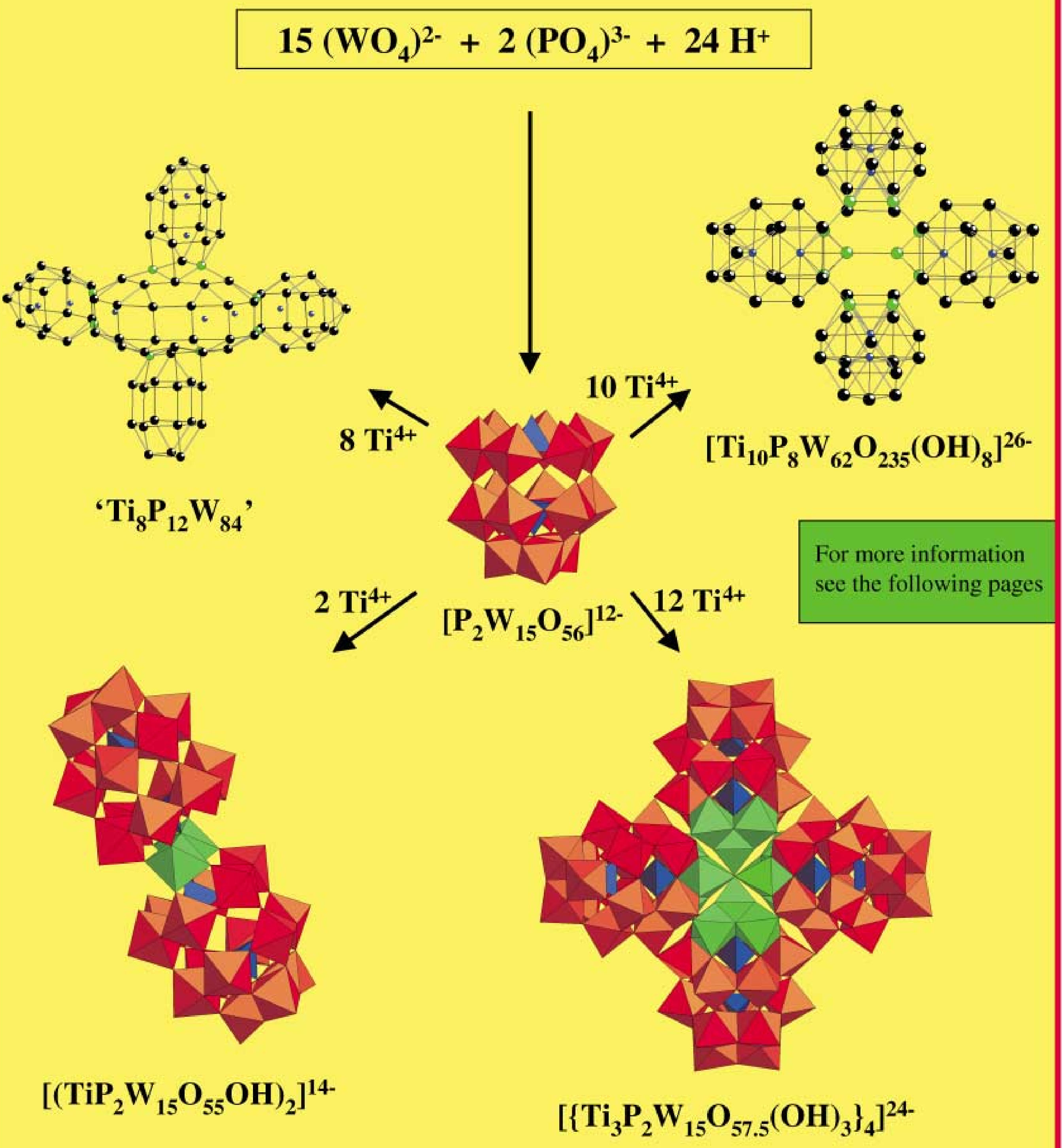
Formation of Supramolecular Polyoxoanions



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Supramolecular Structures of Titanium(IV)-Substituted Wells – Dawson Polyoxotungstates

Ulrich Kortz,*[a] Shadia S. Hamzeh,[b] and Niveen A. Nasser[b]

