DALTON
FULL PAPER

Synthesis and characterization of tri-titanium(IV)-1,2,3-substituted α-Keggin polyoxotungstates with heteroatoms P and Si. Crystal structure of the dimeric, Ti–O–Ti bridged anhydride form $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ and confirmation of dimeric forms in aqueous solution by ultracentrifugation molecular weight measurements†

Kenji Nomiya,*[a] Mizuto Takahashi,[a] Katsunori Ohsawa[a] and Jason A. Widegren[b]

[a] *Department of Materials Science, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-1293, Japan. E-mail: nomiya@chem.kanagawa-u.ac.jp*
[b] *Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA*

Received 2nd April 2001, Accepted 19th June 2001
First published as an Advance Article on the web 6th September 2001

The preparation and characterization of the α-Keggin-type, novel tri-Ti^{IV}-1,2,3-substituted polyoxotungstates with heteroatoms P and Si are described. The molecular structure of $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1**, obtained as a main product (30.4% yield) from the 1 : 3 molar ratio reaction of tri-lacunary precursor $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ with $Ti(SO_4)_2\cdot 4H_2O$ in aqueous solution, was determined by X-ray structure analysis. It had the dimeric, anhydride structure formed by three Ti–O–Ti bonds linking two Keggin $[\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{40}]^{9-}$ units. From the filtrate after **1** was filtered off, a different compound **2** was obtained as a minor product. A related α-Keggin tri-Ti^{IV}-1,2,3-substituted polyoxotungstate with heteroatom Si, the dimeric anhydride form $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3**, was obtained as a main product (31.1% yield) from a 1 : 3 molar ratio reaction of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 15H_2O$ with $Ti(SO_4)_2$. Ultracentrifugation molecular weight measurements under less acidic conditions revealed that **1** and **3** were present as dimers in aqueous solution. Characterization of **1** and **3** was also accomplished by complete elemental analyses, TG/DTA, FTIR and solution (^{31}P and ^{183}W) NMR spectroscopies.

Introduction

Polyoxoanions are molecular metal-oxide clusters which are of current interest as soluble analogs of heterogeneous metal oxides.[1] In particular, the polyoxotungstates substituted with early transition metal (d^0) ions such as V^V and Nb^V have been intensively studied,[2,3] because they allow covalent bonding of organometallic fragments to specific binding sites on the polyoxoanion surface.[3,4]

Substitution of W^{VI} in polyoxoanions with Ti^{IV} is particularly interesting, because of the expected, much higher basicity of the resulting polyoxoanion. The ionic radius of Ti^{IV} (0.75 Å) is close to that of W^{VI} (0.74 Å), a fact which suggests that Ti^{IV} should fit nicely into the polyoxotungstate framework. However, there is a significant issue of Ti–O–Ti anhydride formation.[5c,d,g] Indeed, the tri-Ti^{IV}-1,2,3-substituted Keggin polyoxotungstates heretofore are the dimeric, Ti–O–Ti bridged anhydride forms, *e.g.* $[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$ **4**[5c] which is formed from two $[A\text{-}\beta\text{-}SiW_9Ti_3O_{40}]^{10-}$ Keggin units, and $[\alpha,\alpha\text{-}Ge_2W_{18}Ti_6O_{77}]^{14-}$ **5**[5d] which is formed from two $[A\text{-}\alpha\text{-}GeW_9Ti_3O_{40}]^{10-}$ Keggin fragments. Also, recently prepared tri-Ti^{IV}-substituted Dawson polyoxotungstates were found to be the tetrameric Ti–O–Ti anhydride $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$ **6**,[5g] which is formed from four $[\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62}]^{12-}$ Dawson fragments to give the T_d tetramer. It is difficult to prepare the monomeric forms from these anhydride forms.[5j] On the other hand, interconversion between a monomer and a dimer has been recently found in the mono-Ti^{IV}-substituted Keggin polyoxotungstate, $[\alpha\text{-}PW_{11}TiO_{40}]^{5-}$.[5i] Crystal structures of the monomeric, mono- and di-Ti^{IV}-substituted Keggin polyoxotungstates have been previously determined in $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ [5b,f] and $[\alpha\text{-}PW_{11}TiO_{40}]^{5-}$.[5a,e]

We have examined the reactions of tri-lacunary Keggin precursors $[A\text{-}PW_9O_{34}]^{9-}$ and $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ with $Ti(SO_4)_2$ in aqueous solution. In this work, the crystal structure of the dimeric, Ti–O–Ti bridged anhydride form of the tri-Ti^{IV}-1,2,3-substituted α-Keggin polyoxotungstate, $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1** was determined. It was obtained as the main product from a 1 : 3 molar ratio reaction of $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ with $Ti(SO_4)_2$ in aqueous solution. Compound **2** was obtained as a second crop from the filtrate after the isolation of compound **1**. The further characterization of **2** is in progress.[5k] Also, a related α-Keggin tri-Ti^{IV}-1,2,3-substituted polyoxotungstate, the dimeric anhydride form $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3**, was obtained as the main product from a 1 : 3 molar ratio reaction of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 15H_2O$ with $Ti(SO_4)_2$. Solution molecular weight measurements with ultracentrifugation sedimentation equilibrium have revealed that **1** and **3** are dimers under less acidic conditions, *i.e.* pH 7.0 and 7.6, respectively.

Herein, we report full details of the syntheses, formation and structural characterization of **1** and **3**.

Results and discussion

Syntheses, isolation, and compositional and spectroscopic characterization of 1 and 3

The water-soluble potassium salt **1** was derived from a 1 : 3 molar ratio reaction of $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ with $Ti(SO_4)_2\cdot$

---

† Electronic supplementary information (ESI) available: further bond lengths and angles for compound **1**. See http://www.rsc.org/suppdata/dt/b1/b102942h/

DOI: 10.1039/b102942h

This journal is © The Royal Society of Chemistry 2001

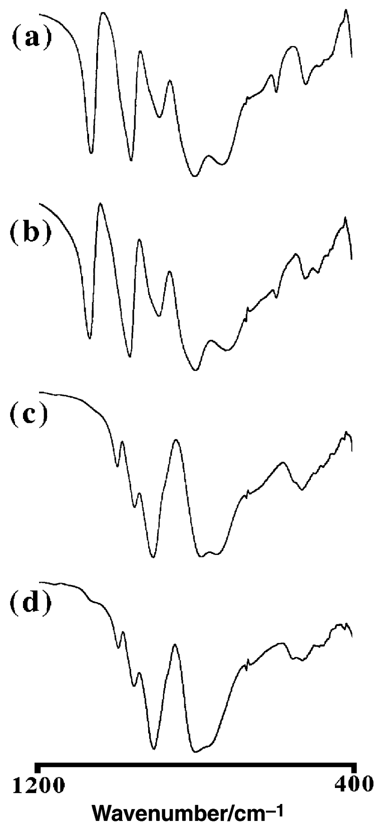

Fig. 1 The FTIR spectra in the polyoxoanion region (1100–400 cm^{-1}), measured as KBr disks of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1**, (b) compound **2**, (c) $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3** and (d) $K_{11}H_3\text{-}[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 20H_2O$.

