

Supporting Information for:

Small Titanium Oxo-Clusters: Primary Structures of Titanium(IV) in Water

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References

EXPERIMENTAL SECTION

Materials. Titanyl sulfate (93%) was obtained from Aladdin Industrial Inc. Analytical grade TiCl_4 and CsCl were obtained from Xiya Reagent Co. All other materials were purchased from commercial sources and used as received. All solutions were prepared using 18.25 M Ω deionized water.

Instruments. Single crystal X-ray diffraction data were collected using a Bruker SMART APEX II diffractometer with graphite-monochromated Mo-K α radiation source ($\lambda=0.71073\text{\AA}$) at 173 K. X-ray powder diffractions were conducted with a Bruker D8 Advance X-ray diffraction instrument using Cu-K α radiation (40KV and 40mA) in the scanning angle (2θ) range of 5-50°. Fourier Transformation Infrared spectra (FTIR) were recorded using a PerkinElmer Spectrum Two IR Spectrometer. UV-vis diffuse reflectance spectra (DRS) were measured on a Shimadzu UV2550 spectrophotometer with BaSO_4 as the reflectance standard. Raman spectra were obtained on a NEXUS 670 FT-IR Raman spectrometer with 532 nm excitation. Elemental analyses (C, H, and N) were measured on a FLASH EA1112 elemental analyzer. Elemental analyses of Ti was performed using a spectrophotometric method and confirmed with energy dispersive spectroscopy (EDS) equipped in a Hitachi S-4800 scanning electron microscope, with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ as an external standard.

Colorimetric determination of Ti%. Quantitative determination of titanium(IV) is based on the characteristic UV-vis absorption of the yellow pertitanic acid complex⁴ of Ti(IV) and H_2O_2 formed in acid aqueous solution. In a volumetric flask (50 mL), the solid sample is dissolved in 25 mL of 50% v/v H_2SO_4 . Then aqueous solutions of 8.0% $(\text{NH}_4)_2\text{SO}_4$ (5.0 mL) and 3.0% H_2O_2 (8.0 mL) are added. Water is then filled to the calibration mark of the flask. The absorbance of the resultant yellow solution at 408 nm is used to quantify concentration of Ti(IV) according to a pre-defined calibration curve using $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ as the authentic substance.

One-pot synthesis of $\text{Cs}_2[\text{Ti}_3(\mu_2\text{-O})_3(\text{OH}_2)_4\text{Cl}_8] \cdot 4\text{CsCl}$ (1) and $\text{Cs}_2[\text{Ti}_4(\mu_2\text{-O})_4(\text{OH}_2)_6\text{Cl}_2(\text{SO}_4)_4] \cdot 4\text{CsCl} \cdot \text{HCl}$ (2). Titanyl sulfate was dissolved in water to make a 20% (w/w) solution. The solution was filtered if not quite clear. Then in 20 mL of the filtrate 2 M CsCl was made. A few seconds after dissolution of CsCl , a greenish precipitate formed and was collected by filtration. HCl (1.5 M) was used to dissolve the precipitate and afterwards 0.5 M CsCl was added. After equilibration for 2-3 hours, the mixture was filtered through a 0.22 μm membrane filter. The filtrate was allowed to evaporate slowly under ambient conditions (ca. 20 °C). After a few days two type of greenish block crystals formed and identified by FTIR.

Optimized synthesis of 2. The precipitate in the above procedure was dissolved in 3 M HCl and afterwards CsCl was added to reach 0.5 M. Then the solution was filtered again with 0.22 μm membrane filter. The resultant clear filtrate was allowed to evaporate slowly under ambient conditions (ca. 20 °C). After several weeks, tiny greenish block crystals began to appear. However, large amounts of spherical crystals (the crude product) might form if evaporation is too fast. The product was collected by filtration and air dried under suction for 10 - 20 minutes (3.2 g, yield 30% based on Ti). Anal. Calcd: Ti, 10.7%. Found: Ti, (10.8 \pm 0.3)%.

Optimized synthesis of 1. To 9.0 mL of 1.0 M TiCl_4 aqueous solution CsCl was added to make $[\text{CsCl}] = 1.0$ M. After equilibration for 2-3 hours, the mixture was filtered through a 0.22 μm membrane filter. The filtrate was allowed to evaporate slowly under ambient conditions (ca. 20 °C). After about two weeks greenish crystals formed. They were collected by filtration and air dried under suction for 10 - 20 minutes (1.5 g, yield 35% based on Ti). Anal. Calcd: Ti, 9.7%. Found: Ti, (10.0 \pm 0.5)%.

