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FULL PAPER

Synthesis and pH-variable ultracentrifugation molecular weight measurements of the dimeric, Ti–O–Ti bridged anhydride form of a novel di-Ti^{IV}-1,2-substituted α-Keggin polyoxotungstate. Molecular structure of the $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{39})_2]^{10-}$ polyoxoanion †

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The preparation and characterization of a Keggin-type, novel di-Ti^{IV}-1,2-substituted polyoxotungstate are described. The dimeric, Ti–O–Ti bridged anhydride form of the di-Ti^{IV}-1,2-substituted α-Keggin polyoxotungstate, $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1**, was unexpectedly found in the varied molar-ratio reactions of tri-lacunary precursor $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ with $Ti(SO_4)_2$ in aqueous solution. Although this compound was first found as a minor product in the preparation of the dimeric, tri-Ti^{IV}-1,2,3-substituted species, $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **3**, it was successfully prepared as a main product in this work and structurally characterized. Compound **1**, as analytically pure, homogeneous colorless needle crystals, was obtained as a major product in 29.2% yield (2.7 g scale) from recrystallization under acidic conditions (at pH 2.2) of the 1 : 2 molar-ratio reaction product. X-Ray structure analysis revealed that the molecular structure of **1** consisted of a dimeric anhydride formed by two Ti–O–Ti bonds linking two $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$ Keggin units. Interestingly, ultracentrifugation molecular weight (MW) measurements of this compound in aqueous solution showed the pH-dependent interconversion between monomer $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$ **2** and dimer $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$ **1**; this compound was present as the monomer under less acidic conditions (pH 7.8), while it was in dimeric form under more acidic conditions (pH 1.0 and 2.2). Characterization of **1** was also accomplished by complete elemental analyses, TG/DTA, FTIR and solution (^{31}P and ^{183}W) NMR spectroscopy.

Introduction

Polyoxoanions are molecular metal-oxide clusters which are of current interest as soluble analogs of heterogeneous metal oxides[1a–c] and for their application to catalysis, medicine and material sciences.[1d–i] In particular, the polyoxotungstates substituted with the 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 prepared 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, and the very recently found $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$ **3** and $[\alpha,\alpha\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$,[5j] which are formed from two $[A\text{-}\alpha\text{-}PW_9Ti_3O_{40}]^{9-}$ Keggin units and two $[A\text{-}\alpha\text{-}SiW_9Ti_3O_{40}]^{10-}$ Keggin units, respectively. Also, the recently found tri-Ti^{IV}-substituted Dawson polyoxotungstates have been elucidated to be a tetrameric, Ti–O–Ti anhydride form, *i.e.* $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$ **6**,[5g] which is composed of four $[\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62}]^{12-}$ Dawson fragments to form the T_d tetramer. On the other hand, the monomeric, mono- and di-Ti^{IV}-substituted Keggin polyoxotungstates have been realized in $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ [5b,f] and $[\alpha\text{-}PW_{11}TiO_{40}]^{5-}$.[5a,e]

In our recent preparation of $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$ **3**,[5j] we found that a di-Ti^{IV}-substituted species, which showed different ^{31}P and ^{183}W NMR spectra from those of **3**, was formed as a minor product. Thus, we carefully examined the reactions of tri-lacunary precursor $[A\text{-}PW_9O_{34}]^{9-}$ with $Ti(SO_4)_2$ in aqueous solution by changing their respective molar ratios and found conditions in which the novel di-Ti^{IV}-1,2-substituted α-Keggin species is the main product. Herein, we report full details of the synthesis and structural characterization of $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$ **1**.

Results and discussion

Synthesis, isolation and compositional characterization

The water-soluble potassium salt of **1**, $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$, was obtained in 29.2% (2.7 g scale) yield by recrystallizing, under acidic conditions (unbuffered pH 2.2 solution), the white powder obtained from 1 : 2 molar-ratio reaction of $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ with $Ti(SO_4)_2\cdot 4H_2O$ in aqueous solution. Compound **1** was first found as a minor product in our recent preparation of **3**.[5j] We examined by ^{31}P NMR the formation of **1** and **3** by changing the molar ratio of $[A\text{-}PW_9O_{34}]^{9-}$ and $Ti(SO_4)_2$ in aqueous solution, and found the optimal molar

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† Electronic supplementary information (ESI) available: further bond lengths and angles for compound **1**. See http://www.rsc.org/suppdata/dt/b2/b204775f/

