# Tetrameric, Trititanium(IV)-Substituted Polyoxotungstates with an $\alpha$-Dawson Substructure as Soluble Metal-Oxide Analogues: Molecular Structure of the Giant "Tetrapod" $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$

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**Abstract:** The preparation and structural characterization of the novel polyoxoanion $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ (**1a**; abbreviated to $\{TiO_6\}_{16}$; FW ~16000) which consists of four tri-$Ti^{IV}$-1,2,3-substituted $\alpha$-Dawson substructures, four $Ti(OH)_3$ bridging groups, and one encapsulated $Cl^-$ ion, are described. A water-soluble, all-inorganic composition compound of the tetrameric Ti-O-Ti-bridged anhydride form, $Na_xH_{45-x}[\mathbf{1a}]\cdot yH_2O$ (**1**; $x = 16-19$, $y = 60-70$), which was afforded by the reaction of the tri-lacunary Dawson polyoxotungstate $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 19H_2O$ with an excess of $TiCl_4$ in aqueous solution, was obtained as analytically pure, homogeneous colorless crystals. Single-crystal X-ray structure analysis revealed that **1a** was an inorganic, giant "tetrapod"-shaped molecule (inscribed to a sphere with a diameter of ~32 Å) with approximately $T_d$ symmetry, in which the 16 edge- and/or corner-shared $TiO_6$ octahedra were contained. This number of $TiO_6$ octahedra was larger than that found in other titanium(IV)-substituted polyoxotungstates. Complex **1** was characterized by complete elemental analysis, TG/DTA, FTIR, UV/Vis absorption, and solution ($^{31}P$ and $^{183}W$) NMR spectroscopy. The longest wavelength band in the UV/Vis absorption spectra of **1** in water was attributed to the $O \rightarrow Ti^{IV}$ ligand-to-metal charge-transfer (LMCT) transition: the wavelength of the LMCT band increased linearly as the number of $TiO_6$ octahedra contained in the Keggin and Dawson polyoxoanions increased. The $Ti_n$ chromophores formed in the Keggin and Dawson polyoxotungstates are water-soluble analogues of solid $TiO_2$ or $SrTiO_3$ as light-semiconductors and photocatalysts.

**Keywords:** titanium • polyoxometalates • UV/Vis spectroscopy • X-ray diffraction

## Introduction

Polyoxoanions are molecular metal-oxide clusters that are of current interest as soluble analogues of heterogeneous metal oxides and because of their applications in catalysis, medicine, and material sciences.[1] Site-selective substitution of $W^{VI}$ atoms in polyoxoanions by $Ti^{IV}$ atoms is particularly interesting because of the multicenter active sites formed with corner- or edge-sharing $TiO_6$ octahedra, and because of the water-soluble molecular modeling of titanium oxides as high-semiconductors and photocatalysts; $TiO_2$[2a–c] consists of edge-sharing $TiO_6$ octahedra, and perovskite $SrTiO_3$[2d–f] consists of corner-sharing $TiO_6$ octahedra.

The ionic radius of $Ti^{IV}$ (0.75 Å) is close to that of $W^{VI}$ (0.74 Å), suggesting that $Ti^{IV}$ should fit nicely into the polyoxotungstate framework. However, there is the significant issue of the formation of oligomeric Ti-O-Ti anhydrides resulting from substitution by several $Ti^{IV}$ atoms, whereas the monomeric, mono- and di-$Ti^{IV}$-substituted Keggin polyoxotungstates have been realized in $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$[3a,b] and $[\alpha\text{-}PW_{11}TiO_{40}]^{5-}$.[3c,d] In fact, the tri-$Ti^{IV}$-1,2,3-substituted Keggin polyoxotungstates heretofore prepared are dimeric, Ti-O-Ti-bridged anhydride forms, for example, $[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$,[3e] $[\alpha,\alpha\text{-}Ge_2W_{18}Ti_6O_{77}]^{14-}$,[3f] and the recently found $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$ (all abbreviated to $\{Ti_6\}$).[3g] The dimeric, Ti-O-Ti-bridged anhydride form of the di-$Ti^{IV}$-1,2-substituted $\alpha$-Keggin polyoxotungstate, $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$, has also recently been elucidated.[3h] The nature of the bonding of the $TiO_6$ octahedra in these Keggin polyoxoanions is corner-sharing, and thus resembles that in perovskite $SrTiO_3$ rather than that in $TiO_2$. Among the titanium(IV)-substituted Keggin polyoxometalates, the largest number of

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Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author. Bond lengths and angles of compound **1**, which are not described in the text, are deposited in Table S1.

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titanium(IV) octahedra contained in one molecule is six, as found in the dimeric, tri-$Ti^{IV}$-substituted polyoxometalates described above.

The oligomeric Ti-O-Ti anhydride forms are very stable and, therefore, isolation of the monomeric forms from these $Ti^{IV}$-substituted polyoxotungstates is very difficult. Thus, the ease of oligomerization observed for the $Ti^{IV}$-substituted polyoxotungstates, in contrast to that for other $d^0$ metal ($V^V$ and $Nb^V$) substituted polyoxotungstates, will be employed for the synthesis of large polyoxotungstate-based inorganic molecules with higher nuclearity and higher molecular weights.

