(Hcit)_2] \cdot 8H_2O$ (**3**), $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti] \cdot 15H_2O$ (**4**), and $Ba[Ti(H_2cit)_3] \cdot 4H_2O$ (**5**), may provide new insight into the preparations of Ti-based ceramic materials using the citrate method. Moreover, a new structural model for the $[BaTi(H_2cit)_3]$ species, inferred from the relevant crystal structures and spectroscopic data, is proposed.

Experimental Section

All of the experiments were carried out in the open air. All of the chemicals were analytical reagents and were used without further purification. Nanopure-quality water was used throughout this work.

Preparation of $(NH_4)_2[Ti(H_2cit)_3] \cdot 3H_2O$ (1). The pH of the solution containing titanium(IV) tetrachloride (1.9 g, 10 mmol) and citric acid monohydrate (6.3 g, 30 mmol) was adjusted to 2.0 by the slow addition of dilute ammonia. After the solution was stirred continuously for 30 min, the microcrystalline material (**1**) that separated was collected and recrystallized from hot water. The yield of purified **1** was 5.7 g (80%). C, H, and N elemental analyses for $C_{18}H_{32}O_{24}N_2Ti$ follow. Found (calcd): C, 30.6 (30.5); H, 4.2 (4.6); N, 3.7 (3.7). IR (KBr): $\nu_{(COOH)}$ 1708.5$_{vs}$; $\nu_{as(COO)}$ 1593.6$_s$; $\nu_{s(COO)}$ 1450.9$_m$, 1369.2$_s$, 1303.1$_s$; $\nu_{(Ti-O)}$ 661.5$_m$, 558.5$_s$. ^1H NMR δ_H (500 MHz, D_2O): 2.947 (d, $J = 13.5$ Hz, CH_2), 2.723 (d, $J = 13.5$ Hz, CH_2). ^{13}C NMR δ_C (D_2O): 188.6 $(CO_2)_{\alpha-carboxyl}$, 176.5 $(CO_2)_{\beta-carboxyl}$, 90.9 $(C-O)_{\alpha-alkoxyl}$, 45.5 $(CH_2)_{methylene}$.

Preparation of $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti] \cdot 3H_2O$ (2). Iron powder (0.36 g, 6 mmol) was slowly added to a continuously stirred solution containing titanium(IV) tetrachloride (1.9 g, 10 mmol) and citric acid monohydrate (6.3 g, 30 mmol). The resulting reaction mixture was adjusted to pH 2.8 with dilute ammonia and was filtered. After the solution was kept in a refrigerator for approximately 1 week, colorless crystals were obtained, washed with water, and dried in air at room temperature to give **2** in a 5.6 g (72%) yield. C, H, and N elemental analyses for $FeTi_2N_5C_{36}H_{71}O_{51}$ follow. Found (calcd): C, 27.9 (28.0); H, 4.7 (4.6); N, 4.3 (4.5). IR (KBr): $\nu_{(COOH)}$ 1711.8$_{vs}$; $\nu_{as(COO)}$ 1626.8$_m$, 1596.6$_s$; $\nu_{s(COO)}$ 1445.5$_m$, 1384.6$_s$, 1305.6$_s$; $\nu_{(Ti-O)}$ 637.2$_m$, 563.0$_s$. The NMR experiments show broad bands due to the paramagnetic effect of the ferrous ion.

Preparation of $Ba_2[Ti(H_2cit)(Hcit)_2] \cdot 8H_2O$ (3). Barium carbonate (4.0 g, 20 mmol) was added slowly to a continuously stirred solution containing titanium(IV) tetrachloride (1.9 g, 10 mmol) and citric acid monohydrate (6.3 g, 10 mmol). The mixture was adjusted to pH 3.5 with ammonia and filtered, then it was concentrated and kept in a refrigerator for several days. The product was filtered, washed with water, and dried in air at room temperature to give colorless crystals. The yield of purified **3** was 7.2 g (70%). C and H elemental analyses for $Ba_2TiN_2C_{18}H_{34}O_{29}$ follow. Found (calcd): C, 21.0 (20.9); H, 3.2 (3.1). IR (KBr): $\nu_{(COOH)}$ 1723.8$_s$; $\nu_{as(COO)}$ 1635.6$_{vs}$, 1557.3$_m$; $\nu_{s(COO)}$ 1401.2$_s$, 1343.7$_s$, 1303.3$_m$; $\nu_{(Ti-O)}$ 629.7$_m$, 557.5$_m$. ^1H NMR δ_H (500 MHz, D_2O): 2.956 (d, $J = 14.5$ Hz, CH_2), 2.723 (d, $J = 14.5$ Hz, CH_2). ^{13}C NMR δ_C (D_2O): 189.5 $(CO_2)_{\alpha-carboxyl}$, 178.2 $(CO_2)_{\beta-carboxyl}$, 92.0 $(C-O)_{\alpha-alkoxyl}$, 46.8 $(CH_2)_{methylene}$.