Dedicated to Professor Michael T. Pope on the occasion of his 70th birthday

Abstract: The novel, dimeric titanium(IV)-substituted phosphotungstate $[(\mathrm{TiP_2W_{15}O_{55}OH})_2]^{14-}$ (**1**) has been synthesized and characterized by IR and ^{31}P NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The polyanion consists of two $[\mathrm{P_2W_{15}O_{56}}]^{12-}$ Wells – Dawson moieties linked through two titanium(IV) centers. Polyanion **1** is a dilacunary species and represents the first Ti-containing sandwich-type structure. The titanium centers are octahedrally coordinated by three oxygen atoms of each $\mathrm{P_2W_{15}O_{56}}$ subunit. The edge-shared $\mathrm{TiO_6}$ units are symmetrically equivalent and have no terminal ligands. Polyanion **1** shows a chiral distortion within each $\mathrm{P_2W_{15}Ti}$ fragment. We also report on the structural characterization of the tetrameric, supramolecular species $[\{\mathrm{Ti_3P_2W_{15}O_{57.5}(OH)_3}\}_4]^{24-}$ (**2**). Polyanion **2** is composed of four equivalent $\mathrm{P_2W_{15}Ti_3}$ fragments, fused together through terminal $\mathrm{Ti{-}O}$ bonds, leading to a structure with T_d symmetry.

Keywords: cluster compounds · polyoxometalates · self-assembly · titanium · tungsten

Introduction

The class of polyoxometalates has been known for almost 200 years, but many more members of this unique family of metal – oxygen clusters remain to be discovered.[1] Interest in polyoxoanions keeps on increasing worldwide, mainly because of the enormous structural variety, and the accompanying multitude of potential applications (e.g. in catalysis, medicine).[2–6] Many novel polyoxoanions have unexpected shapes and sizes, but some consist of subunits or fragments of known species. Indeed, the identity of some species could have been predicted but even in these cases the determination of the required synthetic conditions is far from trivial. The mechanism of formation of polyoxoanions is still not well understood (best described by self-assembly), so that the design of novel polyoxoanions is virtually impossible. An additional complication is the fact that an unequivocal structural characterization of novel polyoxoanions almost always requires single-crystal X-ray diffraction.

During the last couple of years some amazingly large polyoxoanions have been isolated. Müller et al. determined the structures of families of ball- and ring-shaped polyoxomolybdates, some with more than 350 molybdenum atoms.[7] Their synthetic strategy is based on the formation of mixed-valence ($\mathrm{Mo^V/Mo^{VI}}$) building blocks, which contain basic surface oxygen atoms that promote molecular growth to very large clusters of nanoscale dimensions. Pope et al. isolated a large polyoxotungstate containing 148 tungsten atoms, but their strategy relies on lanthanide and actinide ions acting as linkers of polyoxotungstate fragments.[8]

Polyoxometalates substituted by titanium(IV) ions are of interest for structural reasons as well as for their properties. Some Ti-containing polyoxotungstates have shown catalytic activity as well as potential applications in medicine.[9] It is well documented that incorporation of vanadium(V) or niobium(V) ions in a fully oxidized polyoxotungstate increases the basicity of the species. This approach allowed binding of organometallic fragments or even Ir nanoclusters to polyoxoanions.[10] Incorporation of $\mathrm{Ti^{IV}}$ instead of $\mathrm{V^V}$ or $\mathrm{Nb^V}$ ions should lead to an even more pronounced effect. Indeed it has been observed that titanium atoms incorporated in polyoxoanions are reactive sites with a strong tendency towards dimer formation through $\mathrm{Ti{-}O{-}Ti}$ bonds as seen in $[(\alpha\text{-}\mathrm{Ti_3PW_9O_{38.5}})_2]^{12-}$, $[(x\text{-}\mathrm{Ti_3SiW_9O_{38.5}})_2]^{14-}$ ($x = \alpha$, β), $[(\alpha\text{-}\mathrm{Ti_3GeW_9O_{38.5}})_2]^{14-}$, and $[(\alpha\text{-}1,2\text{-}\mathrm{Ti_2PW_{10}O_{39}})_2]^{10-}$.[11] Nevertheless two monomeric species have also been structurally characterized.[12] Interestingly all of these monomeric and dimeric species are polyoxotungstates based on the Keggin structure as a basic building block.

We have been interested in Ti-substituted polyoxometalates for a few years, mainly because of the attractive

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properties that can be expected from such compounds. Our interest was particularly triggered by the paper of Meng and Liu, who reported on the synthesis of a titanium(IV)-substituted Wells–Dawson ion.[13] The authors suggested the formula $[Ti_3P_2W_{15}O_{62}]^{12-}$ based on IR, UV, and ^{183}W NMR spectroscopy, electrochemistry, and elemental analysis. However, the study of Meng and Liu did not rule out a dimeric product, nor did it show any protonation (it is highly likely that some of the oxygen atoms associated with the Ti centers are protonated). Two years later Qu et al. also reported on $[Ti_3P_2W_{15}O_{62}]^{12-}$ without providing experimental proof for the monomeric nature of this species.[14] We decided that a single-crystal X-ray diffraction study was needed to determine the structure of the product unequivocally.