The two tri-$Ti^{IV}$-substituted Dawson polyoxotungstates recently found, that is $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 0.8\,KCl \cdot 56\,H_2O$ and $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 46\,H_2O$, have been suggested to be tetrameric, Ti-O-Ti anhydride forms on the basis of complete elemental analysis, ultracentrifugation molecular weight measurements, and solution ($^{183}W$ and $^{31}P$) NMR spectroscopy.[4] The former, which was prepared in aqueous solution in the reaction of the tri-lacunary Dawson polyoxoanion $[P_2W_{15}O_{56}]^{12-}$ with $Ti(SO_4)_2$ in a 1:3 molar ratio, was obtained as a powder sample containing KCl, whereas the latter was obtained as a crystalline compound without KCl derived from the KCl-adduct, although the crystals of the KCl-free compound were not suitable for X-ray structure analysis. Very recently, we successfully determined the molecular structure of the KCl-adduct, $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot y\,H_2O$ ($x = 21-26$, $y = 60-70$, $\{Ti_{12}\}$), which contained an inorganic, giant "tetrapod" molecule composed of four tri-$Ti^{IV}$-1,2,3-substituted $\alpha$-Dawson substructures and one encapsulated chloride ion.[5] Separately, Kortz et al. have very recently determined the molecular structure of the ammonium potassium salt of the KCl-free compound, $K_4(NH_4)_{20}[(P_2W_{15}Ti_3O_{57.5}(OH)_3)_4] \cdot 77\,H_2O$ ($\{Ti_{12}\}$), which was prepared in aqueous solution by the reaction of $[P_2W_{15}O_{56}]^{12-}$ with $TiO(SO_4)$ in a 1:3 molar ratio.[6] The molecular structure was a giant "tetrapod" without an encapsulated chloride ion.

In this work, we have unexpectedly found a novel "tetrapod"-shaped polyoxotungstate, $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl] \cdot y\,H_2O$ (**1**: $x = 16-19$, $y = 60-70$) $= Na_xH_{45-x}[\mathbf{1a}] \cdot y\,H_2O$, which was prepared by the reaction of $[P_2W_{15}O_{56}]^{12-}$ with an excess amount of $TiCl_4$ in aqueous solution. The polyoxoanion unit, $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ (**1a**; $\{Ti_{16}\}$), was revealed to be an inorganic, giant "tetrapod" molecule composed of four tri-$Ti^{IV}$-1,2,3-substituted $\alpha$-Dawson substructures, four $Ti(OH)_3$ bridging groups, and one encapsulated chloride ion; thus overall the structure contains 16 titanium atoms. Herein, we report full details of the synthesis and characterization of **1** and the molecular structure of **1a**.

## Results and Discussion

Reaction of $Na_{12}[B\text{-}P_2W_{15}O_{56}] \cdot 19\,H_2O$ (5.0 g, 1.15 mmol) with an excess of $TiCl_4$ (ca. 1 mL, ca. 9.10 mmol) in aqueous solution in a water bath at about 80 °C for 30 min afforded the water-soluble sodium salt **1**. Analytically pure, colorless crystals of **1** were obtained in 5.61–5.69 % (0.29 g scale) yield by slow evaporation of the crude product in water at room temperature. Compound **1** was characterized by elemental analysis, TG/DTA, FTIR, $^{31}P$ and $^{183}W$ NMR, UV/Vis absorption measurements, and single-crystal X-ray analysis. The ionic balance for the formation of **1a** is shown in Equation (1).

$$16\,Ti^{4+} + Cl^- + 4\,[P_2W_{15}O_{56}]^{12-} + 36\,H_2O \rightarrow [(P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}\ (\mathbf{1a}) + 60\,H^+ \qquad (1)$$

The FTIR spectrum of **1** ($\tilde{\nu} = 1090, 954, 914, 828, 656, 561, 531, 418\ cm^{-1}$), measured as a KBr disk, showed the characteristic vibrational bands of the Dawson-type "$P_2W_{18}O_{62}{}^{6-}$" polyoxotungstate framework (Figure 1 d).[7] The positions of all bands in the polyoxoanion region in **1** were very similar to those of the recently reported, three tetrameric polyoxotungstates, that is, $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot y\,H_2O$ (x = 21–26, y = 60–70) (Figure 1a: $\tilde{\nu} = 1090, 952, 918, 832, 692, 663\ cm^{-1}$), $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 0.8\,KCl \cdot 56\,H_2O$ (Figure 1b: $\tilde{\nu} = 1089, 950, 917, 833, 692, 661\ cm^{-1}$) and $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 46\,H_2O$ (Figure 1c: $\tilde{\nu} = 1088, 948, 916, 830, 693, 661\ cm^{-1}$).