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ratio of formation for **1** and **3**, respectively. Complex **1** was formed as a main product under relatively limited conditions, *i.e.* 1 : 2 molar ratio, while **3** was formed as a main species when more Ti^{4+} was added, *e.g.* 1 : 3 molar ratio. It should be noted that the unsubstituted ion $[PW_{12}O_{40}]^{3-}$ is always formed under these conditions. The formation of **1** and **3**, deduced from ^{31}P NMR measurements of the 1 : 3 molar-ratio reaction solution, can be shown in the ionically balanced eqn. (1). The pH-dependent interconversion between Keggin monomer **2** and Keggin dimer **1** is shown in eqn. (2).

$$32Ti^{4+} + 18\,[A\text{-}PW_9O_{34}]^{9-} + 30\,H_2O \longrightarrow 4\,[P_2W_{18}Ti_6O_{77}]^{12-}\ \mathbf{3} + 2\,[PW_{10}Ti_2O_{40}]^{7-}\ \mathbf{2} + [P_2W_{20}Ti_4O_{78}]^{10-}\ \mathbf{1} + 4\,[PW_{12}O_{40}]^{3-} + 2\,PO_4^{3-} + 2\,WO_4^{2-} + 60\,H^+ \quad (1)$$

$$[P_2W_{20}Ti_4O_{78}]^{10-}\ \mathbf{1} + 4\,OH^- \rightleftarrows 2\,[PW_{10}Ti_2O_{40}]^{7-}\ \mathbf{2} + 2\,H_2O \quad (2)$$

The dimeric, Ti–O–Ti bridged anhydride composition for **1** was confirmed by X-ray structure analysis, complete elemental analysis, TG/DTA, FTIR, and pH-variable ultracentrifugation molecular weight measurements. In the complete elemental analysis, all elements including oxygen, total 100.26% (repeat analysis on an independent preparation, 99.14%) for **1** with 3 hydrated water molecules of the sample dried at room temperature under 10^{-3}–10^{-4} torr overnight was observed. The weight loss observed during drying before analysis was 3.98% which corresponds to 13 water molecules for each molecule of **1**. TG/DTA measurements performed under atmospheric conditions showed the presence of 12 water molecules for **1** believed to be both intrinsic water of hydration and adsorbed water from the atmosphere. ‡ The solid FTIR spectrum, measured as a KBr disk of **1**, showed the characteristic vibrational bands of the Keggin-type "$XW_{12}O_{40}{}^{n-}$" polyoxotungstate framework (Fig. 1).[6] The ^{183}W NMR of **1** measured in D_2O, which showed a six-line spectrum of −92.8, −101.2, −105.8, −119.9, −131.2 and −139.5 ppm with integrated intensities 2 : 2 : 2 : 2 : 1 : 1 (Fig. 2b), suggests that the two Ti^{IV} octahedra are linked through corner- or edge-sharing in the α-Keggin polyoxoanion (1,2- or 1,4-isomer; C_s symmetry). However, from the X-ray structure analysis, it was shown that the ^{183}W NMR spectrum is due to the corner-sharing species (1,2-isomer). Solution ^{31}P NMR spectra of **1** measured in D_2O showed only one resonance at −11.74 ppm, confirming its purity and single product nature (Fig. 3).

There are five isomers from di-substitution of the α-Keggin structure; two are of C_s, one is of C_2, one is of C_{2v}, and one is C_1 symmetry.[5b] The ^{31}P and ^{183}W NMR of **1** can be compared with the well-known di-Ti^{IV}-substituted Keggin polyoxotungstate with C_2 symmetry (1,5-isomer);[5b] the ^{31}P NMR of $Li_7[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]$ in water has revealed a single resonance at −11.43 ppm and the ^{183}W NMR in H_2O/D_2O has shown five equally intense peaks, which must be ascribed to the C_2 isomer formed by 1,5-substitution. (*Note*: this was described as 1,4-substitution in the original paper.[5b]) The structure of the C_2 isomer has been also confirmed by X-ray structure analysis of $(Et_2NH_2)_4Na[H_2PW_{10}Ti_2O_{40}]\cdot 11H_2O$.[5f]

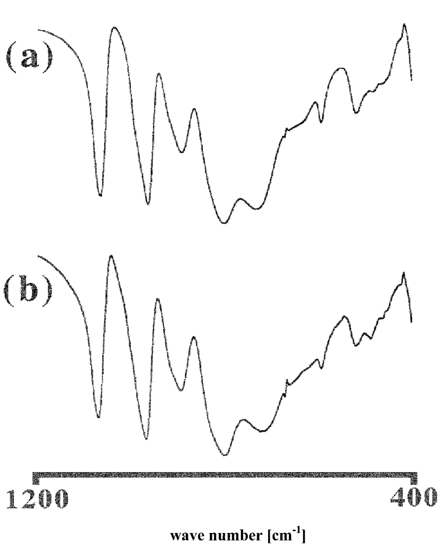

Fig. 1 FTIR spectra in the polyoxoanion region (1200–400 cm^{-1}), measured as KBr disks, of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **3** (for comparison) and (b) $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1**.