Preparation of $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti] \cdot 15H_2O$ (4). Barium carbonate (3.0 g, 15 mmol) was added slowly to the continuously stirred aqueous solution containing titanium(IV) tetrachloride (1.9 g, 10 mmol) and citric acid monohydrate (6.3 g, 30 mmol). The mixture was adjusted to pH 6.0 with ammonia and filtered, and then it was kept in a refrigerator for approximately 1 month. The product was filtered, washed with deionized water, and dried in air at room temperature to give colorless crystals. The yield of purified **4** was 5.7 g (56%). C, H, and N elemental analyses for $Ba_3Ti_2C_{36}H_{79}O_{54}N_7$ follow. Found (calcd): C, 20.8 (21.2); H, 4.5 (4.2); N, 5.0 (4.8). IR (KBr): $\nu_{as(COO)}$ 1628.8$_s$, 1572.0$_{vs}$; $\nu_{s(COO)}$

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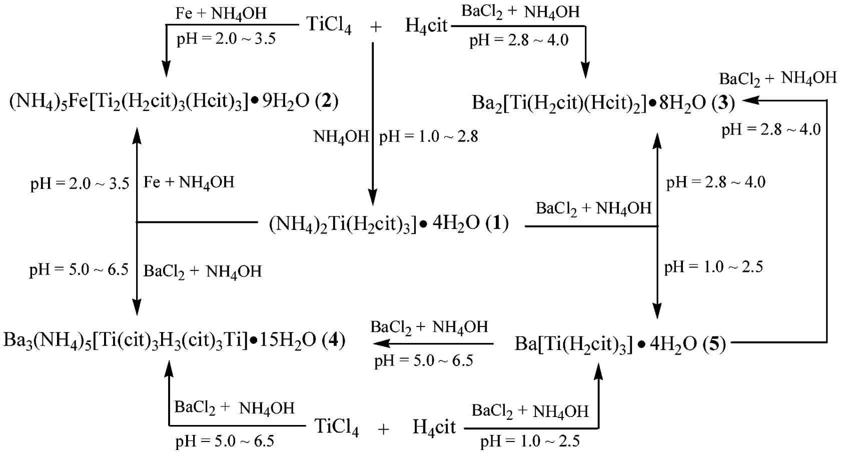
Scheme 1. Syntheses and Transformations of Titanium(IV) Citrate Complexes



1402.1_{vs}, 1344.8_{m}; $\nu_{(Ti-O)}$ 645.6_{m}, 538.7_{m}. ^{1}H NMR δ_H (500 MHz, D_2O): 2.861 (d, $J = 6.5$ Hz, CH_2), 2.491 (d, $J = 6.5$ Hz, CH_2). ^{13}C NMR δ_C (D_2O): 190.1 $(CO_2)_{\alpha-carboxyl}$, 180.4 $(CO_2)_{\beta-carboxyl}$, 92.3 $(C-O)_{\alpha-alkoxyl}$, 47.9 $(CH_2)_{methylene}$.

Preparation of $Ba[Ti(H_2cit)_3]\cdot 4H_2O$ (5). The preparation of **5** followed the previously reported procedures with some modifications.[13] Barium chloride dihydrate (2.5 g, 10 mmol) was added slowly to the continuously stirred solution containing titanium(IV) tetrachloride (2.0 g, 10 mmol) and citric acid monohydrate (6.3 g, 30 mmol). The pH of the mixture was increased with ammonia to 2.0. After the solution was stirred continuously for 30 min, a large quantity of white microcrystalline product was collected and recrystallized from hot water. The product was washed with water and dried in air at 30 °C to give white microcrystallines. The yield of purified **5** was 6.2 g (75%). IR and NMR spectra and elemental analysis identified **5** as $Ba[Ti(H_2cit)_3]\cdot 4H_2O$.[27]

Transformation of 1 to 2. $(NH_4)_2[Ti(H_2cit)_3]\cdot 3H_2O$ (**1**) (2.1 g, 3 mmol) was dissolved in warm water. In a separate flask, iron powder (0.17 g, 3.0 mmol) was dissolved in 5 mL of 2 M HCl and added to the solution of **1**. The mixture was adjusted to pH 2.8 with ammonia and filtered, and then cooled. The crystals that separated were colorless crystals of **2** (1.6 g, 70%). Positive identification of the crystalline material as complex **2** came from the IR spectrum and the X-ray unit-cell determinations carried out by single-crystal structural analysis.

Transformations of 1 to 3 and 4. To the aqueous solution of $(NH_4)_2[Ti(H_2cit)_3]\cdot 3H_2O$ (**1**) (2.1 g, 3 mmol) was added barium chloride dihydrate (1.5 g, 6 mmol). Dilute ammonia was added to bring the solution pH to 3.5. The solution was cooled for several days to deposit colorless crystals of **3** (2.3 g, 75%). The IR spectrum of the product was identical to that of **3**.

In a similar procedure, when barium chloride dihydrate (0.98 g, 4 mmol) was added and the pH adjusted to 5.5, **1** was converted into **4** in 54% (1.6 g) yield. The IR spectrum of the product was identical to that of **4**.

Transformation of 1 to 5. $(NH_4)_2[Ti(H_2cit)_3]\cdot 3H_2O$ (**1**) (2.1 g, 3 mmol) was dissolved in water, and the pH was altered to 2.0 by the addition of 2 M HCl. Barium chloride dihydrate (0.75 g, 3 mmol) was added; the pH was kept at 2.0. The water was partially removed by evaporation to produce a solid material **5** that was recrystallized from water in 70% (1.8 g) yield. The IR spectrum of the product was identical to that of **5**.