$4H_2O$ in aqueous solution, followed by the addition of solid KCl. Colorless needle crystals were obtained in 30.4% yield by recrystallization from pH 2.2 (HCl-acidic) unbuffered aqueous solution. Colorless needle crystals of the water-soluble compound **2** were obtained by concentrating (on an evaporator at 40 °C) the filtrate from the isolation of **1**. Using ^{31}P NMR as the probe, we optimized the reaction for the formation of either **1** or **2** by changing the molar ratio of $[A\text{-}PW_9O_{34}]^{9-}$ and $Ti(SO_4)_2$ in aqueous solution. We found that compound **2** is formed as the main species under relatively limited conditions, *i.e.* with a 1 : 2 molar ratio of $[A\text{-}PW_9O_{34}]^{9-}$ and $Ti(SO_4)_2$, while **1** is formed as the main species with larger amounts of Ti^{4+}, *e.g.* the 1 : 3 molar ratio. It should be noted that the unsubstituted ion $[PW_{12}O_{40}]^{3-}$ formed under all of the conditions tested.

The composition of **1** was confirmed by complete elemental analysis, TG/DTA, FTIR, and ^{183}W and ^{31}P NMR spectroscopy. In the complete elemental analysis of **1** (including oxygen) the observed total for all elements was 99.25%. TG/DTA measurements performed under atmospheric conditions showed the presence of 17 water molecules for **1**, including both intrinsic water of hydration and the adsorbed water from the atmosphere. The solid state FTIR spectrum, measured as a KBr disk of **1**, showed the characteristic vibrational bands of a Keggin-type "$PW_{12}O_{40}{}^{n-}$" polyoxotungstate framework (Fig. 1),[6] which was very similar to that of **2**. The ^{183}W NMR of **1** in D_2O showed a two-line spectrum of −109.7 (12W) and −131.5 (6W) ppm with integrated intensities 2 : 1, which was contrasted to that of **2** in D_2O showing a six-line spectrum of −92.8 (2W), −101.2 (2W), −105.8 (2W), −119.9 (2W), −131.2 (1W) and −139.5 (1W) ppm with integrated intensities 2 : 2 : 2 : 2 : 1 : 1 (Fig. 2). Solution molecular weight measurements have shown that **1** is present as a dimer *even* under less acidic conditions (pH 7.0 solution). In **1**, the integrated intensities are in accord with the presence of a tungsten belt consisting of six WO_6 octahedra and a tungsten cap of three WO_6 octahedra, as expected for the constituent, Keggin polyoxoanion unit with C_{3v} symmetry (overall D_{3h} symmetry for the dimer). Solution ^{31}P NMR spectra of **1** and **2** in D_2O showed only one resonance at −10.49 and −11.75 ppm, respectively, confirming the formation of a single phosphorus-containing compound (Fig. 3).

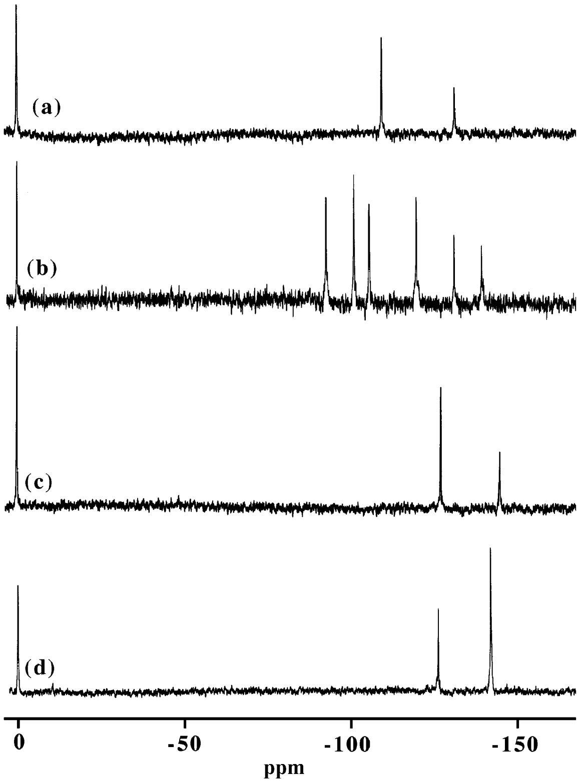

Fig. 2 ^{183}W NMR in D_2O of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1**, (b) compound **2**, (c) $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3** and (d) $K_{11}H_3\text{-}[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 20H_2O$. The resonance at 0.0 ppm is due to the external reference of saturated Na_2WO_4–D_2O solution.

The water-soluble potassium salt **3** was derived from a 1 : 3 molar ratio reaction of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 15H_2O$ with $Ti(SO_4)_2\cdot 4H_2O$ in aqueous solution, followed by the addition of solid KCl. Colorless needle crystals were obtained in 31.1% yield by recrystallization from pH 2.2 (HCl-acidic) unbuffered aqueous solution. The formation of **3** is represented in the ionic balance equation (1).

$$2\,[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-} + 6\,Ti^{4+} + 9\,H_2O \longrightarrow [\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}\ \mathbf{3} + 18\,H^{+} \qquad (1)$$

The composition of **3** was also confirmed by complete elemental analysis, TG/DTA, FTIR and ^{183}W NMR spectroscopy. In the complete elemental analysis of **3** (including oxygen) the observed total for all elements was 98.32%. TG/DTA measurement of **3** performed under atmospheric conditions showed the presence of 15 water molecules. The solid state FTIR spectrum, measured as the KBr disk of **3**, showed the characteristic vibrational bands of a Keggin-type "$SiW_{12}O_{40}{}^{n-}$" polyoxotungstate framework (Fig. 1).[6] Solution molecular weight measurements revealed that **3** is present as the dimer *even* under less acidic conditions (pH 7.6 solution). The ^{183}W NMR of **3** in D_2O (Fig. 2) showed a two-line spectrum of −127.4 (12W) and −145.1 (6W) ppm with integrated intensities 2 : 1, which are in accord with the presence of a tungsten belt consisting of six WO_6 octahedra and a tungsten cap of three WO_6 octahedra, as expected for the Keggin polyoxoanion fragment with C_{3v} symmetry (overall D_{3h} symmetry for the dimer) if protonation is not taken into account.