While our work on this topic was in progress Nomiya et al. reported on the synthesis and characterization of a tetrameric species composed of four tri-titanium(IV)-substituted Wells–Dawson ions.[15] Based on ultracentrifugation molecular weight measurements the authors were able to conclude that the product was a tetramer and they suggested three plausible structures. However, they could not pin down which of these was correct. Then Nomiya et al. tried to obtain single crystals of their product suitable for X-ray diffraction, but without success.

Here we report for the first time on the structural characterization of titanium(IV)-substituted polyoxoanions of the Wells–Dawson type. We isolated dimeric and tetrameric structures of the $Ti^{IV}/[P_2W_{15}O_{56}]^{12-}$ system.

Results and Discussion

The novel polyoxoanion $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$ (**1**) consists of two lacunary $[P_2W_{15}O_{56}]^{12-}$ Wells–Dawson moieties linked through two Ti^{4+} ions (Figure 1). Polyanion **1** belongs to the well known class of sandwich-type structures, but it represents the first Ti-containing species.[16] Interestingly the two Wells–Dawson fragments are linked by only two, instead of four Ti atoms in **1**. The titanium centers are octahedrally coordinated by three oxygen atoms of each $P_2W_{15}O_{56}$ subunit. The edge-shared TiO_6 units are symmetrically equivalent and have no terminal ligands. Almost all known sandwich-type polyoxoanions of the Keggin and Wells–Dawson type contain four transition-metal centers.[16] Very recently a few sandwich-type ions with only two or three incorporated transition metals were reported and all of them are based on the Wells–Dawson structure. Hill et al. were the first to describe the di-iron(III)-substituted polyanion $[Fe_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$, and in this compound the two equivalent exterior positions are occupied by sodium ions in the solid state.[17] Hill et al. also showed that this polyanion reacts with Cu^{2+} or Co^{2+} ions in aqueous solution leading to a trisubstituted, mixed-metal sandwich-type polyanion.[18] Very recently the same authors described the tri-iron(III)-substituted polyanion, $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$.[19] Ruhlmann et al. reported on the di- and trisubstituted cobalt(II) analogues of this polyanion.[20] The first example of a trisubstituted, sandwich-type polyanion based on the Keggin fragment was reported by Kortz et al.[21]

Abstract in German: *Das neuartige, dimere Titanium(IV)-substitutierte Phosphowolframat* $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$ *(**1**) wurde synthetisiert und charakterisiert durch IR,* ^{31}P *NMR Spektroskopie, Elementaranalyse und Einkristallröntgenstrukturanalyse. Das Polyanion besteht aus zwei* $[P_2W_{15}O_{56}]^{12-}$ *Wells-Dawson Einheiten die durch zwei Titanium(IV) Zentren verknüpft sind. Polyanion **1** ist eine dilakunare Spezies und stellt die erste Titan-haltige Verbindung mit einer Sandwich-Struktur dar. Die Titanzentren sind oktaedrisch koordiniert von drei Sauerstoffatomen jeder* $(P_2W_{15}O_{56})$ *Untereinheit. Die kantenverknüpften* TiO_6 *Einheiten sind symmetrisch äquivalent und besitzen keine terminalen Liganden. Das Polyanion **1** zeigt eine chirale Verzerrung innerhalb jedes* $(P_2W_{15}Ti)$ *Fragments. Wir berichten auch von der strukturellen Charakterisierung der tetrameren, supramolekularen Spezies* $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ *(**2**). Das Polyanion **2** ist aus vier äquivalenten* $(P_2W_{15}Ti_3)$ *Fragmenten aufgebaut, die über die terminalen Ti-O Bindungen verknüpft sind. Diese Anordnung resultiert in einer Struktur mit* T_d *Symmetrie.*

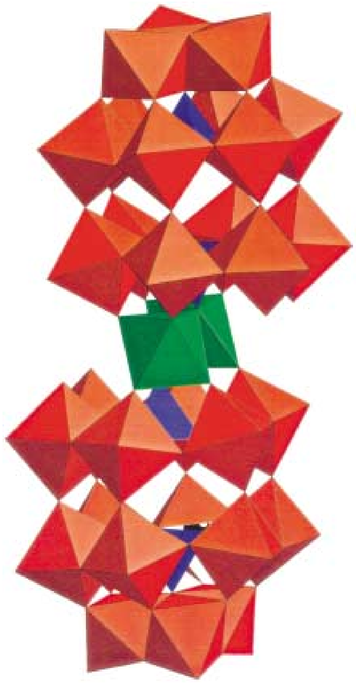

Figure 1. Polyhedral representation of $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$ (**1**). The PO_4, WO_6, and TiO_6 polyhedra are shown in blue, red, and green, respectively.