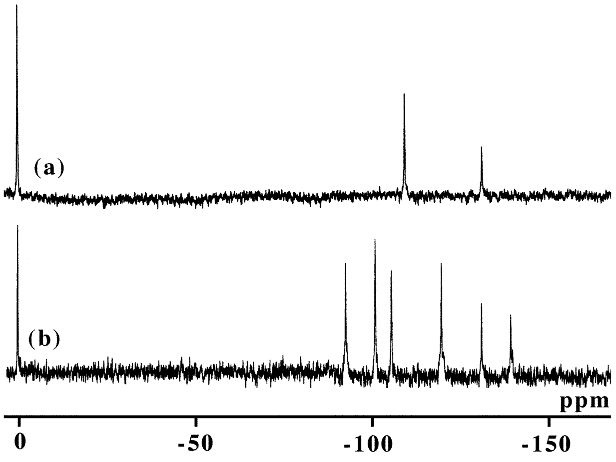

Fig. 2 ^{183}W NMR in D_2O of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **3** (for comparison) and (b) $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1**. The resonance at 0.0 ppm is due to the external reference: saturated Na_2WO_4–D_2O solution.

On the other hand, the pH-dependent interconversion has been confirmed by pH-variable ultracentrifugation molecular weight (MW) measurements; **1** is present as a monomer under less acidic conditions (pH 7.8), while it is present as a dimer under acidic conditions (pH 1.0 and 2.2).

Thus, isolation of the monomer **2** was attempted from an aqueous solution containing the dimer**1**. It was confirmed by ^{31}P NMR (showing a single peak at −12.14 ppm) that species **2** was present in pH 7.01 aqueous solution, however, the analytically pure solid of **2** was difficult to isolate, because the monomer readily reverted to the dimer in solution [see the Experimental section]. The pH 7.01 solution, concentrated by rotary evaporation, showed three ^{31}P NMR signals at −11.55, −11.82 (dimeric $[P_2W_{20}Ti_4O_{78}]^{10-}$) and −12.16 (monomeric $[1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$) ppm. An FTIR spectrum of the solid sample, obtained by evaporation of the solution to dryness, was measured. The 721 cm^{-1} band observed in **1**, which may be due to intermolecular Ti–O–Ti bonds, was weakened, but the two P–O bands (1084, 1062 cm^{-1}) were observed, suggesting that the dimer is contaminated (P–O band for **1**, 1065 cm^{-1}). The re-dissolved D_2O solution of the compound obtained by evaporation to dryness, where pH or pD was not controlled, showed three ^{31}P NMR signals (at −11.49, −11.77 and −12.12 ppm).

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‡ With regard to the composition of compound **1**, the number of hydrated water molecules was changed from sample to sample. In fact, an inconsistency in the amount of hydrated water of **1** (a weight loss on drying before analysis corresponding to 13 waters plus the analytical results showing 3 waters, *i.e.* total 16 hydrated water molecules, are inconsistent with the TG/DTA results of 12 waters) was observed. The measurements were performed in different circumstances, *i.e.* the complete elemental analysis was performed in Germany, while the TG/DTA measurements were conducted in Japan. We have frequently experienced such an inconsistency. Thus, the amount of hydrated water of the title compound was based on the TG/DTA measurement. On the other hand, the single-crystal used for X-ray crystallography was a compound with 17 hydrated waters.

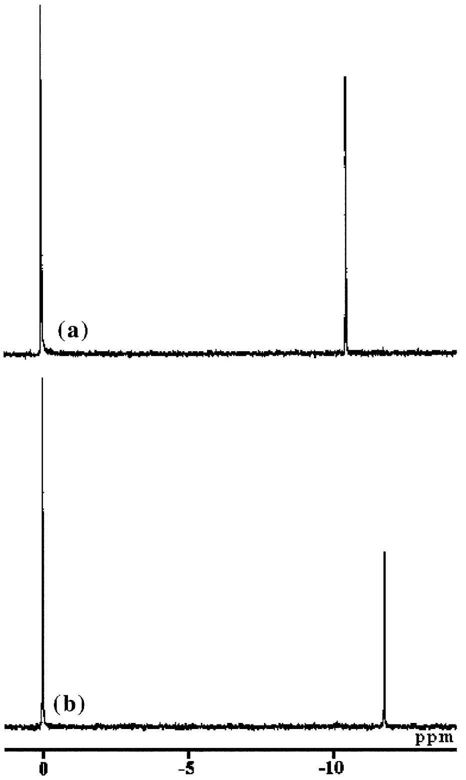

Fig. 3 ^{31}P NMR in D_2O of (a) $K_{10}H_2[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]\cdot 17H_2O$ **3** (for comparison) and (b) $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1**. The resonance at 0.0 ppm is due to the external reference: 25% H_3PO_4 in H_2O. In each case a very high level of purity is indicated (*i.e.*, with respect to any other P-containing polyoxoanions or other materials).