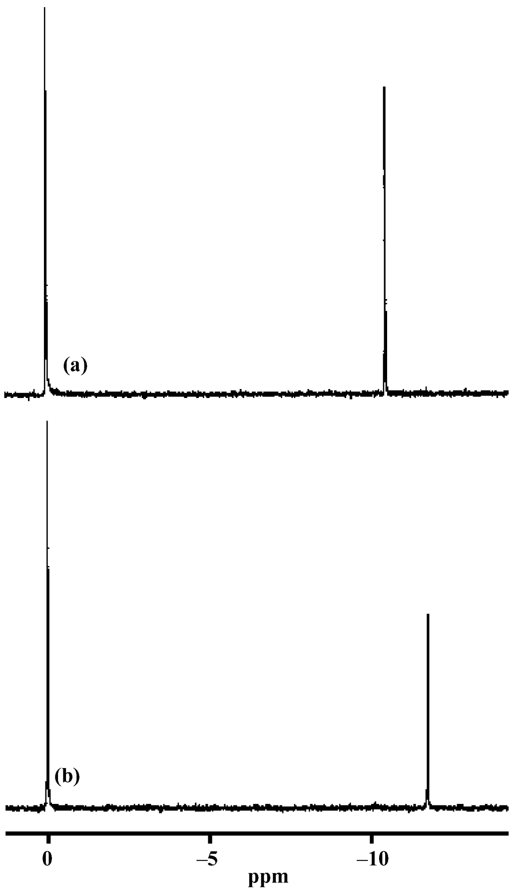

Fig. 3 ^{31}P NMR in D_2O of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1** and of (b) compound **2**. The resonance at 0.0 ppm is due to the external reference of 25% H_3PO_4 in H_2O. In each case a very high level of purity is indicated (*i.e.*, with respect to any other, P-containing polyoxoanions or other materials).

The ^{183}W NMR of **3** in D_2O can be compared with that of the related compound $K_{12}H_2[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 25H_2O$ **4**.‡ It should be noted that the chemical shifts of the two ^{183}W resonances in **3** were reversed compared to those of the well-defined compound **4** in D_2O (Fig. 2);[5c] the latter ^{183}W NMR was reported as a two-line spectrum of two resonances at −131.3 (6W) and −145.8 (12W) ppm, the measurement being performed as the Li^+ salt following metathesis with excess $LiClO_4$ and removal of the insoluble $KClO_4$. It has also been confirmed in our group that the latter spectrum was reproducible for our compound $K_{11}H_3[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 20H_2O$ in D_2O.‡ Liu and co-workers have reported a two-line ^{183}W NMR spectrum with a relative intensity ratio of 2 : 1 at −125.2 and −143.8 ppm for "$K_8H_2[\alpha\text{-}SiW_9Ti_3O_{40}]\cdot 15H_2O$" and at −65.6 and −145.1 ppm for "$K_7H_3[\beta\text{-}SiW_9Ti_3O_{40}]\cdot 15H_2O$", respectively, although the description of the synthesis and characterization were unsatisfactory.[5h] All our attempts to change the Keggin dimeric anion, $[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$ **4**, to its monomeric anion have been unsuccessful.[5j]

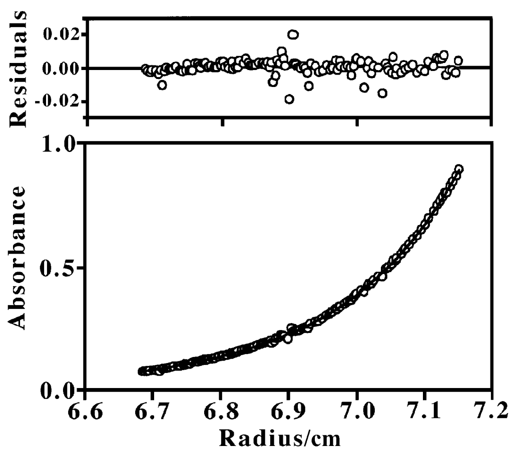

Fig. 4 Ultracentrifugation sedimentation equilibrium plot for compound **1** at 20000 rpm. Note the excellent fit to the data for the calculated curve, which assumes a single-species model, resulting in relatively small, random residuals. The fit gives a solution MW of 5200 (±300) g mol^{-1}.

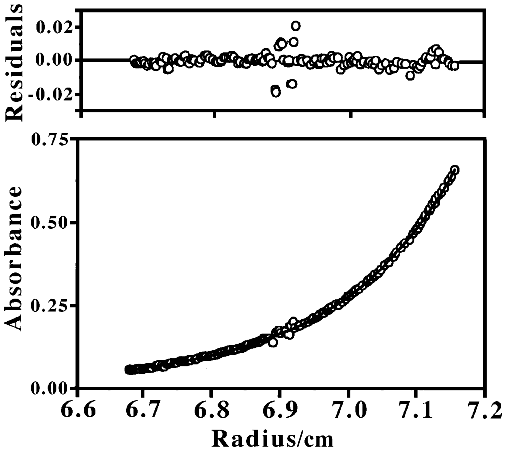

Fig. 5 Ultracentrifugation sedimentation equilibrium plot for compound **3** at 20000 rpm. Note the excellent fit to the data for the calculated curve, which assumes a single-species model, resulting in relatively small, random residuals. The fit gives a solution MW of 5200 (±300) g mol^{-1}.