In all of the above compounds the external lacunary sites are occupied by sodium ions, which seem to fit the octahedral vacancy extremely well. This is further supported by the observation that the di- and trisubstituted species (with two and one sodium centers in the vacancies, respectively) are more stable than their corresponding tetrasubstituted analogues.[17, 19, 21] Polyanion **1** represents the first lacunary sandwich-type polyanion that does not contain a sodium ion substituting for the first-row transition metals. Here the lacunary sites are surrounded and stabilized by ammonium ions and/or water molecules in the solid state (and most likely also in solution). It should be mentioned that our attempts to crystallize **1** as a sodium salt were unsuccessful and the same applies to all other alkali metal ions. The only counterion that resulted in single crystals suitable for X-ray diffraction was the ammonium ion.

Polyanion **1** has a crystallographic inversion center and the asymmetric unit with the labeling scheme is shown in Figure 2. The titanium(IV) centers are coordinated by six oxygen atoms in an octahedral fashion ($d_{Ti-O} = 1.79-2.19(1)$ Å). All bonds involve bridging (μ_2- and μ_3-)oxo groups and as expected the Ti–O bonds to triply bridging oxygen atoms are somewhat longer than those to doubly bridging oxygen atoms.

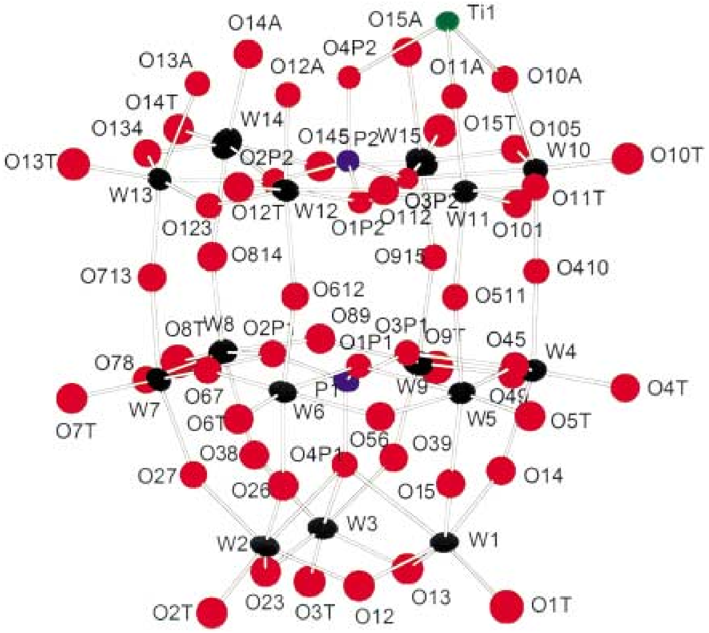

Figure 2. Ball-and-stick representation of the asymmetric unit of $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$ (**1**) showing 50% probability ellipsoids and the labeling scheme.

Bond-valence sum (BVS) calculations confirm that O15A is protonated in the solid state (see Figure 2).[22] Interestingly O14A is not protonated which results in a chiral distortion within each $P_2W_{15}Ti$ half unit of **1**. This subtle phenomenon was first discovered by Pope for molybdophosphates of the 1:9 and 2:18 type.[23] The sequence of alternatingly long and short *trans* O-W-O bond lengths of interest in **1** is: HO15A-W15-O915-W9-O39-W3-O38-W8-O814-W14-O14A (the corresponding bond lengths are: 2.15, 1.81, 2.00, 1.84, 2.00, 1.86, 2.01, 1.81, 2.14, 1.77(1) Å). It becomes apparent that **1** is assembled of a *d*-$(P_2W_{15}Ti)$ and an *l*-$(P_2W_{15}Ti)$ subunit resulting in the *meso* product with C_i symmetry. Most likely this symmetry is maintained in solution and explains why the two vacancies of polyanion **1** are not occupied by sodium ions, which are present in solution.

The above-mentioned BVS calculations suggest that the charge of **1** is minus fourteen which requires an equal number of ammonium counterions in the lattice for charge balance reasons. However, X-ray diffraction did not allow us to distinguish them from water molecules of hydration. Nevertheless the results of elemental analysis are in good agreement with the proposed formula.