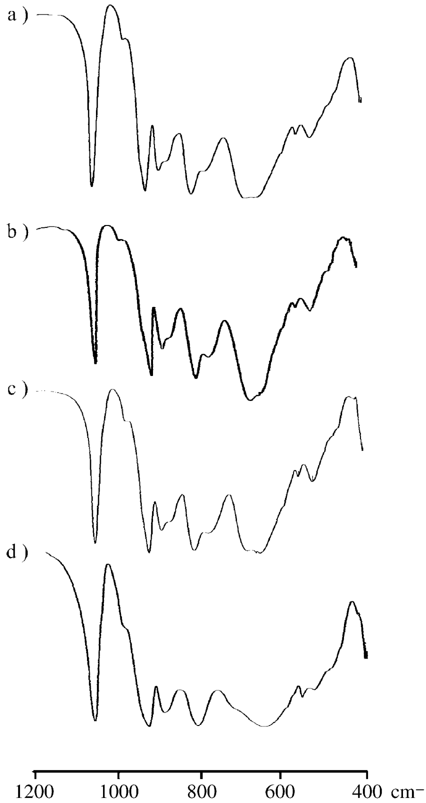

Figure 1. FTIR spectra in the polyoxoanion region (1200–400 $cm^{-1}$), measured as KBr disks, of a) $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot y\,H_2O$ ($x = 21-26$, $y = 60-70$) , b) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 0.8\,KCl \cdot 56\,H_2O$, c) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 46\,H_2O$, and d) $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl] \cdot y\,H_2O$ ($x = 16-19$, $y = 60-70$) (**1**).

The $^{183}W$ NMR spectrum of **1** measured in $D_2O$ at 23.3 °C showed a three-line spectrum with signals at $\delta = -145.0$, $-181.5$, and $-201.4$ ppm with integrated intensities of 1:2:2 (Figure 2d). This spectrum is in accord with the presence of two tungsten belts consisting of six $WO_6$ octahedra and a tungsten cap of three $WO_6$ octahedra ($W_3$ cap). Thus, the three $Ti^{IV}$ octahedra are edge-shared within the $\alpha$-Dawson polyoxoanion, which leads to the formation of the $Ti_3$ cap site.

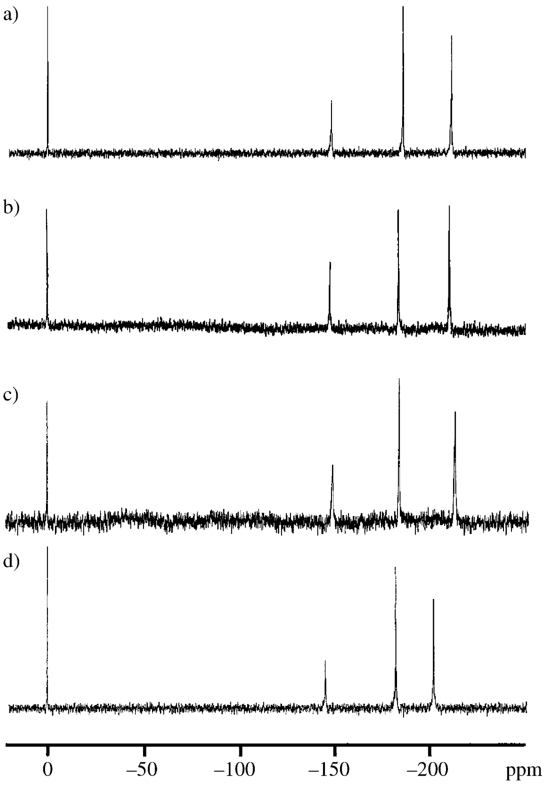

Figure 2. $^{183}$W NMR spectra in $D_2O$ of a) $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl]\cdot yH_2O$ ($x = 21-26$, $y = 60-70$), b) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 0.8\,KCl\cdot 56\,H_2O$, c) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 46\,H_2O$, and d) $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]\cdot yH_2O$ ($x = 16-19$, $y = 60-70$) (**1**). The resonance at 0.0 ppm is due to the external reference: saturated $Na_2WO_4-D_2O$ solution.

The $^{31}$P NMR spectrum of **1** in $D_2O$ at 21.3 °C showed a clean two-line spectrum with signals at $\delta = -7.04$ and $-13.77$ ppm, confirming its purity and single-product nature (Figure 3d). The downfield resonance is assigned to the phosphorus atom closest to the $Ti_3$ cap, whereas the upfield resonance is due to the phosphorus atom closer to the $W_3$ cap. The $^{183}$W and $^{31}$P NMR spectra are consistent with the results of the X-ray structure analysis and are comparable to those of the recently reported, tetrameric $Ti^{IV}$-substituted Dawson polyoxotungstates; $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl]\cdot yH_2O$ ($x = 21-26$, $y = 60-70$) ($^{183}$W NMR in $D_2O$ at 19.7 °C (Figure 2a): $\delta = -148.3 (3\,W\times 4)$, $-185.8$ $(6\,W\times 4)$, $-211.2$ ppm $(6\,W\times 4)$; $^{31}$P NMR in $D_2O$ at 25 °C (Figure 3a): $\delta = -7.6$, $-14.0$ ppm); $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 0.8\,KCl\cdot 56\,H_2O$ ($^{183}$W NMR in $D_2O$ at 25 °C (Figure 2b): $\delta = -147.6$ $(3\,W\times 4)$, $-183.5$ $(6\,W\times 4)$, $-210.8$ ppm $(6\,W\times 4)$; $^{31}$P NMR in $D_2O$ at 25 °C (Figure 3b): $\delta = -7.7$, $-14.0$ ppm); and $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 46\,H_2O$ ($^{183}$W NMR in $D_2O$ at 25 °C (Figure 2c): $\delta = -149.1$ $(3\,W\times 4)$, $-183.9$ $(6\,W\times 4)$, $-$-213.4 ppm $(6\,W\times 4)$; $^{31}$P NMR in $D_2O$ at 25 °C (Figure 3c): $\delta = -7.4$, $-13.9$ ppm).