Transformations of 5 to 3 and 4. $Ba[Ti(H_2cit)_3]\cdot 4H_2O$ (**5**) (2.5 g, 3 mmol) was dissolved in 50 mL of warm water and kept at pH 1.5. In a separate flask, barium chloride dihydrate (0.75 g, 3 mmol) was dissolved in 10 mL of water and added to the solution of **5**. Dilute ammonia was added dropwise to the solution to increase the pH to 3.5. The solution was concentrated and kept refrigerated for several days. The product was collected, washed with water several times, and dried in air at room temperature to give colorless crystals of **3** (2.1 g, 70%). The IR spectrum of the product was identical to that of **3**.

The same procedure above was followed for the transformation of **5** to **4**, except that barium chloride dihydrate (0.37 g, 1.5 mmol) was added and the pH was adjusted to 5.5. Complex **5** was converted into **4** in 60% (1.7 g) yield. The IR spectrum of the product was identical to that of **4**.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates using a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed using EA 1110 elemental analyzers. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian UNITY 500 NMR spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal reference. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were carried out using a Netzsch STA 409EP thermal analyzer with a heating rate 10 °C/min in flowing N_2. Diffraction patterns were obtained using a Rigaku D/Max-C powder diffractometer using Cu Kα radiation at 40 kV and 30 mA at a scan rate of 4°/min.

X-ray Structure Determination. Crystals of **2**, **3**, or **4** in oil were measured on a Bruker Smart Apex CCD area detector diffractometer with graphite monochromate Mo Kα radiation ($\lambda = 0.71\,073$ Å) at 296 K. The data were corrected for Lorentz and polarization effects. An absorption correction was applied using the SADABS program.[28a] The structures were primarily solved by the WinGX program[28b] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all of the non-hydrogen atoms with SHELX-97.[29] Hydrogen atoms, except those of the disordered ammonium ions, were located from a difference Fourier map and refined isotropically.

Results and Discussions

Synthesis. The syntheses of titanium(IV) citrate complexes and their transformations are shown in Scheme 1, which illustrates the sensitivity of the reaction toward pH in aqueous solutions containing titanium(IV) ions and citric acid. The molar ratio of titanium(IV) ions and citric acid does not seem

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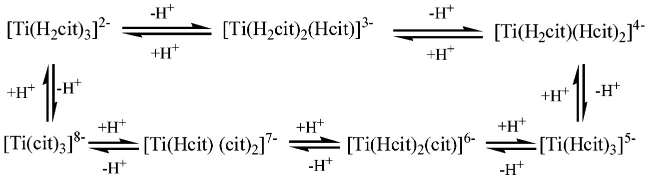
Scheme 2. Possible Species of Titanium(IV) Citrate Anions and Their Transformations in the Ti Citrate System



to be crucial for the formation of these species. Control of the high ratio of citric acid and titanium tetrachloride (3:1) in the synthetic procedures will drive the reaction completely and lead to the isolation of titanium(IV) citrate complexes in high yield. When a pH value of 1.0−2.5 was maintained, the solutions containing titanium(IV) ions, barium ions, and citric acid deposited **5** in 75% yield; in contrast, control pH values of 2.8−4.0 and 5.0−6.5 yielded **3** and **4**, respectively. Under the conditions with pH > 6.5, no titanium(IV) citrate complexes were isolated. Alternately, complexes **3**−**5** were prepared by the reactions of barium chloride with $(NH_4)_2[Ti(H_2cit)_3]\cdot 3H_2O$ (**1**). The transformations also revealed their remarkable sensitivity to pH control; **1** gave **5** at pH 2.0 but **3** and **4** at pH 3.5 and 5.5, respectively. Furthermore, **5** was converted to **3** and **4** at pH 3.5 and 5.5, respectively. These observations are a clear indication that the formations of titanium(IV) citrate complexes are typically pH-dependent reaction patterns.

Compared with the isolated complexes in the vanadium(V) $H_4cit\cdot H_2O$ system,[30−32] Scheme 2 shows that the proposed titanium(IV) citrate species existed in aqueous solutions at different pH values. The proposed titanium citrate species are different from those in the solutions of titanium(IV) and citric acid that were previously reported,[33] such as $[TiO(Hcit)]^-$, $[TiO(Hcit)_2]^{4-}$, $[TiO(H_3cit)]^+$, and $[TiO(H_3cit)_2]$. In our case, in the presence of titanium(IV) tetrachloride and citric acid at different pH levels, five complexes were isolated in pure crystalline forms. X-ray diffraction studies showed that two β-carboxyl groups were deprotonated in **3**. The anion in this complex corresponds to the quadrivalence anion in Scheme 2. However, none of the anionic species in Scheme 2 corresponds to the anions in **2** and **4**. The half-deprotonation of the citrate ligands in **2** and **4** increases the complexity of the titanium(IV) citrate system; that is, the titanium(IV) citrate anionic species may increase because of the formations of half-deprotonated citrate ligands.

It should be emphasized that, based on the available structures of the five titanium(IV) citrate complexes, $K_2Mg[Ti(H_2cit)_3]\cdot 12H_2O$, $(NH_4)_2Mg[Ti(H_2cit)_3]\cdot 12H_2O$,[27] $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti]\cdot 3H_2O$ (**2**), $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**), and $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3]\cdot 15H_2O$ (**4**) in the overall pH range of 1.0−6.5, the basic structural features of the titanium citrate complexes involving the $Ti^{IV}O_6$ core and the bidentate coordination mode of citrate do not change. All of the complexes are soluble in aqueous solutions, especially in hot water, and slightly soluble in organic solvents, such as ethanol and acetone.