Determination of the solution molecular weight of 1 and 3

Analytical ultracentrifugation[7] is a well-established technique for the determination of the solution molecular weight of polyoxoanions.[2c,3a,b,5g] Of special interest is our recent report of the use of analytical ultracentrifugation for the detection of anhydride forms of polyoxoanions.[5g] The results of the solution molecular weight determinations for **1** and **3** are summarized in Table 1. The molecular weight of each compound was determined at two different spinning rates to substantiate the validity of the data. Compound **1** was found to have a molecular weight of 5200 (±300) g mol^{-1} in aqueous solution (pH 7.0), clearly indicating that the anhydride bridged dimer seen in the X-ray crystal structure is also the species present in solution. The molecular weight of **3** was also found to be 5200 (±300) g mol^{-1} in aqueous solution (pH 7.6), indicating that it, too, is present in solution as the expected anhydride bridged dimer.[5c] In every MW experiment an excellent fit to the single-species model was observed, as evidenced by the relatively small, random residuals shown in Fig. 4 and 5. Clearly, the results of these solution molecular weight determinations support the proposed formulations of **1** and **3**.

Crystal and molecular structure of 1

After a few days of standing at room temperature, crystals of sufficient quality for single-crystal X-ray diffraction studies were grown from a solution of **1**.

---

‡ The original paper[5c] reported the composition of **4** as $K_{12}H_2\text{-}[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 25H_2O$, whereas $K_{11}H_3[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 20H_2O$ was obtained in our lab. These compounds have been prepared by the 1 : 3 molar ratio reactions of the precursor $Na_9[A\text{-}\beta\text{-}SiW_9O_{34}H]\cdot 17H_2O$ with different Ti sources; in the former $K_2TiO(ox)_2\cdot 2H_2O$ was used, while in the latter $Ti(SO_4)_2\cdot 4H_2O$ was used. Further, the pH of the recrystallization solution in the former was adjusted to pH 3.1 using acetic acid, while in the latter it was adjusted to pH 2.2 using aqueous HCl.

Table 1 The results of solution molecular weight determinations for **1** and **3**

Compound (solution)	T/K	Calc. MW {minus waters} (of anion alone)/g mol^{-1}	Found MW/g mol^{-1} (spinning rate in rpm)
$K_{10}H_2[\alpha\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot17H_2O$ **1** (0.1 M NaCl in water, pH 7.0)	20	5589.86 {5283.60} (4890.60)	5200 (±300) (20 000)
	30		5100 (±300) (30 000)
$K_{10}H_4[\alpha\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot15H_2O$ **3** (0.1 M NaCl in water, pH 7.6)	20	5550.06 {5279.84} (4884.82)	5200 (±300) (20 000)
	30		5200 (±300) (30 000)

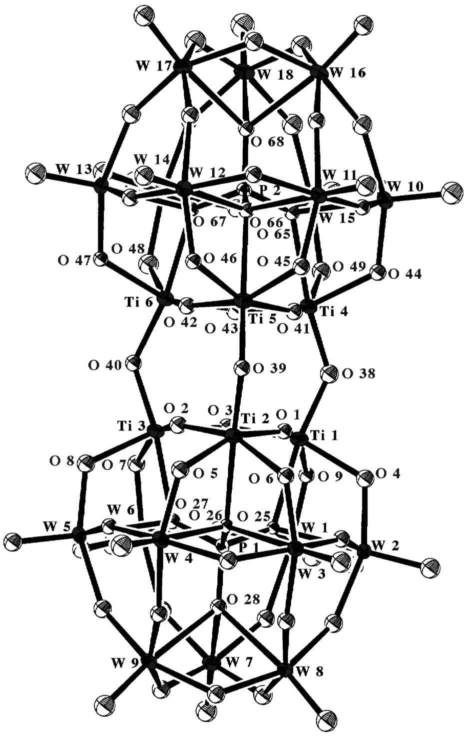

Fig. 6 Molecular structure of **1** with 50% probability ellipsoids.

The crystal system (triclinic), the space group ($P\bar{1}$ (No. 2)) and a disorder-free polyoxometalate unit provided a straightforward solution of the structure and refinement. Structural analysis revealed the molecular structure of $[P_2W_{18}Ti_6O_{77}]^{12-}$ as shown in Fig. 6. The crystals of **1** contain discrete polyoxoanions, potassium cations and lattice water molecules, all in general positions in this space group. 9.5 of the 10 potassium cations were identified in the crystal structure of compound **1**, but 0.5 were not determined because of disorder. The observed electron densities on the Ti and W atoms are quite different, and the data unequivocally distinguish and define the Ti and W atoms.

The molecular structure of **1** is composed of two "$PW_9Ti_3O_{40}$" Keggin-polyoxoanion halves linked *via* three Ti–O–Ti bonds, with each half consisting of the same A-α Keggin structure $[A\text{-}\alpha\text{-}PW_9Ti_3O_{40}]^{9-}$. As expected, the three TiO_6 octahedra in each "$PW_9Ti_3O_{40}$" Keggin unit substitute the three corner-sharing WO_6 octahedra (1,2,3-position, *i.e.* A-site) of $[A\text{-}\alpha\text{-}PW_{12}O_{40}]^{3-}$. Selected bond lengths and angles for the polyoxoanion are given in Table 2 (other bond lengths and angles of **1** are given as ESI†). The three Ti atoms and nine W atoms all exhibit conventional octahedral coordination polyhedra. The W–Ot (Ot: terminal oxygen) [1.70(1)–1.74(1) Å], W–Oc (Oc: corner sharing oxygen) [1.87(1)–2.00(1) Å], W–Oe (Oe: edge-sharing oxygen) [1.81(1)–1.97(1) Å], and W–Oa (Oa: oxygen coordinated to P atom) [2.41(1)–2.47(1) Å] distances are in the normal range.[1b] The polyoxoanion contains two central P atoms in an almost regular tetrahedral environment of PO_4 with P–O distances in the range 1.52(1)–1.55(1) Å, and O–P–O bond angles of 108.5(7)–110.5(7)°. Bond lengths around Ti were Ti–OTi (between monomer units) [1.80(1)–1.86(1), average 1.83 Å], Ti–OTi (within monomer units) [1.79(1)–1.92(1), average 1.87 Å], Ti–Oe(W) [1.98(1)–2.05(1), average 2.01 Å], and Ti–Oa [2.30(1)–2.39(1), average 2.35 Å]. The bond valences at the two P heteroatoms were 4.913 (P1) and 5.043 (P2). The Ti–O–Ti angles between the two α-Keggin units were 130.1(7)–131.3(7)° and those within the Keggin units were 141.7(7)–147.4(8)°. The corresponding bond valences[8a,b] at all Ti and W atoms, based on bond lengths, were 3.898–4.020 for the six Ti atoms and 5.804–6.406 for the 18 W atoms.