Synthesis of $[\text{Ti}_4\text{O}_4(\text{OH}_2)_8(\text{SO}_4)_4] \cdot 2\text{TEAC} \cdot (\text{H}_2\text{SO}_4) \cdot 10\text{H}_2\text{O}$ (3). A mixture of TiCl_4 (1.0 M; 10 mL), H_2SO_4 (3.0 M) and tetraethylammonium chloride (TEAC; 1.0 M) was stirred for 24 h under ambient conditions. After filtration, slow evaporation of the filtrate afforded colorless block crystals of compound

3 in three weeks (based on Ti). The product was collected by filtration and air-dried with suction for 10 minutes. Alternatively, crystals of lower quality can be obtained by rapid evaporation under ambient conditions (2 days; yield 80% based on Ti). Anal. Calcd (%): Ti, 13.8; C, 13.8; N, 2.0; H, 5.6. Found (%): Ti, 13.1; C, 14.1; N, 1.9; H, 5.1.

X-ray single crystal crystallography. Single crystals with appropriate dimensions were collected from the mother liquor, coated with high vacuum grease (Dow Corning Corporation), and transferred to a stream of cold N₂ on the diffractometer as quickly as possible to prevent decomposition due to solvent loss. Data were collected on a Bruker SMART APEX II diffractometer with a CCD area detector using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Indexing was processed with APEX2 through difference vectors method. Data integration and reduction were done using SaintPlus 6.01². Absorption correction was performed using the multi-scan method with SADABS³. Structure solution and refinement were performed using the least-square method implemented in Olex2 v1.2⁴. Crystallographic data are summarized in Table S1. Hydrogen atoms were not included for the terminal water/hydroxide ligands nor for the solvent water because they could not be positively identified.

More comments on compound 3. When structure of compound **3** was solved, the TEA cations and crystal water molecules could not be located. “Squeeze” was applied after other work had been finished completely. Before “squeeze”, R1 was ca. 11%. Then “squeeze” gave a residue electron density of 865e per cell. Based on the elementary analysis results, we then added 8 TEA⁺ (600e) and 40 H₂O (400 e) molecules to each unit cell. Further refinements gave a much better R1 value of 6.35%.

Table S1. Crystallographic data summary

Compound	1	2	3
Empirical formula	H ₈ Cl ₁₂ Cs ₆ O ₇ Ti ₃	H ₁₅ Cl ₇ Cs ₆ O ₂₆ S ₄ Ti ₄	C ₈ H ₇₈ Cl ₂ N ₂ O ₄₂ S ₅ Ti ₄
Formula weight (g/mol)	1486.56	1795.45	1392.8756
Crystal system	orthorhombic	monoclinic	triclinic
Space group (Nr.)	Fdd2	C2	P-1
a (Å)	16.1626(10)	18.994(5)	13.871(4)
b (Å)	30.975(2)	10.217(3)	13.885(4)
c (Å)	12.1951(8)	11.715(3)	23.400(7)
α (°)	90	90	92.679(3)
β (°)	90	114.548(4)	98.013(3)
δ (°)	90	90	90.122(3)
Volume (Å ³)	6116.6(7)	2067.9(10)	4458(2)
Z	8	2	4
D _{calc} (g/cm ³)	3.211	2.861	1.933
Abs. Coeff. μ (mm ⁻¹)	8.871	6.677	1.167
Temperature (K)	173	173.15	173.15
Total reflections	6943	5521	42478
Min-max θ (°)	5.678 to 49.97	4.672 to 49.996	4.69 to 49.998
Unique reflections	5531	4933	15590
Calculated reflection ($I > 2\sigma$)	2179	2718	7161
R ₁ [$I > 2\sigma$] ^a	0.0130	0.0968	0.0635
wR ₂ (all data) ^b	0.0314	0.2660	0.1677
R _{int}	0.0178	0.0253	0.0879
Goodness of fit on F ²	1.073	1.063	0.849
Parameters	129	213	829
Restraints	1	13	208
Largest diff. peak/hole (e Å ⁻³)	0.56/-0.77	6.28/-1.53	1.39/-1.18

^a $R_1 = \sum |F(o) - |F(c)|| / \sum |F(o)|$; ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Table S2. Summarized bond lengths (Å) and bond angles (°)

