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Structure and Stability of Water Soluble $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$

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Ammonium citratoperoxotitanate(IV), $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$, was isolated in the solid form. Its crystal structure was solved and refined using single-crystal X-ray data. The compound crystallizes in a monoclinic cell with $a = 10.237(2)$ Å, $b = 17.537(4)$ Å, $c = 14.713(3)$ Å, $\beta = 100.35(1)°$ ($Z = 2$, fw = 1360.40, $\rho_{calc} = 1.74$ g/cm^3) and space group $P2_1/n$ (No. 14). The determined structure of the titanium complex agrees well with the Raman and NMR spectroscopic data. We speculate that tight coordination of titanium in the complex molecule is responsible for the high stability of this compound against hydrolysis.

Introduction

Titanium is often called as the element of the 21st century because of the extremely broad range of industrial applications of titanium-based materials. The most important products include TiO_2 as a starting reagent for syntheses, a widely used pigment in ultraviolet-protecting cosmetics,[1,2] nonvolatile memories, capacitors, ink printer heads, sensors for laser printers, ultrasonic devices,[3,4] photocatalytic antimolds,[5] catalysts for organic synthesis,[6] etc. The need to control chemical composition and homogeneity of fine multicomponent powders and ceramics, especially for small-scale devices, requires utilization of chemical methods of mixing and, consequently, convenient soluble precursors. One of the suitable techniques is the so-called polymerizable complex method,[7,8] a sol−gel method based on the polyesterification reaction between citric acid and ethylene glycol, originally proposed for the synthesis of $BaTiO_3$.[9] The problem of the soluble titanium source is partly solved by application of titanium tetrachloride or different titanium alkoxides easily subjected to hydrolysis.[10] At the same time peroxocomplexes of titanium are known to be relatively stable in water solutions at different pH,[11,12] and sometimes they are successfully applied in laboratory inorganic syntheses.[13,14] Different titanium peroxocomplexes with organic ligands could be isolated in solid form,[12] and possible stereochemical coordination of titanium, based on the characteristic features in the IR and Raman spectra, was discussed rather intensively.[15−18] However, such compounds are often unstable; only few of them were obtained in single-crystal form for which the reliable structural data were reported.

In our case it turned out that in the presence of citric acid the solution is stable for at least 2 years; gradual evaporation of water allows yellow single crystals to be obtained. Here we report the structure of isolated water-soluble ammonium citratoperoxotitanate(IV), $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$, which can be easily prepared in the solid form, and its water-based solution is stable over a broad range of pH values (∼1−14). A novel stereochemical coordination of titanium is responsible for the high stability of this compound in the presence of water.

Experiment

Synthesis. In a typical synthesis 0.25 g of Ti powder was dissolved in a cold aqueous solution containing 20 mL of 30% hydrogen peroxide and 5 mL of 30% ammonia solution to yield a yellowish transparent titanium peroxo solution:[19]

$$Ti + 3H_2O_2 \rightarrow [Ti(OH)_3O_2]^- + H_2O + H^+ \qquad (1)$$

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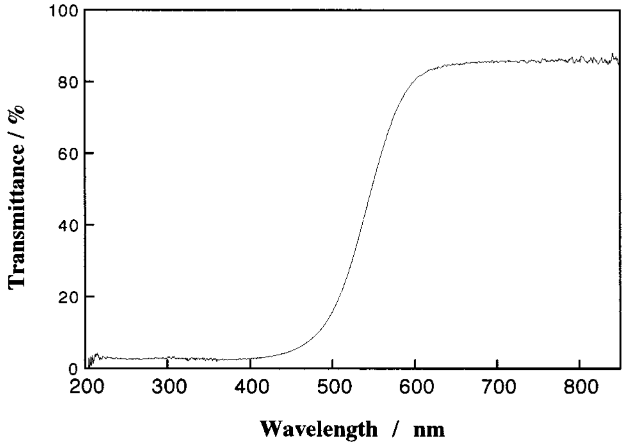

Figure 1. Ultraviolet and visible light absorption spectrum of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ taken at room temperature using a Shimadzu UV-2400PC spectrometer.