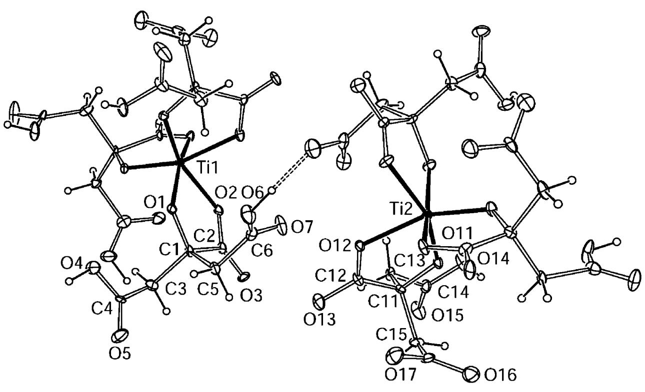


Figure 1. ORTEP plot of the $[Ti(H_2cit)_3(Hcit)_3Ti]^{7-}$ anion in **2** at the 20% probability level.

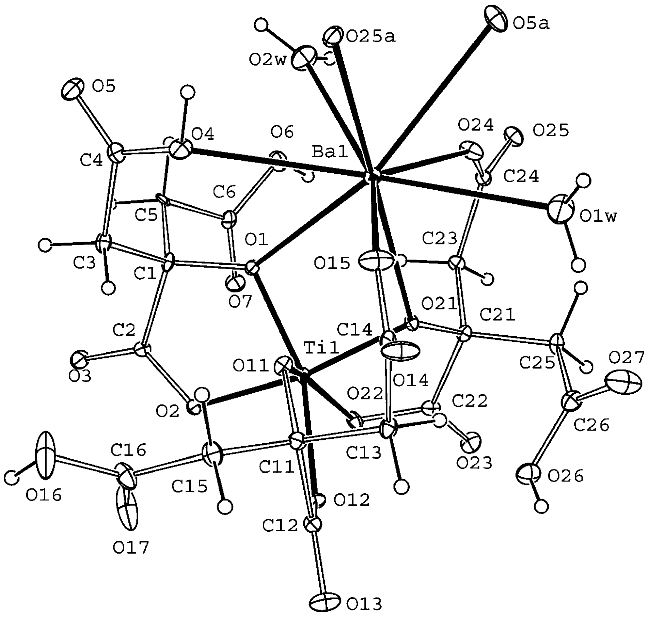


Figure 2. ORTEP plot of the $[BaTi(H_2cit)(Hcit)_2]^{2-}$ anion in **3** at the 20% probability level.

Description of the Crystal Structures. The crystal structures of the titanium(IV) citrate complexes **2**−**4** were determined by single-crystal X-ray crystallography, and the ORTEP diagrams and pertinent crystal data are given in Figures 1−3 and in Tables 1 and 2, respectively. While the data will be discussed later, the uncoordinated protonated β-carboxyl groups are strongly hydrogen bonded to the deprotonated β-carboxyl groups of an adjacent molecule, resulting in the polymeric structures of complexes **2**−**4**. It is most significant that **4** is a centrosymmetric dimer formed through the linear hydrogen bonding of a β-carboxylic acid to a β-carboxyl group [O6···O6^i = 2.478(2) Å; O−H1−O = 180.0(3)°]. The closest analogies are the crystal structures

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Table 1. Crystal Data Summaries of Intensity Data Collections and Structure Refinements for $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti]\cdot 3H_2O$ (**2**), $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**), and $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti]\cdot 15H_2O$ (**4**)

empirical formula	$C_{36}H_{71}O_{51}N_5FeTi_2$	$C_{18}H_{34}O_{29}Ba_2Ti$	$C_{36}H_{85}O_{57}N_7Ba_3Ti_2$
formula weight	1541.63	1035.02	2035.93
crystal color	colorless		
crystal system	hexagonal	monoclinic	hexagonal
cell constants	$a = 15.4413(7)$ Å $c = 7.6252(3)$ Å $V = 1574.52(9)$ Å^3	$a = 11.1605(6)$ Å $b = 10.4522(6)$ Å $c = 21.816(2)$ Å $\beta = 91.311(1)°$ $V = 3127.3(5)$ Å^3	$a = 14.7993(6)$ Å $c = 9.4457(4)$ Å $V = 1791.6(1)$ Å^3
space group	$P\bar{3}$	$P2_1/c$	$P\bar{3}$
formula units/unit cell	1	4	1
D_{calc} (g cm^{-3})	1.626	2.198	1.887
μ (mm^{-1})	0.60	2.86	1.96
max and min transmission	0.9156 and 0.8897	0.8943 and 0.5989	0.6952 and 0.6196
F_{000}	800	2024	1018
diffractometer		Smart Apex CCD	
radiation		Mo Kα ($\lambda = 0.7107$ Å)	
reflections collected/unique	18587/5042 [R(int) = 0.0731]	18516/7256 [R(int) = 0.0636]	20179/2866 [R(int) = 0.0235]
data/restraints/parameters	5042/28/333	7256/28/511	2866/13/189
θ range (deg)	1.52−28.49	1.83−28.30	2.16−28.34
GOF on F^2	0.988	1.100	1.099
R1, wR2 [$I > 2\sigma(I)$]^a	0.052, 0.124	0.060, 0.110	0.043, 0.117
R1, wR2 (all data)^a	0.062, 0.130	0.085, 0.114	0.045, 0.119
largest diff. peak and hole (e Å^{-3})	0.911, −0.414	1.882, −1.870	1.460, −1.799