	1a	2a	3a	ref. values
d(Ti-Cl)	2.34 - 2.49	2.31	-	2.41 in Ti ₂ Cl ₂ (OPr ⁱ) ₄ (HOPr ⁱ) ₂ , ^a ref. 5
d(Ti-OSO ₃)	-	1.89 - 1.99	1.94 - 2.00	1.95-2.05 in TiOSO ₄ , ref. ⁶
d(Ti-O _{μ2})	1.81 - 1.82	1.78 - 1.91	1.80 - 1.82	1.79 - 1.86 in Ti ₈ O ₁₂ (OH ₂) ₂₄ ⁸⁺ , ref. 7
d(Ti-OH ₂)	2.14 - 2.15	2.10 - 2.25	2.08 - 2.10	2.08 - 2.16 in Ti ₈ O ₁₂ (OH ₂) ₂₄ ⁸⁺ , ref. 7
d(Ti ···Ti)	3.45 - 3.47 ^b	3.43 - 3.53 ^b	3.44 - 3.47 ^b	3.52- 3.62 in Ti ₈ O ₁₂ (OH ₂) ₂₄ ⁸⁺ , ref. 7
∠TiO _{μ2} Ti	ca. 144	ca. 144	143 - 147	152 - 156 in Ti ₈ O ₁₂ (OH ₂) ₂₄ ⁸⁺ , ref. 7

^a Not available for aqueous isolated compounds. ^b Distance between the O_{μ2}-bridged Ti.

Table S3. BVS calculations for O atoms in compound **1**.

μ_2 -O / total valence	bonded atoms	distance (Å)	BVS	aqua-O	bonded atoms	distance (Å)	BVS
O1/1.958	Ti1	1.823	0.979	O2	Ti1	2.143	0.412
	Ti1	1.823	0.979	O3	Ti2	2.147	0.408
O9/2.006	Ti1	1.814	1.003				
	Ti1	1.814	1.003				
O9/1.958	Ti2	1.817	0.995				
	Ti2	1.817	0.995				

Table S4. BVS calculations for O atoms in compound **2**.

μ_2 -O / total valence	bonded atoms	distance (Å)	BVS	aqua-O	bonded atoms	distance (Å)	BVS
O1/1.861	Ti1	1.783	1.090	O3	Ti2	2.121	0.437
	Ti2	1.911	0.771	O4	Ti2	2.099	0.464
O2/2.036	Ti1	1.838	0.940	O5	Ti1	2.255	0.304
	Ti2	1.781	1.096				

Table S5. BVS calculations for O atoms in compound **3**.

μ_2 -O / total valence	bonded atoms	distance (Å)	BVS	aqua-O	bonded atoms	distance (Å)	BVS
O1/2.015	Ti1	1.802	1.036	O5	Ti1	2.091	0.474
	Ti2	1.823	0.979	O6	Ti1	2.101	0.462
O2/2.011	Ti2	1.809	1.016	O7	Ti2	2.09	0.476
	Ti3	1.817	0.995	O8	Ti2	2.1	0.463

O3/2.011	Ti3	1.814	1.003	O9	Ti3	2.095	0.469
	Ti4	1.812	1.008	O10	Ti3	2.091	0.474
O4/1.989	Ti1	1.812	1.008	O11	Ti4	2.084	0.483
	Ti4	1.822	0.981	O12	Ti4	2.084	0.483

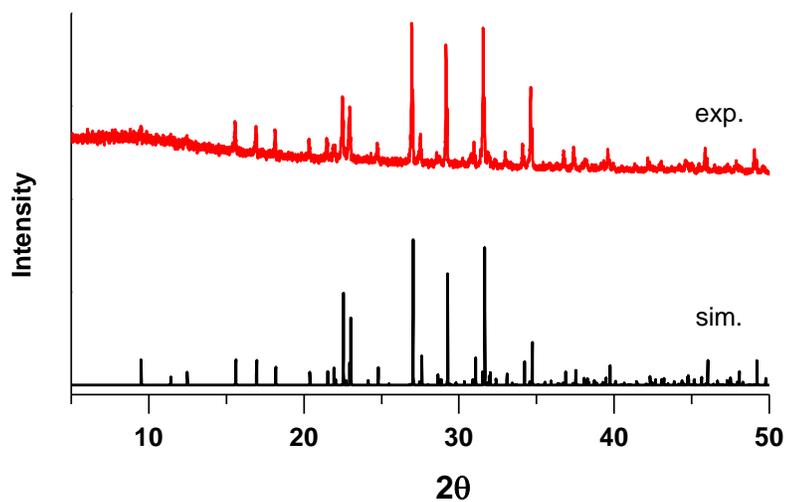


Figure S1. Powder XRD pattern of **1**.