Table 1. Crystallographic Data for $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$

chemical formula	$C_{24}H_{64}N_8O_{44}Ti_4$	fw	1360.40
a, Å	10.237(2)	space group	$P2_1/n$ (No. 14)
b Å	17.537(4)	temp, °C	25 °C
c Å	14.713(3)	λ, Å	0.710 70
β (deg)	100.35(1)	ρ_{calcd}, g/cm^3	1.739
V, Å^3	2598.3(9)	μ, cm^{-1}	7.19
Z	2	R ^{a}	0.066
		R_w ^{b}	0.121

^{a} $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

An equivalent amount of citric acid (CA) with CA/Ti = 1:1 ratio was dissolved into this titanium peroxo solution with continuous stirring. Yellow crystals with dimensions of approximately 4 mm × 2 mm × 1 mm were grown from the saturated solution by slow gradual water evaporation.

Characterization. The obtained single crystals were uniform according to micro-Raman spectroscopic analysis. The results of elemental analysis gave the following: C, 20.02%; N, 8.97%; H, 4.60%. According to thermal gravimetric analysis, the Ti content was 14.08% and the rest was referenced to oxygen (O, 52.33%). Thus, the simplest formula could be described as $C_6H_{16}O_{11}N_2Ti$.

The crystals start to decompose without melting at around 50 °C, losing crystalline water and NH_3. The decomposition process finishes at 540 °C, yielding TiO_2. The new compound absorbs light in virtually the entire ultraviolet light domain (Figure 1). It has high solubility in water (>30 g in 100 g of pure H_2O at room temperature), and surprisingly, it is not subject to hydrolysis; therefore, it is possible to recrystallize it repeatedly.

Single-Crystal Structure Solution and Refinement. Single-crystal X-ray data were collected by a Rigaku RAXIS-IV imaging plate area detector using graphite monochromated Mo Kα radiation at a temperature of 25 ± 1 °C. The crystal size was approximately 0.30 × 0.15 × 0.10 mm^3. Indexing was performed from three oscillations, which were exposed for 4 min. The crystal to detector distance was 105.0 mm with the detector at the zero swing position. Readout was carried out in the 0.100 mm pixel mode. More details of data collection and crystallographic information are summarized in Table 1. The crystal was found to be monoclinic. The systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) allowed a unique choice of the space group $P2_1/n$ (No. 14). Then 30 of 3.50° oscillation images were collected, each being exposed for 6.0 min. In total, 5350 reflections were acquired. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient and a correction for the secondary extinction were performed. The structure was solved by the direct method and expanded using a Fourier difference synthesis technique using the SIR97 package[20] and refined by means of the teXsan crystallographic software package of Molecular Structure Corporation.[21] Hydrogen atoms except those of the disordered ammonium ions were included but not refined (CIF file is available as Supporting Information).

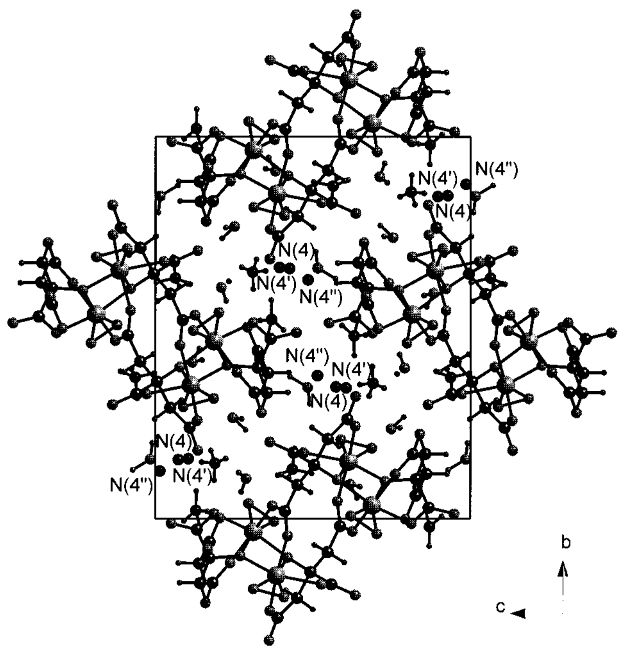

Figure 2. Unit cell of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ determined from single-crystal X-ray diffraction experiments.

Raman and NMR Spectroscopy. The Raman spectrum was measured with the 514 nm excitation line of an Ar laser in a backscattering geometry using microprobe optics (Atago Bussan Co.). The laser beam was focused on the surface of the crystal with a 90× objective lens to a spot of several micrometers in diameter. The scattered light was analyzed with a Jobin-Yvon T64000 triple spectrometer and collected with a CCD detector.