It is of interest to examine the junctions of the two TiO_6 octahedra with both Wells–Dawson fragments in **1** to identify which Baker–Figgis isomers are present.[24] Both junctions are of the α-type so that the complete configuration of this polyanion is best described as αααα-**1**. This is in complete agreement with the observations of Hill et al. for the di-iron substituted species $[Fe_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$.[17a]

The second polyoxoanion $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**) consists of four lacunary $[P_2W_{15}O_{56}]^{12-}$ Wells–Dawson moieties linked through a core of twelve Ti^{4+} ions (see Figures 3–5). The tetrameric, supramolecular polyanion **2** has ideally T_d symmetry and bears a striking resemblance to an sp^3-hybrid orbital. Formation of **2** could be visualized by fusion of four $Ti_3P_2W_{15}$ fragments involving the end of the Wells–Dawson ion that has been activated by insertion of three Ti centers. The $Ti_{12}O_{46}$ core of polyanion **2** consists of four groups of three edge-shared, corner-linked TiO_6 octahedra (Figure 6). This rare arrangement resembles one set of the four corner-shared faces of an octahedron. Some time ago Sasaki and Nishikawa discovered such a geometry for the molybdoarsenate $[As_4Mo_{12}O_{50}]^{8-}$ which was described as a "reversed Keggin structure".[25] Since then some derivatives of the structural type $[Mo_{12}O_{46}(AsR)_4]^{4-}$ ($R = CH_3$, C_2H_4OH, C_6H_5, *p*-$C_6H_4NH_3^+$, *p*-C_6H_4CN, C_6H_4-4-COOH, C_6H_3-4-OH-3-NO_2, C_6H_4-4-OH, C_6H_4-4-NH_2) have been synthesized.[26] It seems that the "reversed" Keggin ion is significantly stabilized by the four tetrahedral groups which occupy the open triangular faces. Interestingly four potassium ions take over this role in polyanion **2** (Figure 6). The potassium ions are bound to a μ_2-oxo group of each of the three adjacent Ti_3O_{13} triads (K$\cdots$O, 3.02–3.28(1) Å). The coordination spheres of the potassium ions are completed by four water molecules (K$\cdots OH_2$, 3.25–3.36(2) Å; Figure 6).

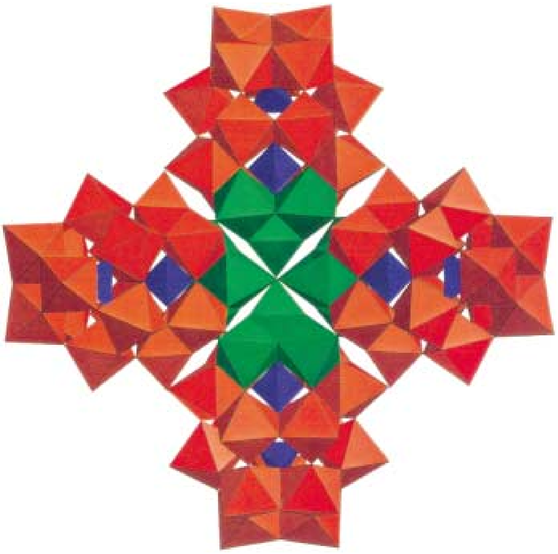

Figure 3. Polyhedral representation of $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**) with a bird's-eye view along a twofold rotation axis. The color code is the same as in Figure 1.

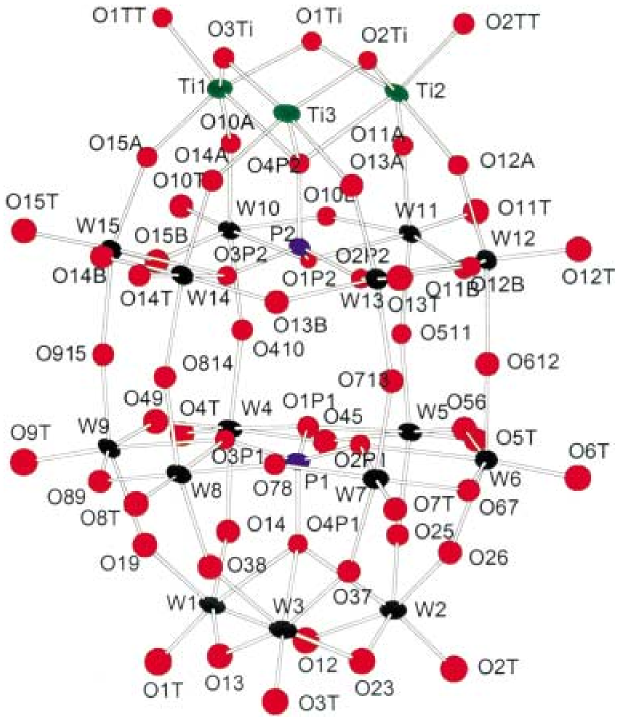

Figure 4. Ball-and-stick representation of the asymmetric unit of $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**) showing 50% probability ellipsoids and the labeling scheme.