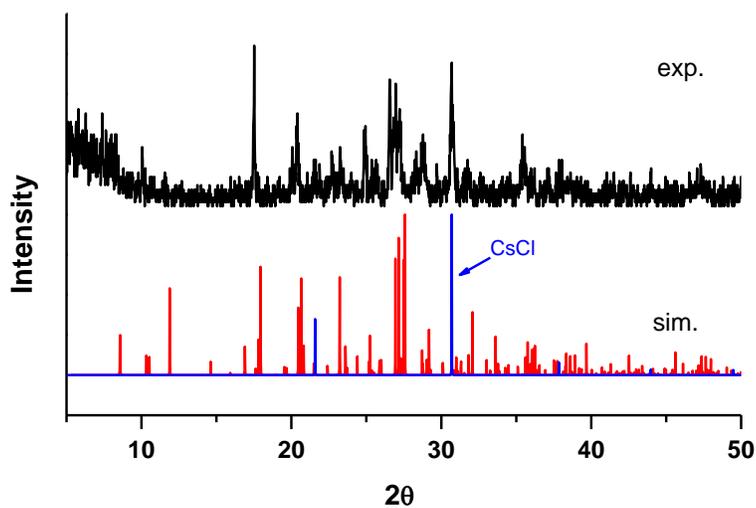


Figure S2. Powder XRD pattern of **2**. This is obtained by using the spherical crystals obtained by relative fast evaporation of solvent. However, the powder pattern indicates the existence of impurities, e.g., CsCl.

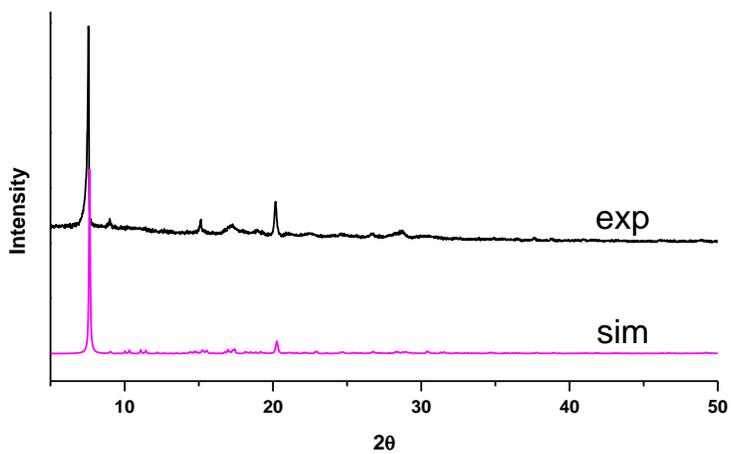


Figure S3. Powder XRD pattern of compound **3**.

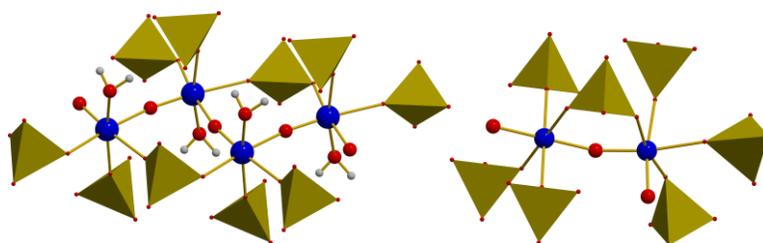


Figure S4. Structures⁶ of **(left)** $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and **(right)** TiOSO_4 . The tetrahedrons are SO_4 moieties. Color Scheme: Blue, Ti; red, O; grey, H.