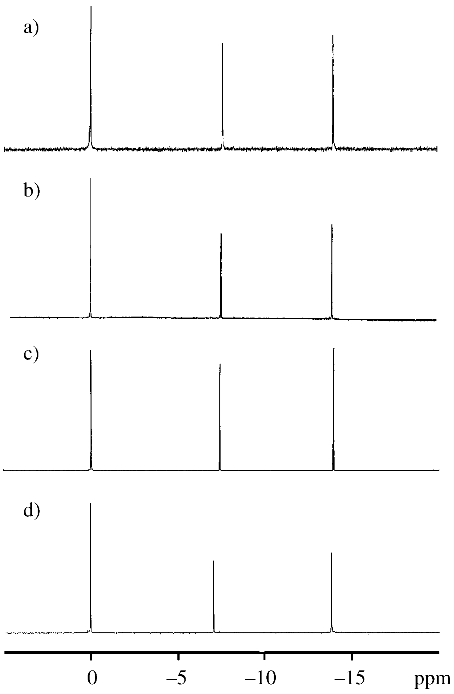

Figure 3. $^{31}$P NMR spectra in $D_2O$ of a) $Na_xH_{33-x}K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl]\cdot yH_2O$ ($x = 21-26$, $y = 60-70$), b) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 0.8\,KCl\cdot 56\,H_2O$, c) $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4\cdot 46\,H_2O$, and d) $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]\cdot yH_2O$ ($x = 16-19$, $y = 60-70$) (**1**). The resonance at 0.0 ppm is due to the external reference: 25 % $H_3PO_4$ in $H_2O$. In each case a very high level of purity is indicated (that is, with respect to any other P-containing polyoxoanions or other materials).

The structure analysis of **1a** revealed that the molecular structure was based on four Dawson units linked through Ti-O-Ti bonds and bridging $\mu_3$-$Ti(OH)_3$ groups such that **1a** displayed $T_d$ symmetry (Figure 4a). The partial structure containing one Dawson unit to which three $Ti(OH)_3$ groups are linked is depicted in Figure 4b. The molecular structure of **1a** was composed of one encapsulated $Cl^-$ ion and four "$P_2W_{15}Ti_3O_{62}$" Dawson-polyoxoanion units (designated as A, B, C, and D) linked to four bridging $\mu_3$-$Ti(OH)_3$ groups (designated as W, X, Y, and Z), each Dawson unit of which has the same $\alpha$-Dawson structure $[\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62}]^{12-}$. As expected, the three $TiO_6$ octahedra ($Ti_3$ cap) in each "$P_2W_{15}Ti_3$" Dawson unit substituted the three edge-sharing $WO_6$ octahedra ($W_3$ cap) of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. The three terminal oxygen atoms of the $Ti_3$ cap were linked to three different $Ti(OH)_3$ groups through Ti-O-Ti bonds, that is Dawson unit A is connected to $Ti(OH)_3$ (X, Y, and Z), Dawson unit B is connected to $Ti(OH)_3$ (Y, Z, and W), Dawson unit C is connected to $Ti(OH)_3$ (Y, X, and W), and Dawson unit D is connected to $Ti(OH)_3$ (W, X, and Z). The four $Ti(OH)_3$ groups occupy the corners of a large tetrahedron in which one $Cl^-$ ion is encapsulated. Thus, the giant "tetrapod" molecule **1a** has approximately $T_d$ symmetry and this molecule was inscribed to a sphere with a diameter of ~32 Å (the longitudinal distance of one Dawson unit is ~12.7 Å). The three Ti atoms and fifteen W atoms in each Dawson unit, as well as the bridging $Ti(OH)_3$ group all exhibited conventional octahedral coordination polyhedra. The polyhedral representation of **1a** is shown in Figure 4c.