Solid-state ^{13}C NMR spectra were recorded on a JEOL NMR-GSX-270 spectrometer operating at 67.9 MHz using a cross-polarization magic angle spinning (CP-MAS) technique. The chemical shifts were externally referenced to adamantan ($C_{10}H_{16}$), but the reported values were rescaled by the TMS (tetramethylsilane) standard for the sake of convenience.

Results and Discussions

The refined atomic positions in the unit cell, the anisotropic thermal parameters, and selected interatomic distances for the $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ single crystal are presented in Tables 2 and 3 and in the crystallographic file in CIF format available as Supporting Information. In the unit cell of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ the complex anions $[Ti_4(C_6H_4O_7)_4(O_2)_4]^{8-}$ are separated from each other (Figure 2) and do not form polymer chains usual for many metal–organic ligand complexes. It should be noted that we were not able to locate hydrogen atoms for the fourth ammonium ion (N4, N4′, N4″) (Table 2 and Figure 2), which may be an indication of free rotation of this ion in the unit cell.

Figure 3 presents the structure of the individual citratoperoxotitanium complex anion determined from single-crystal X-ray diffraction data and the labeling scheme of the tetranuclear metal complex, which consists of the two binuclear fragments interlinked through the bridging carboxylate group (C6–O6–O7) of one citrate ligand. The salient feature of the citrate ligand in this complex is its tridentate nature as a whole molecule. As a result, the deprotonated alcoholic oxygen atom (O10) and the

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Table 2. Refined Atomic Parameters for $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ Single Crystal

atom	*x*	*y*	*z*	B_{eq}[a]	occupancy
Ti(1)	−0.14915(3)	0.14994(2)	0.38683(2)	1.176(7)	1.00
Ti(2)	0.05244(3)	0.03495(2)	0.31278(2)	1.165(7)	1.00
O(1)	−0.0377(1)	0.24264(7)	0.3661(1)	1.89(3)	1.00
O(2)	0.1303(2)	0.3208(1)	0.3645(1)	4.04(4)	1.00
O(3)	0.0367(1)	0.10216(7)	0.42187(8)	1.29(2)	1.00
O(4)	−0.0946(1)	0.17289(8)	0.52761(9)	1.88(3)	1.00
O(5)	0.0804(1)	0.20108(8)	0.6353(1)	2.24(3)	1.00
O(6)	−0.2154(1)	0.04541(7)	0.42166(9)	1.59(2)	1.00
O(7)	−0.0683(1)	−0.03325(7)	0.37346(9)	1.58(2)	1.00
O(8)	0.1290(1)	0.11662(8)	0.2396(1)	2.32(3)	1.00
O(9)	0.1455(2)	0.2221(1)	0.1616(2)	5.43(5)	1.00
O(10)	−0.1156(1)	0.09821(7)	0.27130(8)	1.39(2)	1.00
O(11)	−0.0288(2)	−0.01315(8)	0.1883(1)	2.27(3)	1.00
O(12)	−0.1475(2)	0.0127(1)	0.0516(1)	4.17(4)	1.00
O(13)	−0.3477(2)	−0.00155(9)	0.2063(1)	3.31(4)	1.00
O(14)	−0.5114(2)	0.0812(1)	0.1682(2)	4.49(5)	1.00
O(15)	−0.2930(1)	0.20671(8)	0.4109(1)	2.10(3)	1.00
O(16)	−0.3072(1)	0.18508(8)	0.3136(1)	2.20(3)	1.00
O(17)	0.1768(2)	−0.03980(9)	0.2972(1)	2.57(3)	1.00
O(18)	0.2226(1)	0.00731(9)	0.3789(1)	2.55(3)	1.00
O(20)	−0.0132(2)	0.3948(1)	0.2104(1)	3.60(4)	1.00
O(21)	0.4626(2)	0.0904(2)	0.3820(2)	5.43(6)	1.00
O(22)	−0.0880(2)	0.2645(2)	0.7527(2)	7.72(8)	1.00
O(23)	−0.6659(4)	0.1558(2)	0.0155(2)	7.87(9)	1.00
N(1)	−0.7173(2)	−0.0213(1)	0.1300(1)	2.96(4)	1.00
N(2)	0.1196(2)	0.3703(1)	0.0636(1)	3.10(4)	1.00
N(3)	0.2335(2)	0.1452(1)	0.8099(2)	3.32(4)	1.00
N(4)	−0.4733(4)	0.3453(2)	0.4267(3)	4.05(7)	0.65
N(4′)	−0.531(1)	0.3428(8)	0.395(1)	4.1(2)	0.20
N(4″)	−0.410(2)	0.375(1)	0.485(1)	4.7(3)	0.15
C(1)	0.0851(2)	0.2611(1)	0.3905(1)	2.01(3)	1.00
C(2)	0.1819(2)	0.2090(1)	0.4524(1)	1.83(3)	1.00
C(3)	0.1191(2)	0.14094(9)	0.4946(1)	1.34(3)	1.00
C(4)	0.0300(2)	0.1732(1)	0.5600(1)	1.58(3)	1.00
C(5)	−0.2262(2)	−0.0884(1)	0.4522(1)	1.43(3)	1.00
C(6)	−0.1655(2)	−0.0198(1)	0.4131(1)	1.32(3)	1.00
C(7)	0.0784(2)	0.1693(1)	0.1838(2)	2.49(4)	1.00
C(8)	−0.0704(2)	0.1702(1)	0.1438(1)	2.30(4)	1.00
C(9)	−0.1514(2)	0.1041(1)	0.1739(1)	1.71(3)	1.00
C(10)	−0.1091(2)	0.0291(1)	0.1329(1)	2.22(4)	1.00
C(11)	−0.2994(2)	0.1181(1)	0.1405(1)	2.01(4)	1.00
C(12)	−0.3920(2)	0.0607(1)	0.1743(1)	2.30(4)	1.00