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

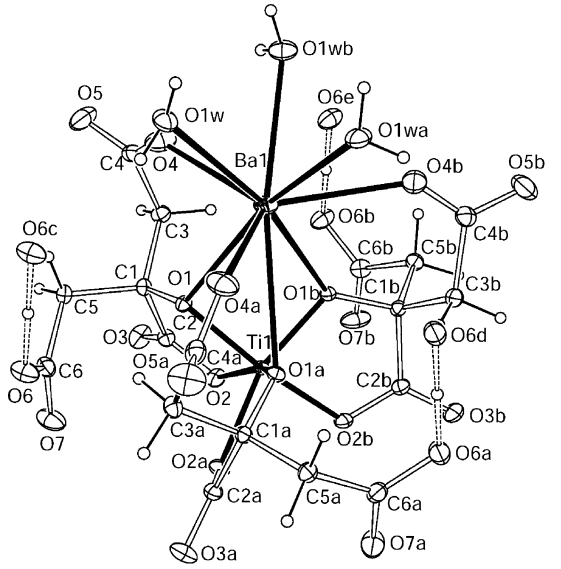

Figure 3. ORTEP plot of the barium titanium(IV) citrate anion in **4** at the 20% probability level.

of potassium tungstate nitrilotriacetate and peroxo citrato molybdate, both of which show intramolecular symmetrical hydrogen-bonded O−H−O linkages [2.54(2) and 2.497(5) Å, respectively].[35,36] The hydrogen bonding in **4** should be extraordinarily strong because of its intermolecular mode[37] and intramolecular hydrogen-bonding distance [O···O = 2.636(7) Å] in salicylic acid[36] and the ordinary OH bond of 0.96 Å. This, in turn, reveals the extraordinary stability of dimer **4**, which is also experimentally demonstrated by its formation and deposition from **3** and **5** in an aqueous solution with a pH value of 5.0−6.5.

The structural features in which the complexes differ from one another are (a) the protonation of the citrate ligands bound to the titanium atom and (b) the overall charge of the complexes' anionic assembly. However, the titanium atom in complexes **2**−**4** is six-coordinated in an octahedral environment by three α-alkoxyl groups and three α-carboxyl groups derived from three citrate ligands. This geometry is similar to that found in $M_2Mg[Ti(H_2cit)_3]\cdot 12H_2O$ ($M = K^+$ or NH_4^+)[27] but differs from those of the seven-coordinated peroxo titanium(IV) citrate complexes, such as $(NH_4)_8[Ti(O_2)(cit)]_4\cdot 8H_2O$,[38] $(NH_4)_4[Ti(O_2)(cit)]_2\cdot 2H_2O$,[39] and $Ba_2(NH_4)_2[Ti(O_2)_4(Hcit)_2(cit)_2]\cdot 10H_2O$.[40] The coordination mode of the titanium atom is a contrast to the previous models inferred from spectroscopic data, in which the titanium atom is coordinated either by three α-alkoxyl groups and three β-carboxyl groups[13] or by three α-alkoxyl groups, one α-carboxyl group, and two β-carboxylic groups.[18,19] Bidentate coordination of the citrate ligand through its α-alkoxyl group and α-carboxyl group with the titanium atom is independent of the pH variations between 1.0 and 6.5. A comparable result is found in vanadate(V) citrate complexes, such as $K_2[V_2O_4(H_2cit)_2]\cdot 4H_2O$, $(NH_4)_2[V_2O_4(H_2cit)_2]\cdot 2H_2O$,[30] $Na_2K_2[V_2O_4(Hcit)_2]\cdot 9H_2O$, $K_4[V_2O_4(Hcit)_2]\cdot 4H_2O$,[31] $(NH_4)_4[V_2O_4(Hcit)_2]\cdot 4H_2O$, $K_2(NH_4)_4[V_2O_4(cit)_2]\cdot 6H_2O$, and $(NH_4)_6[V_2O_4(cit)_2]\cdot 6H_2O$.[32]

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $(NH_4)_5[Fe(H_2O)_6][Ti(H_2cit)_3(Hcit)_3Ti]\cdot 3H_2O$ (**2**), $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**), and $Ba_3(NH_4)_7[Ti(cit)_3H_3(cit)_3Ti]\cdot 15H_2O$ (**4**)[a]