Table 2 Selected bond lengths (Å) and angles (°) for the polyoxoanion **1**

Ti–OTi (within monomer units)		Ti–OTi (between monomer units)	
Ti1–O1	1.83(1)	Ti1–O38	1.85(1)
Ti1–O3	1.90(1)	Ti2–O39	1.86(1)
Ti2–O1	1.85(1)	Ti3–O40	1.83(1)
Ti2–O2	1.87(1)	Ti4–O38	1.80(1)
Ti3–O2	1.79(1)	Ti5–O39	1.82(1)
Ti3–O3	1.92(1)	Ti6–O40	1.83(1)
Ti4–O41	1.87(1)		
Ti4–O43	1.87(1)	Ti–O[a]	
Ti5–O41	1.88(1)	Ti1–O25	2.34(1)
Ti5–O42	1.88(1)	Ti2–O26	2.36(1)
Ti6–O42	1.81(1)	Ti3–O27	2.30(1)
Ti6–O43	1.91(2)	Ti4–O65	2.39(1)
		Ti5–O66	2.37(1)
		Ti6–O67	2.32(1)
Ti1–O1–Ti2	147.2(7)	Ti1–O38–Ti4	131.0(8)
Ti2–O2–Ti3	147.0(8)	Ti2–O39–Ti5	131.3(7)
Ti1–O3–Ti3	141.7(7)	Ti3–O40–Ti6	130.1(7)
Ti4–O41–Ti5	145.9(8)		
Ti5–O42–Ti6	147.4(8)		
Ti4–O43–Ti6	144.5(8)		

[a] Oxygen involved in the bond is coordinated to a P atom.

Although the general structure of the anion of **1** $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$ is, overall, similar to those of the reported polyoxoanions, $[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$ **4**[5c] and $[\alpha,\alpha\text{-}Ge_2W_{18}Ti_6O_{77}]^{14-}$ **5**,[5d] there are several differences in (1) the orientation (α for **1** and **5** *vs.* β for **4**) of the W_3 cap, (2) the Ti–O–Ti angles between the two Keggin units [130.1(7)–131.3(7)° for **1**, all are 141(3)° for **4**, 132–136(2)° for **5**], (3) the Ti–OTi bond lengths between the two Keggin units [1.80(1)–1.86(1), average 1.83 Å for **1**, 1.79(3)–1.83(3), average 1.81 Å for **4**, 1.78(2)–1.85(2), average 1.82 Å for **5**], (4) the Ti–OTi bond lengths within the Keggin units [1.79(1)–1.92(1), average 1.87 Å for **1**, 1.90(3)–1.98(2), average 1.94 Å for **4**, 1.82(3)–1.95(3), average 1.88 Å for **5**], and (5) the dimensions of the polyoxoanions which are ascribable to the different sizes of the heteroatoms (ionic radii; 0.31 Å for

P^{5+}, 0.54 Å for Si^{4+} and 0.68 Å for Ge^{4+})[8c] and, therefore, to the different sizes of the central tetrahedra [P–O distances 1.52(1)–1.55(1) Å in **1**, Si–O distances 1.59(5)–1.68(5) Å in **4**, and Ge–O distances 1.63(2)–1.77(2) Å in **5**].

A crystal structure determination of **3** was attempted *at least* four times using different crystals, but the resolution obtained for the structure was limited by the poor quality of the available crystals and by the considerable disorder of the cations and the solvent molecules in crystals of the polyoxoanion salt. These features are well-known in polyoxoanion crystallography.[5c,8d] Nevertheless, the molecular structure of **3**, *i.e.* the dimeric structure $[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$ possessing three Ti–O–Ti bonds between the two Keggin units $[A\text{-}\alpha\text{-}SiW_9Ti_3O_{40}]^{10-}$, was confirmed. This polyoxoanion is a geometrical isomer of **4** and the general structure is also similar to those of **1** and **5**. The crystal data for **3** at the present stage are shown in the footnote.§ The Ti–O–Ti angles between the two Keggin units [131.0(2)–133.0(2)°], the Ti–O–Ti angles within the Keggin units [138.0(3)–147.0(2)°], the Ti–OTi bond lengths between the two Keggin units [1.78(4)–1.91(4) Å], and the Ti–OTi bond lengths within the Keggin units [1.78(4)–2.02(5) Å], which have been obtained at the present refinement, can be compared with those of **4**.

Conclusion

The novel Ti–O–Ti bridged anhydride forms of two tri-Ti^{IV}-1,2,3-substituted α-Keggin polyoxotungstates, $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1** and $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3**, were synthesized and unequivocally characterized. In the synthesis of **1**, a different compound **2** was unexpectedly obtained as a minor product. The tri-Ti^{IV}-1,2,3-substituted polyoxotungstates so far elucidated are anhydride dimers of the Keggin family,[5c,d] and anhydride tetramers of the Dawson family as observed in $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$ **6**.[5g] All our attempts to change the Keggin dimeric polyoxoanion to its monomeric anion have been unsuccessful.[5j] Thus, it should be noted that the monomeric form of the tri-Ti^{IV}-1,2,3-substituted polyoxometalates is difficult to form.

The complexes **1** and **3** are also of interest as possible solid-base catalysts, perhaps even super-base catalysts. Studies in these directions are in progress. Further studies of **2** including X-ray structure determination and molecular weight measurements are also under way.[5k]

Experimental

Materials

The following were used as received: $Na_2WO_4\cdot 2H_2O$, $Na_2SiO_3\cdot 9H_2O$, NaCl, 85% H_3PO_4, KCl, 12 M, 6 M and 1 M aqueous HCl solutions (quantitative analysis grade), glacial acetic acid, Na_2CO_3, 30% $Ti(SO_4)_2$ aqueous solution (all from Wako); $Ti(SO_4)_2\cdot 4H_2O$ (Junsei); $K_2TiO(ox)_2\cdot 2H_2O$ (Kanto); D_2O (Isotec). The precursors $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 15H_2O$, $Na_9[A\text{-}\beta\text{-}SiW_9O_{34}H]\cdot 17H_2O$ and $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ were prepared according to the literature.[9] $K_{11}H_3[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 20H_2O$ was prepared by a 1 : 3 molar ratio reaction of $Na_9[A\text{-}\beta\text{-}SiW_9O_{34}H]\cdot 17H_2O$ with $Ti(SO_4)_2\cdot 4H_2O$ in aqueous solution and characterized with complete elemental analysis, FTIR, TG/DTA and ^{183}W NMR.‡

Instrumentation/analytical procedures

Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under $10^{-3} - 10^{-4}$ Torr overnight before analysis. Infrared spectra were recorded on a Jasco 300 FTIR spectrometer as KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were made in air with a temperature ramp of 4 °C min^{-1} between 20 and 500 °C.