However, when 0.2 mL of KOH solution (pH 14) was added to the D_2O solution showing the three ^{31}P resonances, a single ^{31}P resonance at −12.14 ppm was re-observed. Thus, it is clear that the monomer readily changes to the dimer in aqueous solution.

The monomeric form can allow covalent bonding of organometallic fragments to the polyoxoanion surface, because it possesses sufficient negative-charge density on its surface oxygen atoms as observed in the tri -V^{V}- and tri-Nb^{V}-substituted polyoxotungstates.[2j,l,3a,d,g]

Crystal and molecular structure of 1

Crystals of **1** contained discrete polyoxoanions, potassium cations and lattice water molecules ‡. The observed electron densities of the Ti and W atoms were quite different, and the data unequivocally distinguished and defined the Ti and W atoms. Thus, the main features of the structure of the polyoxoanion were clear. However, the resolution obtained for the structure of the salt was limited by the poor quality of the available crystals and by the considerable disorder of the cations and the solvent of crystallization. These features are all too common in polyoxoanion crystallography.[5c,7d]

Structural analysis revealed the molecular structure of $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$ as shown in Fig. 4a. The molecular structure of **1** was composed of two "$PW_{10}Ti_2O_{40}$" Keggin-polyoxoanion halves linked *via* two Ti–O–Ti bonds, each half of which has the same α-Keggin structure $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$. The overall symmetry of **1** is C_{2v}, because two mirror planes are present, and it is consistent with a 2 : 2 : 2 : 2: 1 : 1 ^{183}W NMR spectrum. As expected, the two TiO_6 octahedra in each "$PW_{10}Ti_2$" Keggin unit substituted the two corner-sharing WO_6 octahedra of $[\alpha\text{-}PW_{12}O_{40}]^{3-}$. Selected bond lengths and angles for the polyoxoanion are given in Table 1 (other bond lengths and angles of **1** are provided in Table S1 in the ESI †). The two Ti atoms and ten W atoms all exhibited conventional octahedral coordination polyhedra (Fig. 4b). The W–Ot (Ot: terminal oxygen) [1.68(2)–1.77(2) Å], W–Oc (Oc: corner sharing oxygen) [1.82(1)–1.98(2) Å], W–Oe (Oe: edge-sharing oxygen) [1.81(2)–2.02(2) Å], and W–Oa (Oa: oxygen coordinated to P atom) [2.41(1)–2.47(2) Å] distances were in the normal range.[1b] The polyoxoanion contained one central P atom in an almost regular tetrahedral environment of PO_4 with P–O distances in the range of 1.50(2)–1.57(2) Å, and O–P–O bond angles of 108.5(9)–112.4(9)°. In Fig. 4a, the terminal oxygens O3 and O41 have an interaction with the same potassium atom K2 [K2–O3 2.94(2), K2–O41 2.87(2), K2–$O3^{i}$ 2.81(2) and K2–$O41^{i}$ 2.81(2) Å; symmetry operation i: $1 - x, -y, -z$]. Bond lengths around Ti were Ti–O–Ti (between monomer units) [1.80(2)–1.84(2), average 1.82 Å], Ti–O–Ti (within monomer units) [1.81(1)–1.84(1), average 1.83 Å], Ti–Oe (W) [1.96(2)–2.04(2), average 2.00 Å], Ti–Oc(W) [1.92(2)–1.95(2), average 1.94 Å] and Ti–Oa [2.31(2)–2.37(2), average 2.34 Å]. The Ti–O–Ti angles between the two α-Keggin units were 136.3(8), 136.4(8)° and those within the Keggin units were 149.8(9), 153.0(1)°. [*Note*: Ti–O–W (within monomer unit); 143.7(9)–145.7(9)°.] The bond valence sums (BVS)[7a,b] at the four Ti, twenty W and two P atoms, calculated based on observed bond lengths, were in the range 3.887–4.065, 5.642–6.400 and 4.923–5.019, respectively, which reasonably correspond to formal valences of Ti^{4+}, W^{6+} and P^{5+}, respectively.