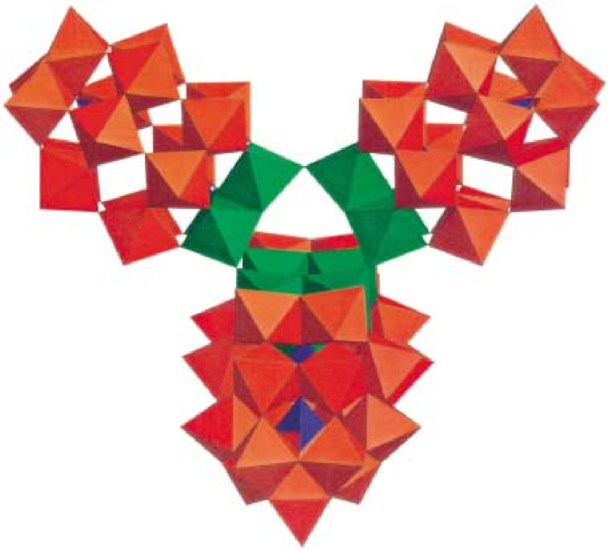

Figure 5. Polyhedral representation of $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**) with a view along a mirror plane. The color code is the same as in Figure 1.

Polyanion **2** represents the first example of a tetrameric polyoxoanion based on the Wells–Dawson structure. The only other known tetrameric tungstophosphate is $[P_8W_{48}O_{184}]^{40-}$, but it is a cyclic species composed of four $[H_2P_2W_{12}O_{48}]^{12-}$ fragments.[27] Interestingly Hill et al. reported on a niobium-substituted, Keggin-based tungstosilicate with T_d symmetry, $[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]^{20-}$.[28] In this case the four (Nb_3SiW_9) Keggin fragments are linked to each other through a central Nb_4O_6 core.

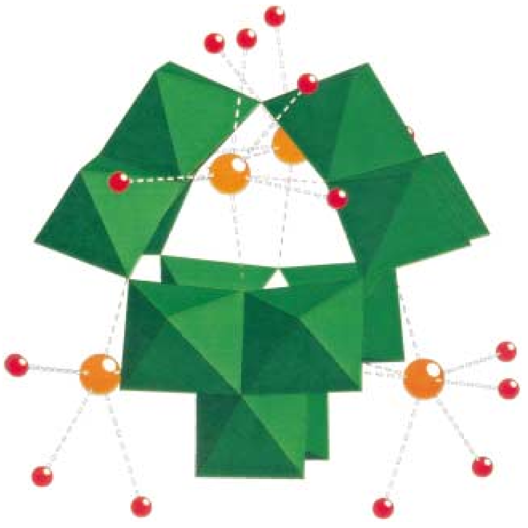

Figure 6. Polyhedral representation of the central $(Ti_{12}O_{46})$ fragment of $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**) showing the arrangement of the twelve TiO_6 octahedra. Potassium ions are shown in orange and their terminal water molecules are red.

The 12 equivalent titanium(IV) centers in **2** are coordinated by six oxygen atoms in a distorted octahedral fashion (d_{Ti-O} = 1.81–2.31(1) Å). As expected the distortion is of an axial type, because the Ti–O–P (μ_4-oxo) bonds are the longest and the bonds *trans* to them (Ti–O–Ti, μ_2-oxo) are the shortest. The four equatorial bonds (Ti–O–Ti and Ti–O–W, all μ_2-oxo) are fairly similar in length. This observation reflects the coordination environment of the tungsten sites in **2**. The bond lengths and angles of the tungsten–oxo framework are within the usual ranges.

Recently Nomiya et al. identified the tetrameric nature of **2** based on ultracentrifugation studies.[15] They were unable to obtain single crystals suitable for X-ray diffraction and therefore they proposed three different structures: two cyclic arrangements with C_{2v} and C_{4v} symmetry, respectively, and a third structure with T_d symmetry. The authors considered the latter structural type as the most plausible and we have proven them to be right. However, the formula and the charge Nomiya proposed ($[\{Ti_3P_2W_{15}O_{60.5}\}_4]^{36-}$ versus $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$ (**2**)) was not exactly correct because of protonation.

Bond-valence sum calculations indicate that a total of twelve protons are bound to surface oxygen atoms of **2**.[22] Interestingly, the μ_2-oxo sites of all three Ti–O–Ti bridges within each Wells–Dawson fragment are protonated, whereas the μ_2-oxo sites of the six Ti–O–Ti bridges linking the four Wells–Dawson fragments to each other are not protonated. This means that the total charge of the tetrameric polyanion **2** is −24. For charge balance a total of twenty ammonium counterions must be present in the lattice in addition to the four K^+ ions identified by X-ray diffraction. The remaining 77 oxygen atoms in the lattice are labeled as water molecules of hydration. It was impossible to distinguish the ammonium ions from water molecules by X-ray diffraction.