^{31}P NMR (161.70 MHz) spectra were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data-processing system, and were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts were reported as negative for resonances upfield of H_3PO_4 (δ 0). ^{183}W NMR (16.50 MHz) spectra were recorded in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system. ^{183}W NMR spectra were referenced to an external standard of saturated Na_2WO_4–D_2O solution. Chemical shifts were reported on the δ scale with resonances upfield of Na_2WO_4 (δ 0) as negative.

Preparations

$K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ 1. To a stirred solution of 2.00 g (6.40 mmol) of solid $Ti^{IV}(SO_4)_2\cdot 4H_2O$ dissolved in 50 mL water was slowly added 5.90 g (2.12 mmol) of $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ (it took *ca.* 10 min). The colorless solution was evaporated to *ca.* 25 mL on a steam bath. After cooling the solution to room temperature, 10.0 g (0.13 mol) of solid KCl was slowly added over 10 min and the solution was stirred for 1 h. The white precipitate formed was collected on a membrane filter (JG 0.2 μm). By evaporating this filtrate at 40 °C to 20 mL volume and placing it in a refrigerator at 5 °C overnight, a different compound **2** was isolated as colorless needle crystals of a minor product. The white precipitate was dissolved in 40 mL of unbuffered pH 2.2 water (prepared with 1 M aqueous HCl solution) in a water bath at 50 °C, followed by filtering through a folded filter paper (Whatman No. 5). The clear colorless filtrate was cooled to room temperature and placed in a refrigerator at 5 °C. The colorless clear needle crystals formed were collected on a membrane filter (JG 0.2 μm) and dried *in vacuo* for 2 h. The water-soluble colorless needle crystals were obtained in 1.8 g (30.4%) yield. After drying *in vacuo*, the crystals changed to a white powder (repeat trials of different lots) {Found: H, 0.17 (0.14); K, 7.31 (8.23); P, 1.11 (1.20); W, 61.9 (60.6); Ti, 5.42 (5.28); O, 23.6 (23.8); total 99.51% (99.25%). Calc. for $K_{10}H_6P_2W_{18}Ti_6O_{79}$ or $K_{10}H_2[P_2W_{18}Ti_6O_{77}]\cdot 2H_2O$: H, 0.11; K, 7.35; P, 1.16; W, 62.21; Ti, 5.40; O, 23.76%}. A weight loss of 4.48% (weakly solvated or adsorbed water) was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis, suggesting the presence of 14–15 water molecules. TG/DTA under atmospheric conditions: a weight loss of 5.52% was observed below 500 °C with an endothermic point at 65 °C; calc. 5.17% for $x = 16$ and 5.78% for $x = 18$ in $K_{10}H_2[P_2W_{18}Ti_6O_{77}]\cdot xH_2O$. IR (KBr) (polyoxometalate region): 1061s, 960s, 889m, 799vs, 731s, 593m, 519m cm^{-1}. ^{31}P NMR (25.7 °C, D_2O): δ −10.49. ^{183}W NMR (25.0 °C, D_2O): δ −109.7 (12W), −131.5 (6W). Ultracentrifugation molecular weight measurements: an average MW of 5200 (± 300) at a spinning rate of 20000 rpm and 5100 (± 300) g mol^{-1} at a spinning rate of 30000 rpm; calc. 5283.60 for $K_{10}H_2[P_2W_{18}Ti_6O_{77}]$ without water and calc. 4890.60 for the anion alone.

When 30% $Ti(SO_4)_2$ aqueous solution was used as the Ti source, compound **2** was obtained as the first crop, although the yield was unchanged.

Compound 2. Water-soluble, colorless needle crystals were

---

§ Crystal data for $H_{38}K_{10}Si_2W_{18}Ti_6O_{94}$ **3**, $M = 5279.84$, triclinic, space group $P\bar{1}$ (no. 2), $a = 18.206(5)$, $b = 21.490(4)$, $c = 12.792(2)$ Å, $\alpha = 100.88(2)$, $\beta = 104.33(2)$, $\gamma = 109.08(2)°$, $V = 4379(2)$ Å^3, $Z = 2$, $D_c = 3.975$ g cm^{-1}, μ(Mo-Kα) = 246.24 cm^{-1}. Final $R1 = 0.152$, $R_w = 0.373$, and GOF = 2.35 (20758 total reflections, 20754 unique reflections of which 20751 with $I > -10.0\sigma(I)$ were used in all calculations).

obtained as the second crop from the filtrate in the preparation of **1**.

IR (KBr) (polyoxometalate region): 1065s, 964s, 891m, 798vs, 721s, 593m, 519m, 487m cm^{-1}. ^{31}P NMR (25.5 °C, D$_2$O): δ −11.75. ^{183}W NMR (24.7 °C, D$_2$O): δ −92.8 (2W), −101.2 (2W), −105.8 (2W), −119.9 (2W), −131.2 (1W), −139.5 (1W).