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

Ti–O–Ti distances (within monomer units)		(between monomer units)	
Ti1–O5	1.81(1)	Ti1–O1	1.81(2)
Ti2–O5	1.83(1)	Ti2–O2	1.80(2)
Ti3–O43	1.82(1)	Ti3–O1	1.83(2)
Ti4–O43	1.84(1)	Ti4–O2	1.84(2)
Ti–O–W distances (within monomer units)		Ti–Oa distances	
Ti1–O4	1.93(2)	Ti1–O38	2.37(2)
Ti2–O6	1.92(2)	Ti2–O39	2.35(2)
Ti3–O44	1.94(2)	Ti3–O77	2.31(2)
Ti4–O42	1.95(2)	Ti4–O76	2.34(2)
W1–O4	1.84(1)		
W1–O6	1.83(2)		
W11–O42	1.82(1)		
W11–O44	1.84(1)		
Angles			
Ti1–O5–Ti2	153.0(1)	Ti1–O1–Ti3	136.4(8)
Ti2–O6–W1	145.5(9)	Ti2–O2–Ti4	136.3(8)
Ti1–O4–W1	145.7(9)		
Ti3–O43–Ti4	149.8(9)		
Ti4–O42–W11	145.0(8)		
Ti3–O44–W11	143.7(9)		

The general structure of the dimeric, di-Ti^{IV}-substituted Keggin polyoxoanion $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$**1** is, overall, similar to those of the reported, dimeric tri-Ti^{IV}-substituted species $[\alpha,\alpha\text{-}P_2W_{18}Ti_6O_{77}]^{12-}$ **3**,[5j] $[\beta,\beta\text{-}Si_2W_{18}Ti_6O_{77}]^{14-}$ **4**[5c] and $[\alpha,\alpha\text{-}Ge_2W_{18}Ti_6O_{77}]^{14-}$ **5**,[5d] but there are several differences in (i) the orientation (α for **1**, **3** and **5** *vs.* β for **4**) of the W_3 cap; (ii) the Ti–O–Ti angles between the two Keggin units [136.3(8)–136.4(8)° for **1**, 130.1(7)–131.3(7)° for **3**, all are 141(3)° for **4**, 132–136(2)° for **5**]; (iii) the Ti–O–Ti bond lengths between the two Keggin units [1.80(2)–1.84(2), average 1.82 Å for **1**; 1.80(1)–1.86(1), average 1.83 Å for **3**; 1.79(3)–1.83(3), average 1.81 Å for **4**; 1.78(2)–1.85(2), average 1.82 Å for **5**]; (iv) the Ti–O–Ti bond lengths within the Keggin units [1.81(1)–1.84(1), average 1.83 Å for **1**; 1.79(1)–1.92(1), average 1.87 Å for **3**; 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 (v) the dimensions of the polyoxoanions 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+})[7c] and, therefore, to the different sizes of the central tetrahedra [P–O distances 1.50(2)–

Table 2 The results of solution molecular weight determination for **1**.

Solution in which sample **1** was dissolved	Found MW (spinning rate in rpm)	Calcd MW {minus waters} (anion alone)
		$K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1**
{adjusted to pH 2.2 with concentrated HCl}	{5200 (± 300) g mol^{-1}} (20000)	5785.7 g mol^{-1} {5569.5 g mol^{-1}}
[adjusted to pH 1.0 with concentrated HCl]	[5000 (± 300) g mol^{-1}] (20000)	(5178.5 g mol^{-1})
		"$K_7[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]\cdot 8H_2O$" **2**
{0.1 M aqueous NaCl solution, pH 7.8}	{2800 (± 100) g mol^{-1}} (30000)	3023.1 g mol^{-1} {2878.9 g mol^{-1}}
	{2700 (± 100) g mol^{-1}} (40000)	(2605.3 g mol^{-1})