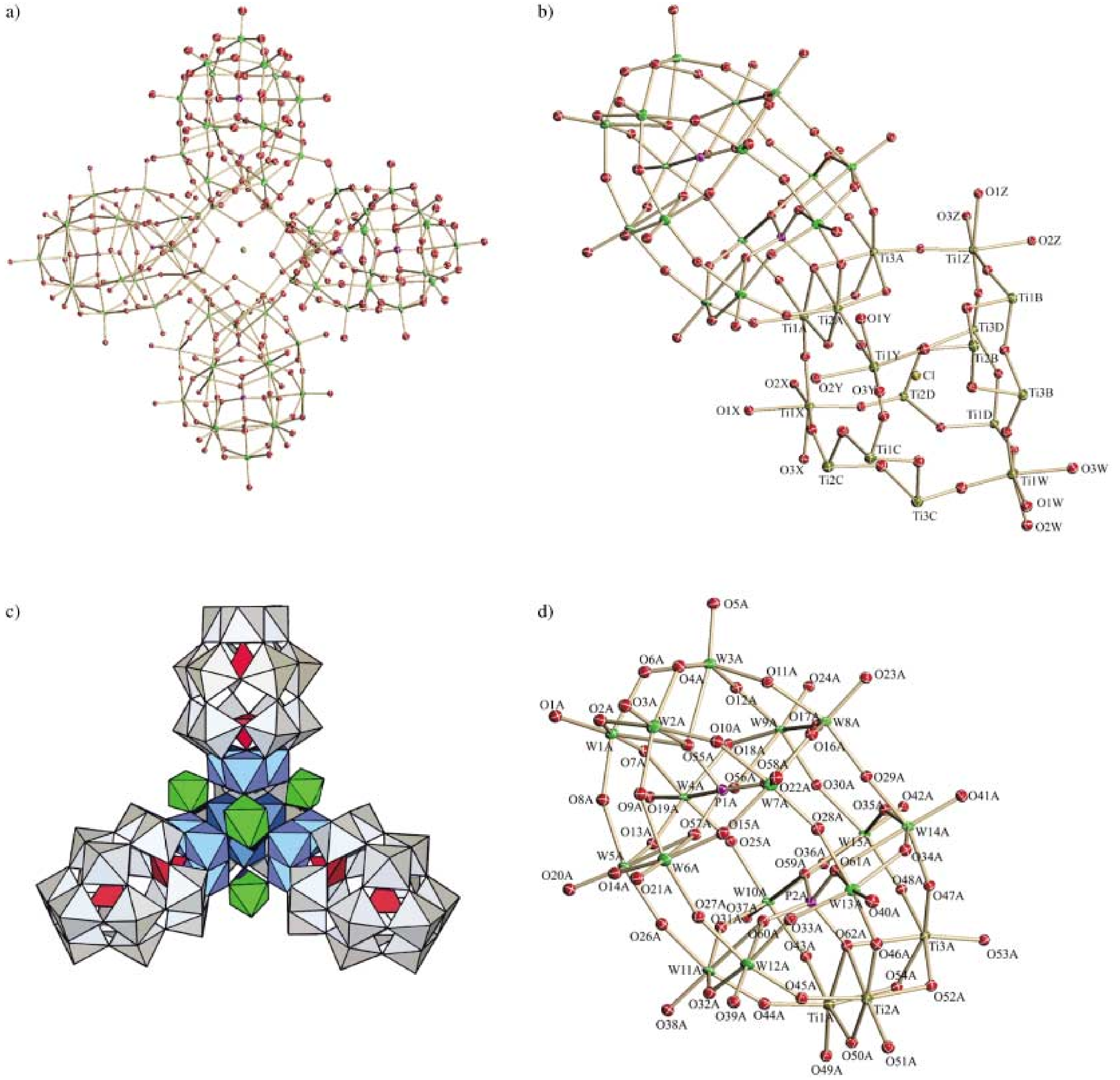

Figure 4. a) Molecular structure with 50% probability ellipsoids of the tetrameric, Ti-O-Ti-bridged anhydride form $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ (**1a**) containing one $Cl^-$ ion encapsulated in the central cavity, b) the partial structure containing one Dawson unit to which the three $Ti(OH)_3$ groups are linked, c) the polyhedral representation of **1a**, and d) the partial structure of Dawson unit A and the atom numbering.

With respect to Dawson unit A (Figure 4d), in the $W_3$ cap, the W–Ot (Ot: terminal oxygen) [1.69(2) – 1.74(2) Å], W–Oe (Oe: edge-sharing oxygen) [1.92(2) – 1.99(2) Å], W–Oc (W belt) (Oc: corner-sharing oxygen) [1.86(2) – 1.91(2) Å], and W–Oa (Oa: oxygen coordinated to P atom) [2.35(2) – 2.39(2) Å] distances are in the normal range.[1b] In the belt W(4 – 9), the W–O bond lengths were as follows: W–Ot [1.66(2) – 1.75(2) Å], W–Oe [1.89(2) – 1.95(2) Å], W–Oc (M cap) [1.91(2) – 1.97(2) Å], W–Oc in the same belt [1.87(2) – 1.92(2) Å], W–Oc between the belts [1.84(2) – 1.90(2) Å], and W–Oa [2.32(2) – 2.38(2) Å]. In the belt W(10 – 15), the W–O bond lengths were as follows: W–Ot [1.69(2) – 1.73(2) Å], W–Oe [1.88(2) – 1.97(2) Å], W–Oc (M cap) [1.81(2) – 1.88(2) Å], W–Oc in the same belt [1.88(2) – 1.95(2) Å], W–Oc between the belts [1.91(2) – 1.98(2) Å], and W–Oa [2.34(2) – 2.39(2) Å].

In the $Ti_3$ cap, the Ti–O bond lengths were as follows: Ti–Ot [1.77(2) – 1.79(2) Å], Ti–Oe [1.98(2) – 2.05(2) Å], Ti–Oc (W belt) [1.87(2) – 1.94(2) Å], and Ti–Oa [2.27(2) – 2.30(2) Å]. The Ti–O bond lengths between the three terminal oxygen atoms (O49A, O51A, O53A) of the $Ti_3$ cap and the bridging $Ti(OH)_3$ group were Ti1X–O49 1.81(2), Ti1Y–O51A 1.81(2), and Ti1Z–O53A 1.84(2) Å. The Ti-O-Ti angles between the $Ti_3$ cap and the three bridging $Ti(OH)_3$ groups were Ti1A-O49A-Ti1X 158.2(14), Ti2A-O51A-Ti1Y 152.0(14), and Ti3A-O53A-Ti1Z 160.0(14)°. Dawson unit A contains two central P atoms which reside in almost regular $PO_4$ tetrahedral environments: the $PO_4$ tetrahedron closest to the $Ti_3$ cap has P–O distances of 1.51(2)–1.59(2) Å and O-P-O angles of 106.4(13)–112.3(13)°, and the $PO_4$ tetrahedron closer to the $W_3$ cap has P–O distances of 1.51(2)–1.60(2) Å and O-P-O angles of 105.9(13)–113.3(13)°.