$K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ 3. To a stirred solution of 2.00 g (6.40 mmol) of solid Ti^{IV}(SO$_4$)$_2$·4H$_2$O dissolved in 50 mL water was slowly added 6.00 g (2.20 mmol) of $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 15H_2O$ over *ca.* 10 min. For 1 h the solution was stirred on a water bath at 70 °C. After cooling the solution to room temperature, 10.0 g (0.13 mol) of solid KCl was slowly added over 10 min and the solution was stirred for 1 h. The white precipitate formed was collected on a membrane filter (JG 0.2 µm). The white precipitate was dissolved in 20 mL of unbuffered pH 2.2 water (prepared with 1 M aqueous HCl solution) in a water bath at 50 °C, followed by filtering through a folded filter paper (Whatman No. 5). The clear colorless filtrate was cooled to room temperature and placed in a refrigerator at 5 °C. The colorless clear needle crystals formed were collected on a membrane filter (JG 0.2 µm) and dried *in vacuo* for 2 h. The recrystallization was performed once more. Water-soluble colorless needle crystals were obtained in 1.9 g (31.1%) yield. After drying *in vacuo*, the crystals changed to a white powder {Found: H, 0.29; K, 7.50; Si, 0.93; W, 61.70; Ti, 5.30; O, 22.60; total 98.32%. Calc. for $K_{10}H_{10}Si_2W_{18}Ti_6O_{80}$ or $K_{10}H_4[Si_2W_{18}Ti_6O_{77}]\cdot 3H_2O$: H, 0.19; K, 7.33; Si, 1.05; W, 62.04; Ti, 5.39; O, 23.00%}. A weight loss of 4.26% (weakly solvated or adsorbed water) was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before analysis, suggesting the presence of 13–14 water molecules. TG/DTA under atmospheric conditions: a weight loss of 5.04% was found below 500 °C with endothermic points at 63 and 103 °C; calc. 4.56% for $x = 14$ and 5.17% for $x = 16$ in $K_{10}H_4[Si_2W_{18}Ti_6O_{77}]\cdot xH_2O$. IR (KBr) (polyoxometalate region): 996m, 953m (Si–O), 907vs, 785vs, 747vs cm^{-1}. ^{183}W NMR (25.0 °C, D$_2$O): δ −127.4 (12W), −145.1 (6W). Ultracentrifugation molecular weight measurements: an average MW of 5200 (± 300) for a spinning rate of 20000 rpm and 5200 (± 300) g. mol^{-1} for a spinning rate of 30000 rpm; calc. 5279.84 for $K_{10}H_4[Si_2W_{18}Ti_6O_{77}]$ without water and calc. 4884.83 for the anion alone.

In the synthesis, if 6.0 g of commercial 30% Ti(SO$_4$)$_2$ aqueous solution were used, instead of solid Ti(SO$_4$)$_2$, it resulted in a 1.5 g (24.6%) yield of the same compound.

Ultracentrifugation solution molecular weight measurements

Samples of $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **1** and $K_{10}H_4[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]\cdot 15H_2O$ **3** were prepared by dissolving *ca.* 3 mg of material in sufficient 0.1 M aqueous NaCl so that the absorbance in a 1 cm quartz cuvette was between 0.26 and 0.38 at λ = 250 nm (the final concentrations were *ca.* 20 µg mL^{-1}).

Sedimentation equilibrium experiments were performed at 25 °C in a Beckman XL-I ultracentrifuge using an An 60 Ti rotor. Absorbance data were collected at λ = 250 nm using quartz windows and a two-channel charcoal-filled Epon centerpiece with a 12 mm pathlength. Prior to use, the centerpiece was "siliconized" by dipping it into a 5% solution of dimethyldichlorosilane (Fluka) in CH$_2$Cl$_2$ (Fisher) for 2 min. For each experiment 200 µL of the sample solution was placed in one channel of the centerpiece and 220 µL of 0.1 M aqueous NaCl was placed in the other channel. Following an initial 8–10 h of centrifugation to approach equilibrium, every 2 h 25 radial scans (with a 0.003 cm step size) were obtained and averaged. Verification that equilibrium had indeed been reached was checked by subtracting successive data sets and showing that the sedimentation data were no longer changing.

Data analysis was performed in the XL-A/XL-I Data Analysis Software, Version 4.0 (Beckman Instruments, Inc.) operating within Origin 4.1. The data were fit to an ideal, single-species model using the following equation:

$$C_r = C_m \exp\,[M\,(1 - \tilde{v}\rho)\omega^2\,(r^2 - r_m{}^2)/2RT] \qquad (2)$$

where C$_r$ is the concentration at some radial position, C$_m$ is the concentration at some reference position, M is the weight-average molecular weight, $\tilde{v}$ is the partial specific volume, ρ is the solvent density, ω is the angular velocity, r is the radial distance from the center of rotation, r_m is the radial distance from the center of rotation to the reference position, R is the gas constant, and T is the temperature in Kelvin. The solution density was taken to be 1.0 g mL^{-1}.[3a] The partial specific volume was approximated as 0.145 mL g^{-1}. This value for the partial specific volume corresponds to an average value for compounds and conditions similar to those used herein;[3a] for a class of compounds under similar conditions the partial specific volume is not expected to vary significantly.[3a,7a]

All of the solution molecular weights were given 5% error bars, a value that encompasses the maximum experimental error observed in repeat measurements, Table 1. This is true even if the extreme values of partial specific volume from ref. 3*a* are used instead of the average values.

X-Ray crystallography

A colorless needle crystal (0.10 × 0.10 × 0.20 mm) obtained by slow evaporation was used for X-ray diffraction measurements. The single crystal was mounted on a glass fiber and transferred to a Rigaku AFC5S four-circle diffractometer. The reflection data were collected using ω–2θ scans with Mo-Kα radiation (λ = 0.71069 Å) at room temperature in the range of $6 < 2\theta < 55°$. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods followed by subsequent difference Fourier calculations and refined by a full-matrix least-squares procedure using the TEXSAN package.[10] Non-hydrogen atoms were refined anisotropically. Crystal data for $H_{36}K_{10}P_2W_{18}Ti_6O_{94}$ **1**, M = 5589.86, triclinic, space group $P\bar{1}$ (No. 2), a = 18.586(6), b = 20.544(7), c = 12.877(9) Å, α = 99.50(4), β = 105.71(4), γ = 105.54(2)°, V = 4408(4) Å^3, Z = 2, D_c = 4.211 g cm^{-1}, μ(Mo-Kα) = 245.45 cm^{-1}. Final $R1$ = 0.056 (R = 0.103), R_w = 0.160, and GOF = 1.45 (20861 total reflections, 20239 unique reflections of which 20236 with $I > -10.0\sigma(I)$ were used in all calculations).

CCDC reference number 165396.

See http://www.rsc.org/suppdata/dt/b1/b102942h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

K. N. gratefully acknowledges financial support from Grant-in-Aid for Scientific Research (C) (10640552) of the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also thank the Department of Energy, Chemical Sciences Division, Office of Basic Energy for providing financial support to J. A. W. *via* grant DOE FG06-089ER13998.