We believe that the counterions play a crucial role in the formation and crystallization of **2**. This is supported by the fact that the atom labeled O32W is located on a special crystallographic position exactly in the middle of the central cavity of **2**. Most likely it is an ammonium ion, which acts as a template for the formation of **2**. It must be realized that the NH_4^+ ion has the same T_d symmetry as polyanion **2**. The central ammonium ion is surrounded by the twelve protonated oxygen atoms of the titanium–oxo fragment ($d_{N\cdots OH} = 3.09-3.12(1)$ Å). Furthermore the ($Ti_{12}O_{46}$) core of polyanion **2** is stabilized by four equivalent potassium ions, which probably play an important role during the self-assembly process of this supramolecular species (see Figure 6). We also discovered that the presence of ammonium ions aids significantly in the crystallization of **2**. Interestingly, polyanion **2** can be synthesized and crystallized in a one-pot, one-step procedure if ammonium and potassium ions are both present (see Experimental Section). Therefore we observe a unique interplay of two different counterions during the formation and crystallization of polyoxoanion **2**.

All attempts to obtain a pure compound following the synthetic method of Meng and Liu failed.[13] Nevertheless we attempted to identify the speciation of their product mixture by ^{31}P NMR spectroscopy and crystallization. Redissolution of Meng and Liu's potassium salt in D_2O at pH 2 resulted in a ^{31}P NMR spectrum with predominantly two singlets ($\delta = -7.1$, -13.5 ppm) which is attributed to the presence of polyanion **2**. However, in addition we observed several weaker signals between $\delta = -5$ and -14 ppm, indicating the presence of by-products. We attempted to grow single crystals from this solution to obtain structural information about the compounds present. The presence of ammonium ions was again essential for good crystal growth. We were able to identify three different crystalline phases which we investigated by single-crystal X-ray diffraction. In addition to polyanion **2** we discovered another tetrameric species **3** for which we could only identify the positions of all heavy atoms (W, Ti, P) due to poor crystal quality.[29] Nevertheless, we obtained a reliable skeleton of this structure and we suggest the molecular formula $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_2\{Ti_2P_2W_{16}O_{60}(OH)\}_2]^{26-}$.[30] Polyanion **3** consists of two ($Ti_3P_2W_{15}$) and two ($Ti_2P_2W_{16}$) fragments leading to a structure with C_{2v} symmetry. We also discovered the supramolecular polyoxoanion **4**, but the poor quality of the data set allowed only to locate the tungsten, titanium and phosphorus atoms.[31] We describe polyanion **4** by the preliminary and incomplete formula "$Ti_8P_{12}W_{84}$" or "$(Ti_2P_2W_{15})_2(Ti_2P_2W_{16})_2(P_2W_{11})_2$". The latter description indicates better that this polyanion is composed of four Wells–Dawson fragments and two fused (P_2W_{12}) fragments. Currently we are in the process of identifying reaction conditions that lead to pure **3** and **4**.

Our results indicate that interaction of titanium(IV) with the Wells–Dawson ion $[P_2W_{15}O_{56}]^{12-}$ in aqueous solution can lead to a variety of products with unexpected, supramolecular structures. The title compounds **2**, **3**, and **4** represent the largest phosphotungstates known to date and **4** is the second largest polyoxotungstate ever reported. They emphasize the strong tendency of titanium(IV) to form Ti–O–Ti bonds in aqueous solution.

Experimental Section

Synthesis: All reagents were used as purchased without further purification. $Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ was synthesized according to the method of Contant.[32]

$(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12H_2O$: A sample of $TiO(SO_4)$ (0.200 g, 1.25 mmol) was added to H_2O (40 mL) and the mixture was stirred. Then 6M HCl (1.4 mL), followed by $Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ (5.00 g, 1.13 mmol) were added in small portions. The solution was stirred for 4 h at room temperature and then refluxed for 1 h. After the mixture had been cooled to room temperature, 10.0 g NH_4Cl was added and after 10 min a white precipitate was isolated by filtration and air dried. The solid was redissolved in H_2O (ca. 40 mL) upon heating and the pH was adjusted to 2 by addition of 6M HCl. Then the solution was left standing open to the air. After about 3–4 weeks a white crystalline solid was isolated (1.60 g, yield 35%). IR for $(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12H_2O$: $\tilde{\nu} = 1090$(s), 1017(sh), 972(sh), 954(s), 908(s), 819(s), 739(sh), 639(s), 560(m), 526(m), 480(sh) cm^{-1}. Elemental analysis (%) calcd for $(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12H_2O$: P 1.6, W 69.0, Ti 1.2, N 2.5; found: P 1.6, W 68.2, Ti 1.1, N 3.0; ^{31}P NMR (D_2O, 293 K) of $(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12H_2O$: $\delta = -10.5$ (singlet, 2P), -13.3 (singlet, 2P).