2	Ti(1)−O(1)	1.876(4)	Ti(1)−O(2)	2.032(4)		
	Ti(2)−O(11)	1.835(4)	Ti(2)−O(12)	2.037(4)		
	Fe(1)−O(1w)	2.056(4)	Fe(1)−O(2w)	2.135(4)		
	O(1)−Ti(1)−O(1a)	95.7(2)	O(1)−Ti(1)−O(2)	78.6(2)		
	O(1)−Ti(1)−O(2a)	156.5(2)	O(1)−Ti(1)−O(2b)	107.5(2)		
	O(2)−Ti(1)−O(2b)	81.4(2)	O(11)−Ti(2)−O(12)	78.6(2)		
	O(11)−Ti(2)−O(11c)	95.8(2)	O(11)−Ti(2)−O(12c)	156.1(2)		
	O(11)−Ti(2)−O(12d)	107.9(2)	O(12)−Ti(2)−O(12d)	81.0(2)		
3	Ti(1)−O(1)	1.883(4)	Ti(1)−O(2)	2.013(4)		
	Ti(1)−O(11)	1.848(3)	Ti(1)−O(12)	2.000(4)		
	Ti(1)−O(21)	1.874(4)	Ti(1)−O(22)	2.007(4)		
	Ba(1)−O(1)	2.926(4)	Ba(1)−O(4)	2.879(4)		
	Ba(1)−O(5a)	2.939(4)	Ba(1)−O(11)	3.108(4)		
	Ba(1)−O(15)	2.622(5)	Ba(1)−O(21)	2.761(3)		
	Ba(1)−O(24)	2.685(4)	Ba(1)−O(25a)	2.856(4)		
	Ba(1)−O(1w)	2.876(6)	Ba(1)−O(2w)	2.774(4)		
	O(1)−Ti(1)−O(2)	78.4(1)	O(1)−Ti(1)−O(11)	90.5(1)		
	O(1)−Ti(1)−O(12)	113.3(1)	O(1)−Ti(1)−O(21)	88.3(1)		
	O(1)−Ti(1)−O(22)	154.9(2)	O(2)−Ti(1)−O(11)	151.33(1)		
	O(2)−Ti(1)−O(12)	81.4(1)	O(2)−Ti(1)−O(21)	113.8(1)		
	O(2)−Ti(1)−O(22)	87.1(1)	O(11)−Ti(1)−O(12)	78.9(1)		
	O(11)−Ti(1)−O(21)	92.0(1)	O(11)−Ti(1)−(22)	111.2(1)		
	O(12)−Ti(1)−O(21)	156.3(1)	O(12)−Ti(1)−O(22)	84.2(1)		
	O(21)−Ti(1)−O(22)	78.7(1)				
4	Ti(1)−O(1)	1.871(2)	Ti(1)−O(2)	2.026(2)		
	Ba(1)−O(1)	2.992(2)	Ba(1)−O(4)	2.747(3)		
	Ba(1)−O(1W)	2.797(3)				
	O(1)−Ti(1)−O(2)	79.18(9)	O(1)−Ti(1)−O(1a)	92.82(9)		
	O(1)−Ti(1)−O(2a)	105.55(9)	O(1)−Ti(1)−O(2b)	160.23(9)		
	O(2)−Ti(1)−O(2a)	85.4(1)				
hydrogen bondings						
2	O4···O3(e)	2.619(6)	158(4)	O6···O17(c)	2.634(8)	173(4)
	O14···O13(f)	2.601(6)	151(4)			
3	O4···O24(a)	2.482(6)	175(4)	O6···O3(b)	2.649(6)	168(5)
	O26···O14(c)	2.552(6)	157(4)			
4	O6···O6(c)	2.478(2)	180.0(3)			

[a] Symmetric transformation for **2**: (a) $-y, x - y - 1, z$; (b) $-x + y + 1, -x, z$; (c) $-y, x - y, z$; (d) $-x + y, -x, z$; (e) $x, y, -1 + z$; (f) $x, y, 1 + z$. Symmetric transformation for **3**: (a) $-x - 1, y + {}^1/_2, -z + {}^1/_2$; (b) $-x, y - {}^1/_2, -z + {}^1/_2$; (c) $-x - 1, -y, -z$. Symmetric transformation for **4**: (a) $-y + 1, x - y, z$; (b) $-x + y + 1, -x + 1, z$; (c) $1 - x, -y, 1 - z$.

The six apexes around the iron atom in **2** are completed by six water molecules, and the geometry of the iron atom is in a normal octahedron. The two barium atoms in complexes **3** and **4** show two coordination modes. It should be mentioned that, despite the difference of the coordination number (10-coordination in **3** and 9-coordination in **4**), the Ba1 atoms (as shown in Figures 2 and 3, respectively) are hexacoordinated by three α-alkoxyl groups and three β-carboxyl groups in a six-member ring. The other four coordination sites of the Ba1 atom in **3** are occupied by two water molecules and two β-carboxyl groups from the other citrate ligands, and the other three coordination sites of the Ba1 atom in **4** are occupied with three water molecules.

Compared with those of other titanium(IV) citrate complexes, the average $Ti-O_{\alpha-\mathrm{alkoxyl}}$ bond distances [1.856(4) Å for **2**, 1.868(3) Å for **3**, and 1.871(2) Å for **4**] are similar to those found in related titanium citrate complexes, such as $K_2Mg[Ti(H_2cit)_3]\cdot 12H_2O$ [1.865(1) Å] and $(NH_4)_2Mg[Ti(H_2cit)_3]\cdot 12H_2O$ [1.866(2) Å][27] or titanium lactate complex $(NH_4)_2[Ti(lact)_3]$ [1.848(5) Å][41] (H_2lact = lactic acid), but are much shorter than those found in $(NH_4)_8[Ti(O_2)(cit)]_4\cdot 8H_2O$ [2.085(1) Å],[38] $(NH_4)_4[Ti(O_2)(cit)]_2\cdot 2H_2O$ [2.054(2) Å],[39] and $Ba_2(NH_4)_2[Ti(O_2)_4(Hcit)_2(cit)_2]\cdot 10H_2O$ [2.027(3) Å].[40] The average $Ti-O_{\alpha-\mathrm{carboxyl}}$ bond distances [2.034(4) Å for **2**, 2.007(4) Å for **3**, and 2.026(3) Å for **4**] are normal, with the distances being similar to those in the above titanium(IV) complexes. The average Ba−O bond distances [2.838(5) Å for Ba1 and 2.806(4) Å for Ba2 in **3**; 2.845(3) Å for Ba1 and 2.87(1) Å for Ba2 in **4**] are comparable with those found in complexes $Ba_2(NH_4)_2[Ti(O_2)_4(Hcit)_2(cit)_2]\cdot 10H_2O$ [2.823(3) Å][40] and $Ba_4[TiO(C_2O_4)_2]_4\cdot 20H_2O$ [2.82(1) and 2.87(1) Å].[42]