The bond valence sums (BVS),[8] calculated based on the observed bond lengths for Dawson units A, B, C, and D, corresponded reasonably to the formal valences of $Ti^{4+}$, $W^{6+}$, and $P^{5+}$, respectively. The BVS for Dawson unit A were in the range of 3.955–4.100 for the three Ti atoms, 5.649–6.455 for the fifteen W atoms, and 4.826–4.928 for the two P atoms, those of Dawson unit B were in the range of 4.052–4.129 for the three Ti atoms, 5.796–6.480 for the fifteen W atoms, and 4.780–4.902 for the two P atoms, those of Dawson unit C were in the range of 3.914–4.130 for the three Ti atoms, 5.639–6.566 for the fifteen W atoms, and 4.867–4.869 for the two P atoms, and those for Dawson unit D were in the range of 3.881–4.131 for the three Ti atoms, 5.733–6.599 for the fifteen W atoms, and 4.814–4.994 for the two P atoms. The BVS for the Ti atoms of the four bridging $Ti(OH)_3$ groups were in the range of 3.999–4.164.

The molecular weight of **1**, which contains 76 metal atoms ($W_{60}Ti_{16}$ nuclei), was more than 16000 and thus of the same order as those of the recently reported polyoxomolybdate-based giant molecules, $[H_xPMo_{12}\subset O_{40}CH_4Mo^{V}_{172}Fe^{III}_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}]\cdot ca.60\,H_2O$ (FW ~17000),[9a] $[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot ca.150\,H_2O$ (FW ~15900), and $[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}]\cdot ca. 80\,H_2O$ (FW ~16000),[9b] but is much smaller than those of $O_{40}CH_4Na_{16}[Mo^{VI}_{124}Mo^{V}_{28}O_{429}(\mu_3\text{-}O)_{28}H_{14}(H_2O)_{66.5}]\cdot ca. 300\,H_2O$ (FW ~23474.6)[9c] and $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$ (FW~26800).[9d] Complex **1** is different from the recently reported anhydride tetramers with tri-$Ti^{IV}$-substituted Dawson structures $[(P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$ (FW: 15700),[4, 5] and $[\{P_2W_{15}O_{57.5}Ti_3(OH)_3\}_4]^{24-}$,[6] which do not contain bridging $Ti(OH)_3$ groups. Thus at present there are at least two types of analytically pure polyoxotungstate-based giant "tetrapod" molecules that are based on tetrameric Ti-O-Ti-bridged anhydride forms of the tri-$Ti^{IV}$-substituted Dawson polyoxotungstate (if the encapsulated $Cl^-$ ion is not taken into account), namely, one with and one without bridging $Ti(OH)_3$ groups.

The number of titanium atoms and the structures of the titanium centers have a remarkable influence on the UV absorption properties in both solution and the solid state. For example, the positions of the adsorption edge energies for low-energy charge-transfer transitions in DR-UV spectra of various transition-metal oxides have been shown to correlate with the domain size of semiconductors and insulators.[10] The individual adsorption edge energies of anatase and rutile $TiO_2$ and $SrTiO_3$ have also been determined and the values are 3.2 eV (corresponding wavelength: 384 nm),[2c] 3.0 eV (410 nm),[2c] and 3.4 eV (364 nm),[2f] respectively. However, the correlation between the number of titanium atoms present in corner- or edge-sharing $TiO_6$ octahedra and the UV absorption properties at atomic/molecular levels has not hitherto been reported.