[a] $B_{eq} = ({}^{8}/_{3})\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 3. Selected Interatomic Distances for Ammonium Citratoperoxotitanate(IV) Determined from X-ray Single Crystal Structural Data

atoms	*d*, Å	atoms	*d*, Å
Ti2−Ti1	3.212(1)	Ti2−O3	2.021(1)
Ti1−O1	2.040(1)	Ti2−O7	2.037(1)
Ti1−O3	2.058(1)	Ti2−O8	2.032(1)
Ti1−O4	2.085(1)	Ti2−O10	2.046(1)
Ti1−O6	2.051(1)	Ti2−O17	1.870(2)
Ti1−O10	2.010(1)	Ti2−O18	1.899(2)
Ti1−O15	1.863(1)	O16−O15	1.463(2)
Ti1−O16	1.880(1)	O18−O17	1.464(2)

two oxygen atoms (O11, O8) from C10 and C7 carboxylate groups build up fused five- and six-membered chelate rings (Ti2−O11−C10−C9−O10 and Ti2−O8−C7−C8−C9−O10, respectively), providing the maximum stability of the complex. The coordinated peroxo groups (O15−O16 and O17−O18) may play two important roles: (i) they retard further polymerization of the tetrameric anion by occupying the free sites in the equatorial pentagonal plane that can also be active sites for nucleofilic attack and hydrolysis; (ii) they provide negative charge to the complex, thus making possible formation of the ammonium salt, which is soluble in water.

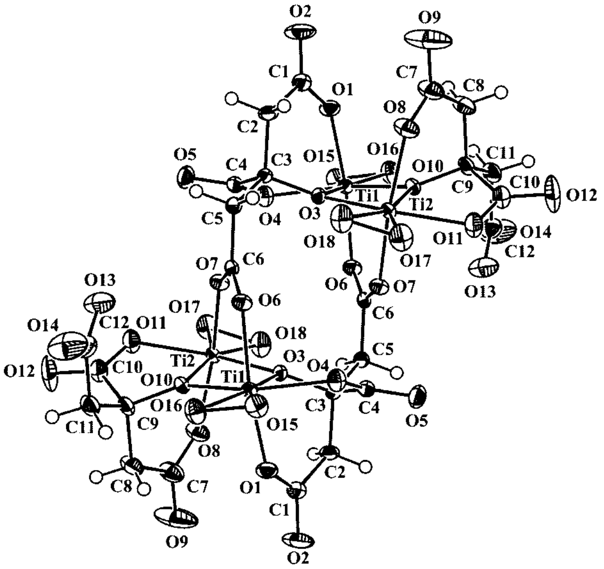

Figure 3. Structure and labeling scheme for the tetrameric anion $[Ti_4(C_6H_4O_7)_4(O_2)_4]^{8-}$. The thermal ellipsoids are displayed for 50% probability.