Solution NMR Spectroscopy. Due to the obvious dissociation when the compounds were dissolved in H_2O (D_2O), the ^{13}C NMR spectra of **1**, **3**, **4**, and **5** showed two sets of resonances, which can be attributed to the bound citrate in the titanium citrate complexes and the decomposed free citrate ligand. Figure 4 illustrates the ^{13}C NMR spectra of **1** taken after 1, 24, and 66 h, which displays that the dissociation of **1** changes with time. Specifically, the intensities of the free citrate resonances increased with time, whereas the intensity of those peaks belonging to the

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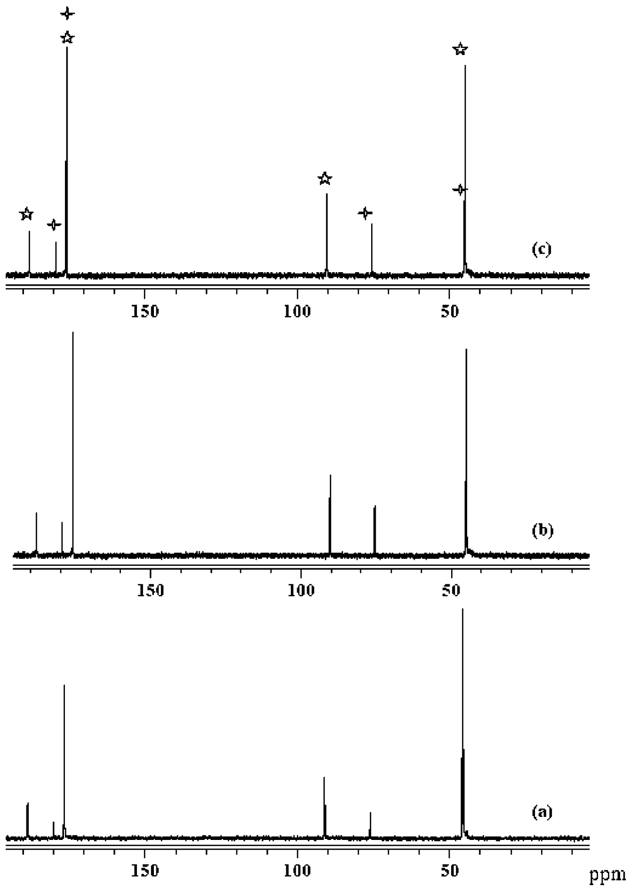

Figure 4. ^{13}C NMR spectrum of a 0.2 M solution of **1** in D_2O after (a) 1 h, (b) 24 h, and (c) 66 h, following the dissolution of the complex. Free citrate (+). Coordinated titanium citrate complex (☆).

coordinated titanium citrate complex decreased gradually. Complex **1** shows large downfield shifts of some ^{13}C resonances via coordination. This is compared with the corresponding carbons in K_3Hcit at a similar pH 3.4 [^{13}C NMR δ_C (D_2O): 180.0 $(CO_2)_{\alpha-\mathrm{carboxyl}}$, 176.3 $(CO_2)_{\beta-\mathrm{carboxyl}}$, 76.1 $(C-O)_{\alpha-\mathrm{hydroxyl}}$, 46.0 $(CH_2)_{\mathrm{methylene}}$]. The shifts of the α-alkoxyl carbon ($\Delta\delta$ 14.8 ppm) at 90.9 ppm and the α-carboxyl carbon ($\Delta\delta$ 8.6 ppm) at 188.6 ppm indicate that the α-alkoxyl and α-carboxyl groups in citric acid coordinate to the titanium atom simultaneously. A small shift ($\Delta\delta$ 0.2 ppm) is observed for the uncoordinated β-carboxyl groups. This observation is in agreement with the conclusion derived from the X-ray crystal structure. The ^{1}H NMR spectrum of complex **1** shows two groups of sharp AB quartets for methylene protons, which corroborates the idea of the dissociation of the titanium(IV) citrate complex in aqueous solution. The ^{13}C NMR and ^{1}H NMR spectra of **3**−**5** resembled that of complex **1**. Large downfield shifts of the α-alkoxyl ($\Delta\delta$ 14.8, 14.4, and 14.7 ppm) and α-carboxyl ($\Delta\delta$ 7.4, 6.4, and 8.3 ppm) carbons related to the free citrate are observed for **3**, **4**, and **5**, respectively. The similarities of the NMR spectra of the isolated titanium(IV) citrate complexes suggest that the coordination mode of the citrate is similar not only in the solid state but also in the solution.

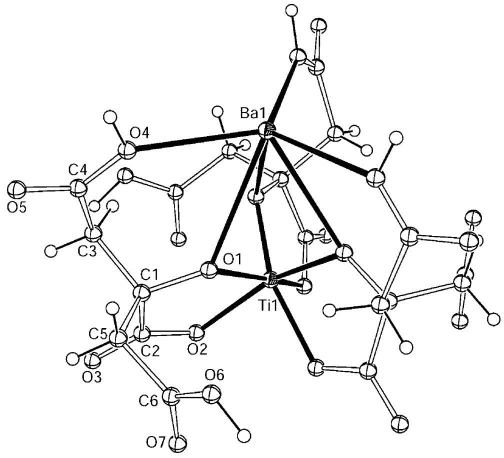

Figure 5. Proposed model for the structure of $[BaTi(H_2cit)_3]$.