The UV/Vis absorption spectrum of **1** in water diplays an absorption at 289 nm ($\varepsilon = 4.13-4.19\times10^5\,mol^{-1}dm^3cm^{-1}$ based on the formula weight with $x = 16-19$, $y = 60-70$), which is ascribed to the $O\rightarrow Ti^{IV}$ LMCT band. This absorption band is shifted to a longer wavelength than that measured in water for the previously reported $Na_{26}H_7K_4[(P_2W_{15}Ti_3O_{60.5})_4Cl]\cdot 70\,H_2O$ (269 nm; $\varepsilon = 4.28\times10^5\,mol^{-1}dm^3cm^{-1}$). The wavelength of the LMCT band of **1** was also much longer than those of the Keggin-type dimeric Ti-O-Ti anhydride forms $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17\,H_2O$ ($\lambda_{max} = 257$ nm, $\varepsilon = 1.11\times10^5\,mol^{-1}dm^3cm^{-1}$) and $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12\,H_2O$ ($\lambda_{max} = 259$ nm, $\varepsilon = 1.48\times10^5\,mol^{-1}dm^3cm^{-1}$). Notably, the increased number of titanium(IV) octahedra in the polyoxoanion correlates linearly to the longer wavelength absorption in the UV/Vis absorption spectrum (Figure 5). The isolated $TiO_6$ octrahedra, which are surrounded by many $WO_6$ octahedra, construct $Ti_2$, $Ti_4$, and $Ti_6$ chromophores with corner-shared $TiO_6$ octahedra for the monomeric di-$Ti^{IV}$-substituted Keggin polyoxoanion $[1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$,[3a,b] dimeric di- and tri-$Ti^{IV}$-substituted Keggin polyoxoanions $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$[3h] and $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$,[3g] respectively. In addition, a $Ti_6$ chromophore with edge-shared $TiO_6$ octahedra with two $Ti(C_2O_4)_2$ bridging groups is constructed in the di-$Ti^{IV}$-substituted Dawson polyoxoanion $[P_4Ti_6W_{32}O_{132}]^{28-}$,[11] a $Ti_{12}$ chromophore with the edge-shared $Ti_3$ caps, and corner-sharing aggregation among the four Dawson units is present in the tri-$Ti^{IV}$-substituted Dawson polyoxoanion $[(P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$,[4, 5] and a $Ti_{16}$ chromophore with edge-shared $Ti_3$ caps and corner-sharing aggregation among the Dawson units and the bridging $Ti(OH)_3$ groups occurs in **1a**.

In conclusion, the water-soluble sodium salt **1** of a giant "tetrapod" inorganic molecule with approximately $T_d$ symmetry, $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ (**1a**), which contains 76 metal atoms ($W_{60}Ti_{16}$ nuclei) and has a molecular weight of more than 16000, was prepared and the molecular structure of **1a** was determined. Interestingly, UV/Vis absorption spectra suggest that the $Ti_{16}$ center in complex **1** shows the longest wavelength to date for the $O\rightarrow Ti^{IV}$ LMCT band in titanium-containing polyoxometalate-based molecules, and the wavelength of the LMCT band increased linearly with the increase in the number of titanium atoms in one molecule. These facts suggest that the $Ti_n$ chromophores formed in the Keggin and Dawson polyoxotungstates might be water-soluble, molecular models of solid $TiO_2$ or $SrTiO_3$ as light-semiconductor and/or photocatalysts.

## Experimental Section

**Synthesis of 1**: In a fume hood, $TiCl_4$ (ca. 1 mL, ca. 9.10 mmol) was added to water (50 mL) in an ice bath, and the white suspension was filtered through a folded filter paper (Whatman No. 5). Solid $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 19\,H_2O$[12] (5.0 g 1.15 mmol) was added to the clear colorless filtrate. The clear pale yellow solution was stirred for 30 min on a water bath at about 80 °C. After the pale yellow solution had been cooled to room temperature, the solvent was removed by using a rotary evaporator at 40 °C, until a powder began to form (ca. 10 mL volume). The volume was further concentrated to about 7 mL on a water bath at about 90 °C. The resulting clear yellow solution was left to stand at room temperature overnight. White crystalline solids that formed were collected on a medium glass frit