$K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77H_2O$: A sample of $TiO(SO_4)$ (0.600 g, 3.80 mmol) was added to H_2O (40 mL) and the mixture was stirred. Then 6M HCl (1.4 mL) followed by KCl (0.112 g, 1.50 mmol), NH_4Cl (0.321 g, 6.00 mmol), and $Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ (5.00 g, 1.13 mmol) were added. The solution was stirred for 60 min at room temperature and then filtered. The solution was left standing open to the air. After about 3–4 weeks a white crystalline solid was isolated (1.60 g, yield 32%). IR for $K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77H_2O$: $\tilde{\nu} = 1122$(sh), 1089(s), 1015(sh), 967(sh), 949(s), 918(s), 891(sh), 832(s), 793(sh), 694(s), 658(s), 598(sh), 564(m), 525(m) cm^{-1}. Elemental analysis (%) calcd for $K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77H_2O$: P 1.4, W 62.5, Ti 3.3, N 1.6, K 0.9; found P 1.6, W 63.2, Ti 3.5, N 1.8, K 0.8; ^{31}P NMR (D_2O, 293 K) of $K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77H_2O$: $\delta = -7.3$ (singlet, 4P), -13.8 (singlet, 4P).

Elemental analysis was performed by Kanti Labs Ltd. in Mississauga, Canada. The IR spectrum was recorded on a Nicolet Avatar spectrophotometer using KBr pellets. ^{31}P NMR spectra were obtained on a Bruker AC300 spectrometer at 121.5 MHz using D_2O as a solvent in 5 mm tubes.

Table 1. Crystal data and structure refinement for $(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12H_2O$ (**NH₄-1**) and $K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77H_2O$ (**KNH₄-2**).

	NH_4-1	**KNH_4-2**
formula	$H_{80}N_{14}O_{124}P_4Ti_2W_{30}$	$H_{246}K_4N_{20}O_{319}P_8Ti_{12}W_{60}$
M_w [$g\,mol^{-1}$]	7996.1	17642.6
crystal color	colorless	colorless
crystal system	triclinic	tetragonal
crystal size [mm^3]	0.24 × 0.16 × 0.06	0.20 × 0.16 × 0.14
space group (no.)	$P\bar{1}$ (2)	$I4_1/a$ (88)
unit cell dimensions		
a [Å]	12.743(3)	25.085(2)
b [Å]	12.759(3)	25.085(2)
c [Å]	19.770(4)	49.367(6)
α [°]	91.843(4)	90
β [°]	93.491(5)	90
γ [°]	105.881(5)	90
volume [Å^3]	3082.2(12)	31065(5)
Z	1	4
ρ_{calcd} [$Mg\,m^{-3}$]	4.297	3.728
abs. coeff. [mm^{-1}]	28.159	22.621
reflections (unique)	14673	19181
reflections (obs.)	9969	14607
$R(F_o)$[a]	0.059	0.060
$R_w(F_o)$[b]	0.143	0.133
diff. peak [eÅ^3]	3.800	4.969
diff. hole [eÅ^3]	−4.350	−2.994

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

Chemical shifts are reported with respect to external 85% H_3PO_4 as a standard.

X-ray crystallography: Crystal data and structure refinement details for $(NH_4)_{14}[(TiP_2W_{15}O_{55}OH)_2]\cdot 12\,H_2O$ (**NH_4–1**) and $K_4(NH_4)_{20}[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]\cdot 77\,H_2O$ (**KNH_4–2**) are summarized in Table 1. The respective crystals were mounted on a glass fiber for indexing and intensity data collection at 173 K on a Bruker SMART-CCD single-crystal diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve the structures and to locate the heavy atoms (SHELXS86). Then the oxygen atoms were found from successive difference maps (SHELXL93). It was not unexpected that the ammonium counterions could not be distinguished from water molecules by X-ray diffraction. The actual number of NH_4^+ ions was determined from charge-balance considerations and elemental analysis. Routine Lorentz and polarization corrections were applied and an absorption correction was performed by using the SADABS program.[33]

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-412880 and CSD-412881, respectively.

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[29] Crystal data for **3**: colorless needle, $0.30 \times 0.08 \times 0.05$ mm^3, $a = 27.110(5)$, $b = 34.365(7)$, $c = 36.821(7)$ Å, $V = 34303(12)$ Å^3, $T = 20\,^\circ$C, *Imma*, $Z = 4$.

[30] The molecular formula for **3** is based on the assumption that only the Ti–O–Ti bonds within a Wells–Dawson fragment are protonated (in agreement with **2**).

[31] Crystal data for **4**: colorless block, $0.24 \times 0.18 \times 0.12$ mm^3, $a = 21.855(4)$, $b = 28.211(5)$, $c = 38.850(7)$ Å, $\alpha = 104.017(3)$, $\beta = 104.746(4)$, $\gamma = 90.551(4)^\circ$, $V = 22409(11)$ Å^3, $T = -100\,^\circ$C, $P\bar{1}$, $Z = 1$.

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