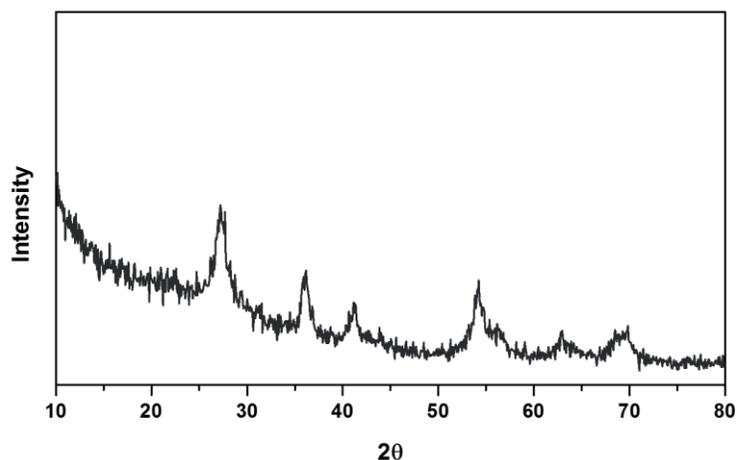


Figure S5. XRD of the precipitate obtained by aging of 1.0 M TiCl_4 at room temperature for a month. Data indicate it is rutile TiO_2 .

Vibrational Spectra. Vibrational spectra including FT-IR (Figure S7) and Raman (Figure S8) are provided herein. By examining the vibrational moieties in the crystal structures, the main features/modes in the spectra are assigned. As shown in Figure S7, the strong and wide peak in the range of $2700\text{--}3600\text{ cm}^{-1}$ and the relatively weaker peaks located at ca. 1620 cm^{-1} are stretch and bending modes of OH_2 groups in compounds **1**, **2** and **3**. A strong vibrational peak centered at ca. 809 cm^{-1} for compound **1** should be assigned to a mixture of stretch modes of the Ti-O_μ and Ti-O_t moieties. The peak centered at ca. 760 cm^{-1} of **2** and **3** should also be assigned Ti-O moieties. Other peaks like 1232 , 1158 , 1126 , 1019 and 952 cm^{-1} for **2** and **3** are assigned to stretch modes of SO_4 groups, and those located at 672 , 582 and 477 cm^{-1} are assigned to bending modes of SO_4 groups.

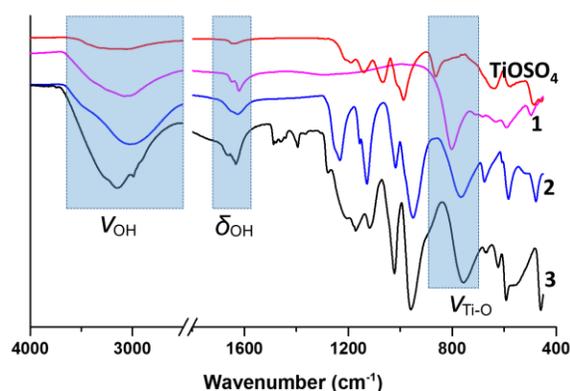


Figure S6. IR of **1**, **2**, **3** and TiOSO_4 .

In their Raman spectra, **1**, **2**, **3** and TiOSO_4 all feature a strong peak near 500 cm^{-1} . By comparing their structures, this mode is tentatively assigned to Ti-O_μ bond.

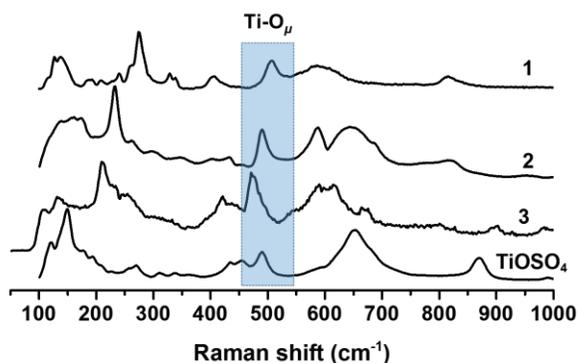


Figure S7. Raman spectra of **1**, **2**, **3** and TiOSO_4 .

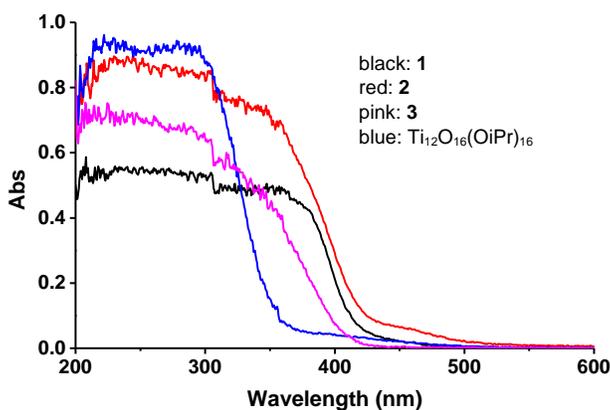


Figure S8. DRS of **1**, **2**, **3** and $\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}$.⁸

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