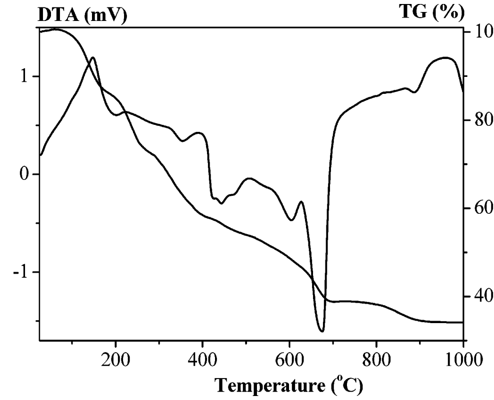

Figure 6. TG and DTA data for $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**) with a heating rate of 10 °C/min.

Proposed Structural Model for $[BaTi(H_2cit)_3]$. On the basis of the $Ti^{IV}O_6$ core, which is independent of the pH variation, and the basic feature of the barium atoms (six-coordinated by three negatively charged α-alkoxyl groups and three β-carboxyl groups of the citrate ligands) in complexes **3** and **4**, Figure 5 shows the proposed model for the structure of $[BaTi(H_2cit)_3]$, which displays a six-coordinated titanium center, and the salient feature of the citric acid ligand is a tridentate citrate anion that coordinates to the titanium and barium atoms through its negatively charged α-alkoxyl, α-carboxyl, and β-carboxylic acid groups. The deprotonated alcoholic oxygen atom (O1) and the other oxygen atom (O2) from the α-carboxyl group build up a fused five-member chelated ring, such as Ti1−O1−C1−C2−O2. Furthermore, the deprotonated alcoholic oxygen atom (O1) and the other oxygen atom from the β-carboxyl group (O4) further build up a fused six-member chelated ring with the barium atom, such as Ba1−O1−C1−C3−C4−O4. This coordination mode of the citrate ligand provides the maximum stability for $[BaTi(H_2cit)_3]$, which is an important precursor for the preparation of barium titanate.

Thermal Studies. The TG analysis and DTA of complexes **3** and **4** are treated in N_2 with a heating rate of 10 °C/min in the temperature range of 25−1000 °C. Figure 6 displays the results of the differential thermal analysis (DTA) and thermogravimetric (TG) analysis for $Ba_2[Ti(H_2cit)(Hcit)_2]\cdot 8H_2O$ (**3**). The first decomposition in complex **3**, occurring at 148 °C, is associated with the eight crystallized water molecules and is followed by the thermal decomposition of the dehydrated $Ba_2[Ti(H_2cit)(Hcit)_2]$ in the temperature range of 150−700 °C. The DTA in this temperature range shows five events at 223, 338, 446, 604, and 676 °C. Another thermal event was observed at ∼900 °C without weight loss, which is probably the transformation of orthorhombic Ba_2TiO_4 to monoclinic Ba_2TiO_4.[43] The powder of **3**, annealed in air at 1000 °C, had XRD patterns typical for the well-crystallized monoclinic Ba_2TiO_4 phase (ICSD #2625). Complex **4** also undergoes several decomposition steps. The loss of H_2O molecules occurs at 137 °C and is followed by the next three decomposition stages at 229, 456, and 647 °C in the temperature range of 150−700 °C. The powder of complex **4**, annealed in air at 1000 °C, had XRD patterns for the mixture of the $BaTiO_3$ and Ba_2TiO_4 phases. It is probably the $Ba_3Ti_2O_7$ phase that is unstable in the binary BaO TiO_2 system.

Conclusions

The detailed isolation, spectroscopic, and structural studies of the pH-dependent titanium(IV) citrate systems in aqueous solution are presented.

Isolated complex **1** can be converted into various titanium(IV) citrate precursors as a raw material, which is further decomposed into different titanium-based materials. Spectroscopic and structural studies show that different protonated citrate ligands in titanium citrate complexes **2**−**4** retain their basic chelation mode via the negatively charged α-alkoxyl and α-carboxyl oxygen atoms. The basic features of barium atoms in complexes **3** and **4** are six-coordinated with three negatively charged α-alkoxyl groups and three β-carboxyl groups of the citrate ligands, which can serve as a proposed model for the structure of $[BaTi(H_2cit)_3]$.

In the preparation of the titanium-based materials using the citrate process, the pH of the precursor solutions is a very important factor for acquiring a single molecular precursor, which is the key step for affording the exact chemical stoichiometry in the final materials. For example, the pH is the key factor for acquiring the pure and exact stoichiometry with regard to the exact Ba:Ti ratio precursor of $BaTiO_3$. Below pH 2.5, the Ba:Ti ratio of the molecular precursor can be easily controlled as a 1:1 ratio, whereas above pH 3.0, the Ba:Ti ratio in the molecular precursors is changed with the alteration of the pH of the solution.

Acknowledgment. This work is supported by the Ministry of Science and Technology (001CB108906, G1999022408) and the National Science Foundation of China (20021002).

Supporting Information Available: X-ray crystallographic files in CIF format, IR and NMR spectra, thermogravimetric analysis, and XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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