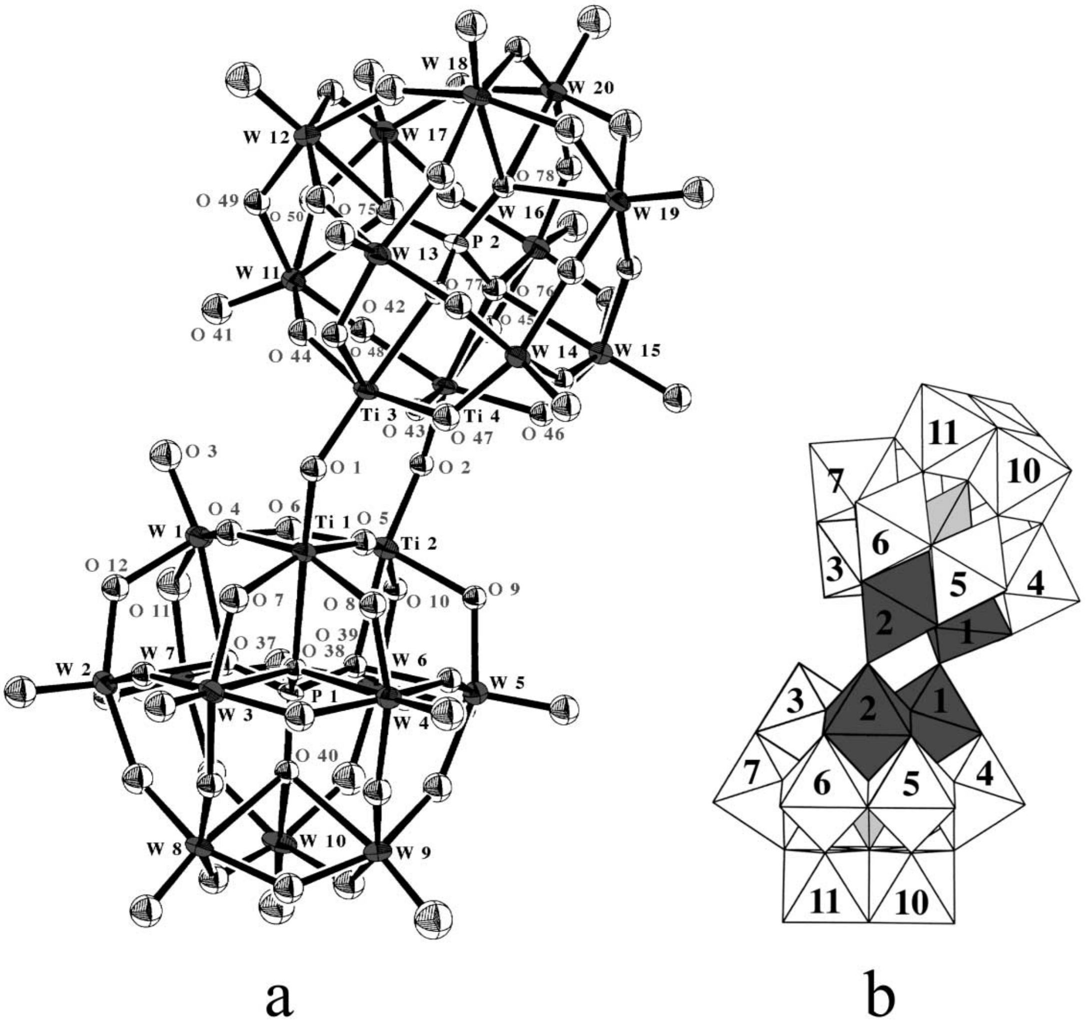

Fig. 4 (a) Molecular structure of the dimeric, Ti–O–Ti bridged anhydride form **1** with 50% probability ellipsoids and (b) the polyhedral representation of the same polyoxoanion $[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]^{10-}$. In (b), the two titaniums are represented by the dark gray octahedra in the 1,2-positions. The WO_6 octahedra occupy the white octahedra in 3–12 positions and the PO_4 group is shown as the internal light gray tetrahedron. The overall symmetry C_{2v} is consistent with a six-line ^{183}W NMR with integrated intensities 2 : 2 : 2 : 2 :1 : 1 (Fig. 2b).

1.57(2) Å for **1**, 1.52(1)–1.55(1) Å in **3**, 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**].

Determination of the solution molecular weight

Analytical ultracentrifugation[8] is a well-established technique for the determination of the solution molecular weight of polyoxoanions.[2c,3a,3b,5g] Of special interest is our recent report of the use of analytical ultracentrifugation for the detection of anhydride forms of polyoxoanions.[5g,j] The results of the solution molecular weight determinations for **1** are summarized in Table 2. The molecular weight of each compound was determined at two different spinning rates to assure the validity of the data. Interestingly, the molecular weight of **1** under less acidic conditions (pH 7.8) was found to be only 2800 (± 100) g mol^{-1}, indicating that it is monomeric in solution (*i.e.*, it does not form a Ti–O–Ti anhydride dimer). Under more acidic conditions (pH 1.0 and 2.2) the molecular weight was found to be 5000 (± 300) and 5200 (± 300) g mol^{-1}, respectively, indicating it is present in solution as the anhydride bridged dimer.[5c] Thus, under more acidic conditions the anhydride bridged dimer seen in the X-ray crystal structure is also the species present in solution. In every MW experiment an excellent fit to the single-species model was observed, as evidenced by the relatively small, random residuals shown in Figs. 5a and 5b. Clearly, the results of these solution molecular weight determinations support the proposed formulation of **1**.