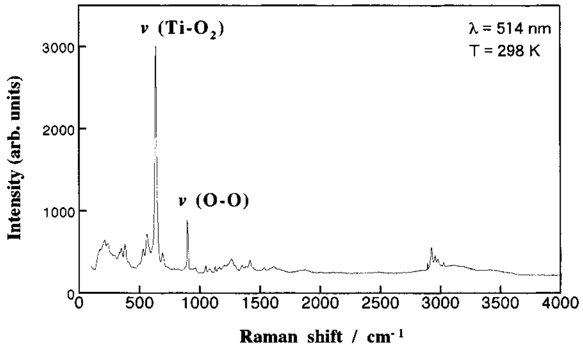

Figure 4. Raman spectrum of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ taken at room temperature.

The determined structure of this compound is in harmony with the corresponding Raman and solid-state ^{13}C NMR spectra. The Raman spectrum in Figure 4 of the crystal clearly demonstrates characteristic features of coordinated peroxo (O_2^{2-}) species.[15,18] A sharp peak near 950 cm^{-1} is assigned to the ν(O−O) stretching vibration, while the one near 650 cm^{-1} corresponds to the ν(Ti−O_2) mode of coordinated peroxo ions. The observed positions of ν(O−O) and ν(Ti−O_2) are in accordance with the signal expected for nonbridging η^2-peroxo ligands (for η^2, O_2^{2-} is bonded to Ti in a triangular bidentate manner; for η^1, the one bonded to Ti is in a linear monodentate manner).[15,18]

An inspection of the central ternary carbon with attached alcoholic group region (70−95 ppm) of citric acid (CA) in a solid-state ^{13}C NMR spectrum of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ demonstrates the complete absence of the resonance at 73 ppm observed in the corresponding spectrum of noncoordinated pure CA (Figure 5a); instead, a new sharp peak appears at 88 ppm (Figure 5b). The resonance at 73 ppm is characteristic of the central ternary carbon with alcoholic group of CA, while the one observed near 88 ppm has been assigned to a carbon with deprotonated alcoholic group of CA.[22] This observation indicates that the alcohol group OH^- of CA in $(NH_4)_8[Ti_4$-

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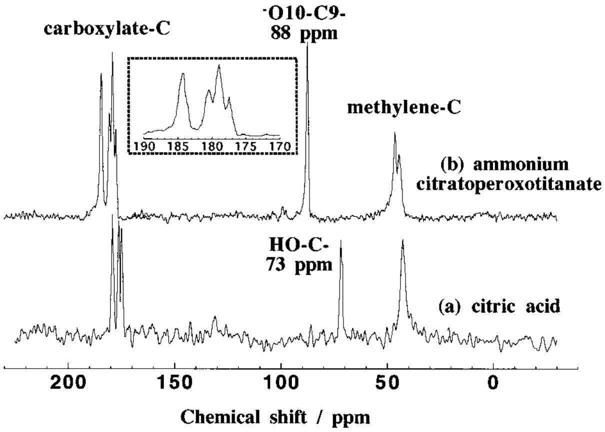

Figure 5. Solid-state ^{13}C NMR spectra of (a) anhydrous citric acid and (b) $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$. Inset shows the magnified low magnetic field region (the carboxylate carbon region) between 170 and 190 ppm.

$(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ is fully deprotonated, thus giving rise to a tight coordination of titanium by a citrate ligand with a bridging μ-alcoholic group. A characteristic splitting of the carboxylic group peaks with an approximate integrated intensity ratio of 2:1:2:1 has been observed for $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ at the lowest magnetic field region of 170−190 ppm (see inset in Figure 5). This signal comes from the six carboxylate carbon atoms of the two CA in the complex with four magnetically different environments.

We have applied the synthesized compound for preparation of different ceramic materials including $BaTiO_3$, $Bi_4Ti_4O_{14}$, thin films of TiO_2, and bismuth titanate.[23] It should be emphasized that the very important practical and environmentally beneficial aspect of $(NH_4)_8[Ti_4(C_6H_4O_7)_4(O_2)_4]\cdot 8H_2O$ is connected with the economical and safe use of water as a solvent for syntheses of high-quality ceramics via chemical solution routes. The described titanium compound is highly stable toward hydrolysis and therefore has potential applications in inexpensive and convenient syntheses of a variety of titanate materials for industrially important products through aqueous precursors; it can be handled and stored with greater convenience than the other known titanium compounds such as highly moisture-sensitive alkoxides or $TiCl_4$.

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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