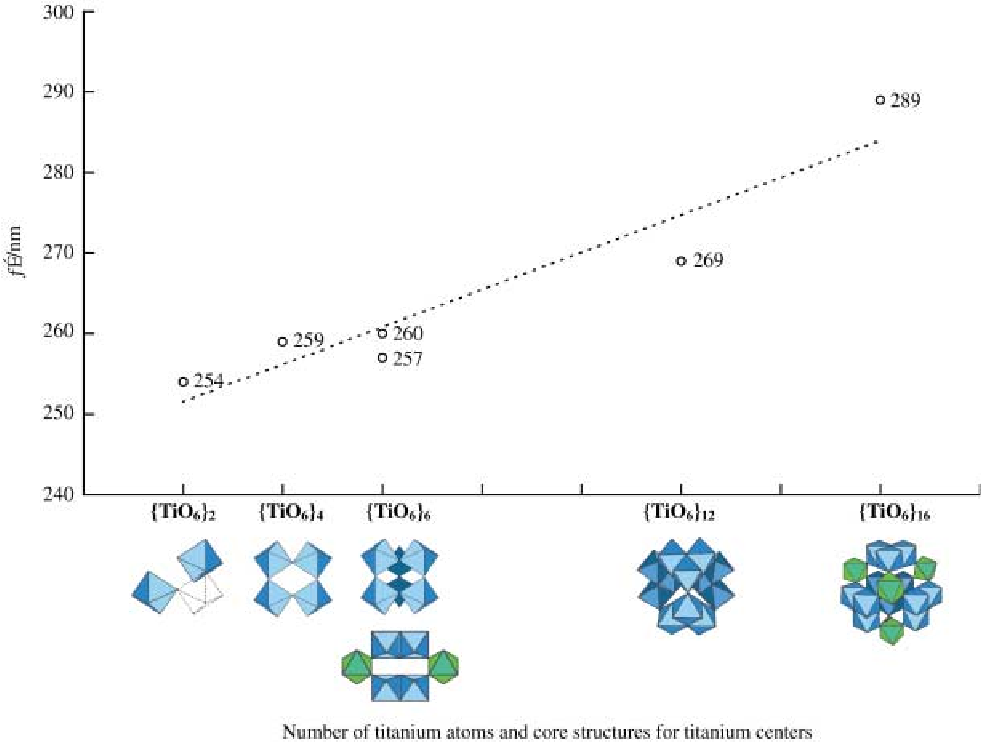

Figure 5. Plot of the wavelength of the O → Ti$^{IV}$ LMCT band ($\lambda$, nm) versus the number of titanium atoms, and the associated core structures for titanium centers in the titanium-containing polyoxometalate-based molecules. The blue octahedra represent $TiO_6$ substituted in polyoxometalate frameworks and the green octahedra represent bridged $Ti(C_2O_4)_2$ groups and $Ti(OH)_3$ groups for $[P_4Ti_6W_{32}O_{132}]^{28-}$ and $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ (**1a**), respectively. The UV absorption bands were observed at 254 nm for $[1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$, at 259 nm for $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$, at 257 nm for $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$, at 260 nm for $[P_4Ti_6W_{32}O_{132}]^{28-}$, at 269 nm for $[(P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$, and at 289 nm for **1a**.

(G3) and dried in vacuo for 2 h. The crude product was obtained as a white powder (2.2 – 2.8 g).

**Crystallization of 1**: The crude product (5.5 g) was dissolved in water (4 mL) by warming on a water bath at 90 °C. The clear pale yellow solution was evaporated to about 3 mL by using a water bath at 90 °C. The solution was divided into two portions, which were slowly evaporated at room temperature. After about 24 h, clear colorless granular crystals formed; one portion was used for X-ray diffraction measurements, and the other portion was used for the characterization as described below. The white powder was obtained in 5.61 – 5.69 % yield (0.29 g scale). Elemental analysis (%): found: H 0.18, Na 2.51, P 1.48, W 67.0, Ti 4.61, O 23.5, Cl 0.27; total 99.6 %. Calculated values were fitted within allowed errors for all $x = 16 - 19$ in $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}TiO_3\}_4Cl]$. Calcd for $x = 19$ or $H_{38}Na_{19}P_8W_{60}Ti_{16}O_{260}Cl$: H 0.23, Na 2.61, P 1.48, W 66.0, Ti 4.58, O 24.9, Cl, 0.21; calcd for $x = 16$ or $H_{41}Na_{16}P_8W_{60}Ti_{16}O_{260}Cl$: H 0.25, Na 2.21, P 1.49, W 66.3, Ti 4.60, O 25.0, Cl 0.21}. A weight loss of 6.39 % was observed during the course of drying at room temperature at $10^{-3} - 10^{-4}$ Torr overnight before analysis, suggesting the presence of 63 – 64 water molecules weakly solvated or adsorbed. TG/DTA under atmospheric conditions: a weight loss of 7.38 % was observed below 433 °C with endothermic points at 93 and 135 °C; calcd 7.39 % for $y = 74$ in $Na_{19}H_{26}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl] \cdot y H_2O$; IR (KBr disk) (polyoxometalate region): $\tilde{\nu} = 1090$vs, 954vs, 914s, 828vs, 656vs (br), 561s, 531s, 418w cm$^{-1}$; $^{31}P$ NMR (21.3 °C, $D_2O$): $\delta = -7.04, -13.77$; $^{183}W$ NMR (23.3 °C, $D_2O$): $\delta = -145.0$ (3 W × 4), $-181.5$ (6 W × 4), $-201.4$ (6 W × 4); UV/Vis absorption (water): $\lambda_{max} = 289$ nm ($\varepsilon$ 4.13 – 4.19 × $10^5$ mol$^{-1}$dm$^3$ cm$^{-1}$ based on the formula weight with $x = 16 - 19$, $y = 60 - 70$).

**X-ray crystallography for 1**: A colorless granular crystal of **1** (0.49 × 0.40 × 0.37 mm) was picked up with a cryo loop TM (from Hampton Research). The crystal was coated with liquid paraffin to prevent its degradation. Data were collected on a Bruker SMART APEX CCD diffractometer at 90 K in the range $4.7 < 2\theta < 43.9°$. The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (SHELXS-97, G. M. Sheldrick, **1990**) followed by subsequent difference Fourier calculations and refined by full-matrix least-squares procedure (SHELXS-97, G. M. Sheldrick, **1997**) (both programs from G. M. Sheldrick, University Göttingen, **1997**). The site occupancy factor of the oxygen as solvent water was refined. The site occupancy factor of the sodium was fixed at 0.5. Crystal data for $ClNa_{14.50}O_{369.12}P_8Ti_{16}W_{60}$, $M_r = 18319.88$, monoclinic, space group $P2(1)/c$ (no. 14), $a = 26.785(3)$, $b = 50.471(5)$, $c = 27.721(3)$ Å, $\beta = 94.525(2)°$, $V = 37359(7)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 3.253$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 18.88$ mm$^{-1}$. $R_{int} = 0.2301$, $R1 = 0.0804$, $wR2 = 0.1995$, GOF = 0.992 (189346 total reflections, 45560 unique reflections were $I > 2\sigma(I)$). The maximum and minimum residual density (14.12 and $-6.77$, respectively) holes were located at 0.85 Å from W2B and 0.54 Å from W2B, respectively. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germeny (fax: (+49) 7247-808-666); e-mail crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-3912214.

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