Conclusions

The dimeric, Ti–O–Ti bridged anhydride form, $K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1** with overall C_{2v} symmetry of the polyoxoanion, composed of the novel di-Ti^{IV}-1,2-substituted

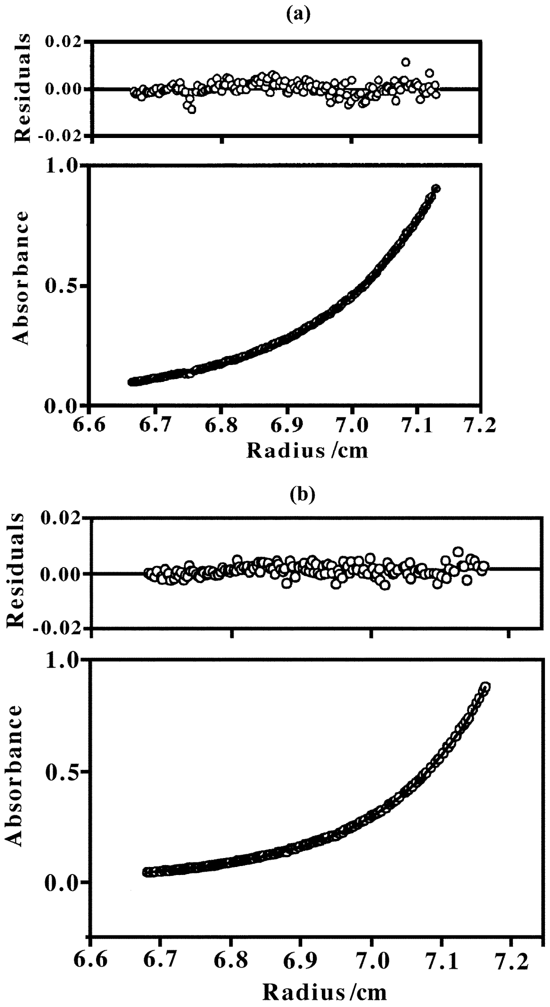

Fig. 5 Ultracentrifugation sedimentation equilibrium plot for compound **1** (a) at 20000 rpm and (b) at 30000 rpm. In (a) the sample solution was adjusted to pH 2.2 with concentrated HCl prior to the MW determination, and in (b) the pH of the sample solution was measured to be 7.8. Note the excellent fit to the data for the calculated curve, which assumes a single-species model, resulting in relatively small, random residuals. The fit in (a) gives a solution MW of 5200 (± 300) g mol^{-1}, corresponding to the MW of the anhydride dimer and the fit in (b) gives a solution MW of 2800 (± 100) g mol^{-1}, corresponding to the MW of the monomer.

α-Keggin polyoxotungstate, was isolated and structurally characterized. The pH-variable solution molecular weight measurements showed that **1** is present as a dimer under more acidic conditions, while it is a monomer under less acidic conditions. ^{31}P NMR verified that a single species, the monomer **2**, was present in a pH 7.01 (KOH) aqueous solution of dissolved **1**. However, during evaporation of the aqueous solution, the monomer readily changed to the dimer and, thus, isolation of the analytically pure solid of the monomer **2** is difficult. Nevertheless, the fact that the presence of the monomeric form $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$ was confirmed is of significance. The complex **1** is also of interest as a possible solid-base catalyst, perhaps a super-base catalyst. Studies in these directions are in progress.

Experimental

Materials

The following were used as received: $Na_2WO_4\cdot 2H_2O$, 85% H_3PO_4, KCl, 12 M aqueous HCl solution (quantitative analysis grade) (all from Wako); $Ti(SO_4)_2\cdot 4H_2O$ (Junsei); D_2O (Isotec). $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$ was prepared according to the literature.[9]

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 in 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 run under air with a temperature ramp of 4 °C per min 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. These spectra were referenced to an external standard (saturated Na_2WO_4–D_2O solution) by the substitution method. Chemical shifts were reported on the δ scale with resonances upfield of Na_2WO_4 (δ 0) as negative. In Fig. 2, the spectra were drawn by overlapping the reference peaks with the spectra measured by the substitution method.

Preparations

$K_{10}[\alpha,\alpha\text{-}P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ 1. To a stirred, clear 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 8.90 g (3.20 mmol) of $Na_9[A\text{-}PW_9O_{34}]\cdot 19H_2O$, where the addition 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 added over 10 min and the solution was stirred for 1 h. The white precipitate which formed was collected on a membrane filter (JG 0.2 μm). The compound at this stage was obtained in *ca.* 8 g yield.