References

1 (*a*) M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34; (*b*) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York, 1983; (*c*) V. W. Day and W. G. Klemperer, *Science*, 1985, **228**, 533.

2 (*a*) S. P. Harmalker, M. A. Leparulo and M. T. Pope, *J. Am. Chem. Soc.*, 1983, **105**, 4286; (*b*) P. Domaille, *J. Am. Chem. Soc.*, 1984, **106**, 7679; (*c*) R. G. Finke, B. Rapko, R. J. Saxton and P. J. Domaille, *J. Am. Chem. Soc.*, 1986, **108**, 2947; (*d*) P. J. Domaille and G. Watunya, *Inorg. Chem.*, 1986, **25**, 1239; (*e*) P. J. Domaille and R. L. Harlow, *J. Am. Chem. Soc.*, 1986, **108**, 2108; (*f*) J. Canny, R. Thouvenot, A. Teze, G. Herve, M. Leparulo-Loftus and M. T.

Pope, *Inorg. Chem.*, 1991, **30**, 976; (*g*) I. Kawafune, H. Tamura and G. Matsubayashi, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 2455; (*h*) R. G. Finke, B. Rapko and P. J. Domaille, *Organometallics*, 1986, **5**, 175; (*i*) R. G. Finke, M. W. Droege, J. C. Cook and K. S. Suslick, *J. Am. Chem. Soc.*, 1984, **106**, 5750; (*j*) R. G. Finke, C. A. Green and B. Rapko, *Inorg. Synth.*, 1990, **27**, 128; (*k*) P. J. Domaille, *Inorg. Synth.*, 1990, **27**, 96; (*l*) B. M. Rapko, M. Pohl and R. G. Finke, *Inorg. Chem.*, 1994, **33**, 3625.

3 (*a*) R. G. Finke and M. W. Droege, *J. Am. Chem. Soc.*, 1984, **106**, 7274; (*b*) D. J. Edlund, R. J. Saxton, D. K. Lyon and R. G. Finke, *Organometallics*, 1988, **7**, 1692; (*c*) K. S. Suslick, J. C. Cook, B. Rapko, M. W. Droege and R. G. Finke, *Inorg. Chem.*, 1986, **25**, 241; (*d*) R. G. Finke, K. Nomiya, C. A. Green and M. W. Droege, *Inorg. Synth.*, 1992, **29**, 239; (*e*) R. G. Finke, D. K. Lyon, K. Nomiya and T. J. R. Weakley, *Acta Crystallogr., Sect. C*, 1990, **46**, 1592; (*f*) K. Nomiya, M. Kaneko, N. C. Kasuga, R. G. Finke and M. Pohl, *Inorg. Chem.*, 1994, **33**, 1469; (*g*) K. Nomiya, M. Pohl, N. Mizuno, D. K. Lyon and R. G. Finke, *Inorg. Synth.*, 1997, **31**, 186; (*h*) H. Weiner, J. D. Aiken, III and R. G. Finke, *Inorg. Chem.*, 1996, **35**, 7905; (*i*) K. Nomiya, C. Nozaki, K. Miyazawa, Y. Shimizu, T. Takayama and K. Nomura, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1369; (*j*) K. Nomiya, K. Ohsawa, T. Taguchi, M. Kaneko and T. Takayama, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2603.

4 L. Barcza and M. T. Pope, *J. Phys. Chem.*, 1973, **77**, 1795.

5 (*a*) W. H. Knoth, P. J. Domaille and D. C. Roe, *Inorg. Chem.*, 1983, **22**, 198; (*b*) P. J. Domaille and W. H. Knoth, *Inorg. Chem.*, 1983, **22**, 818; (*c*) Y. Lin, T. J. R. Weakley, B. Rapko and R. G. Finke, *Inorg. Chem.*, 1993, **32**, 5095; (*d*) T. Yamase, T. Ozeki, H. Sakamoto, S. Nishiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 103; (*e*) T. Yamase, T. Ozeki and S. Motomura, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1453; (*f*) T. Ozeki and T. Yamase, *Acta Crystallogr., Sect. C*, 1991, **47**, 693; (*g*) K. Nomiya, Y. Arai, Y. Shimizu, M. Takahashi, T. Takayama, H. Weiner, T. Nagata, J. A. Widegren and R. G. Finke, *Inorg. Chim. Acta*, 2000, **300–302**, 285; (*h*) J.-F. Liu, L. Meng, W.-Y. Zhao, J.-C. Li and B.-L. Zhao, *Acta Chim. Sin. (Chin. Ed.)*, 1995, **53**, 46; (*i*) O. A. Kholdeeva, G. M. Maksimov, R. I. Maksimovskaya, L. A. Kovaleva, M. A. Fedotov, V. A. Grigoriev and C. L. Hill, *Inorg. Chem.*, 2000, **39**, 3828; (*j*) K. Nomiya, M. Matsuoka and I. Yoshiwara, unpublished results; (*k*) K. Nomiya, M. Takahashi and J. A. Widegren, manuscript in preparation.

6 (*a*) C. Rocchiccioli-Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta, Part A*, 1976, **32**, 587; (*b*) C. Rocchiccioli-Deltcheff and R. Thouvenot, *Spectrosc. Lett.*, 1979, **12**, 127.

7 (*a*) T. M. Laue, in *Methods in Enzymology*, ed. M. L. Johnson and G. K. Ackers, Academic, San Diego, 1995, vol. 259, p. 427; (*b*) H. Colfen, *Crit. Rev. Opt. Sci. Technol.*, 1997, **CR69**, 525; (*c*) S. E. Harding, *Methods Mol. Biol.*, 1994, **22**, 75; (*d*) T. M. Laue and D. G. Rhodes, in *Methods in Enzymology*, ed. M. P. Deutscher, Academic, San Diego, 1990, vol. 182, p. 566.

8 (*a*) I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244; (*b*) I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, 1973, **29**, 266; (*c*) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925; (*d*) T. J. R. Weakley and R. G. Finke, *Inorg. Chem.*, 1990, **29**, 1235.

9 (*a*) A. Teze and G. Herve, *Inorg. Synth.*, 1990, **27**, 85; (*b*) W. J. Randall, M. W. Droege, N. Mizuno, K. Nomiya, T. J. R. Weakley and R. G. Finke, *Inorg. Synth.*, 1997, **31**, 167.

10 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.