The white powder was suspended in 40 mL of unbuffered pH 2.2 water, prepared with 1 M aqueous HCl solution, on 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 as **1** were collected on a membrane filter (JG 0.2 μm) and dried *in vacuo* for 2 h. [When ^{31}P NMR in D_2O of this compound at this stage showed contamination with compound **3**, the recrystallization from unbuffered pH 2.2 water at 50 °C was repeated once more. Compound **3** was insoluble in MeOH, while compound **1** was soluble in MeOH. This fact can also be utilized to separate **1** from **3**.] Yield: 2.7 g (29.2%). Compound **1** was soluble in water and MeOH, but insoluble in EtOH and diethyl ether {Found (repeat analysis on an independent preparation): H, 0.12 (0.13); K, 6.97 (7.38); P, 1.13 (1.16); W, 65.20 (63.80); Ti, 3.74 (3.57); O, 23.10 (23.10); total 100.26% (99.14%). Calc. for $H_6K_{10}P_2W_{20}Ti_4O_{81}$ or $K_{10}[P_2W_{20}Ti_4O_{78}]\cdot 3H_2O$: H, 0.11; K, 6.95; P, 1.10; W, 65.39; Ti, 3.41; O, 23.05%}. A weight loss of 3.98% was observed during the course of drying at room temperature at 10^{-3}–10^{-4} torr overnight before analysis, suggesting the presence of 13 water molecules weakly solvated or adsorbed. TG/DTA under atmospheric conditions: a weight loss of 3.74% was observed below 500 °C with an endothermic point at 110 °C; calcd 3.74% for x = 12 in $K_{10}[P_2W_{20}Ti_4O_{78}]\cdot xH_2O$. IR (KBr) (polyoxometalate region): 1065s, 964s, 891m, 798vs, 721s, 593m, 519m, 487m cm^{-1}. ^{31}P NMR (24.2 °C, D_2O): δ −11.74. ^{183}W NMR (24.7 °C, D_2O): δ −92.8 (2W), −101.2 (2 W), −105.8 (2 W), −119.9 (2 W), −131.2 (1 W), −139.5 (1 W). [*Note*: 0.23 g (0.041 mmol) of

$K_{10}[P_2W_{20}Ti_4O_{78}]\cdot 12H_2O$ **1** dissolved in 10 mL water showed pH 4.1.]

Attempt to isolate the monomer "$K_7[PW_{10}Ti_2O_{40}]\cdot 8H_2O$" 2. This compound was not isolated as an analytically pure solid. 0.71 g of the dimeric compound **1** was dissolved in 10 mL of pH 7.0 aqueous solution prepared with 1.0 M KOH aqueous solution. After dissolving, the resulting solution showed pH 4.7. By dropwise adding 0.5 M KOH aqueous solution, the pH of the solution was adjusted to pH 7.01. [*Note*: It took a long time (more than 10 h) to stabilize the pH of the solution at 7.01. This fact suggests that the transformation from dimer to monomer is very slow.] The ^{31}P NMR in H_2O, measured at this stage, showed a single peak at −12.14 ppm due to **2**. The solution was evaporated to dryness by rotary evaporation at 50 °C. The residue was washed with 5 mL of EtOH and dried *in vacuo* for 2 h. A very hygroscopic, white powder was obtained in more than 0.022 g yield {Found: H, 0.12; K, 10.5; P, 1.06; W, 61.4; Ti, 3.34; O, 22.1; total 98.52%. Calc. for $H_2K_7PW_{10}Ti_2O_{41}$ or $K_7[PW_{10}Ti_2O_{40}]\cdot H_2O$: H, 0.07; K, 9.45; P, 1.07; W, 63.46; Ti, 3.31; O, 22.64%}. A weight loss of 4.48% was observed during the course of drying at room temperature at 10^{-3}–10^{-4} torr overnight before analysis, suggesting the presence of 7–8 water molecules weakly solvated or adsorbed. TG/DTA under atmospheric conditions: a weight loss of 4.95% was observed below 500 °C without a clear endothermic point; calcd 4.76% for $x = 8$ in $K_7[PW_{10}Ti_2O_{40}]\cdot xH_2O$. IR (KBr) (polyoxometalate region): 1084m, 1062m, 962m, 891m, 818s, 721m, 624m, 480m cm^{-1}. ^{31}P NMR (21.2 °C, H_2O, pH 7.0 (KOH)): δ −12.14. ^{31}P NMR (21.2 °C, D_2O): δ −11.49, −11.77 (dimer), −12.12 (monomer). ^{31}P NMR (21.2 °C, D_2O after addition of 0.2 mL of KOH solution (pH 14) to the above solution): δ −12.14.

Ultracentrifugation solution molecular weight measurements

A solution (pH 7.8) of **1** was 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 $\lambda = 250$ nm (the final concentration was *ca.* 20 μg mL^{-1}). The solutions at pH 1.0 and 2.2 were prepared similarly, and their pH adjusted with concentrated HCl prior to the MW determination.

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 $\lambda = 250$ 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_2Cl_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 the 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 using the XL-A/XL-I Data Analysis Software, Version 4.0 (Beckman Instruments, Inc.) operating within Origin 4.1. The data were fitted to an ideal, single-species model using the following equation:

$$C_r = C_m \exp[M(1 - \upsilon\rho)\omega^2(r^2 - r_m^2)/2RT] \qquad (3)$$

where C_r is the concentration at some radial position and C_m is the concentration at some reference position, M is the weight-average molecular weight, υ 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,8a]

All of the solution molecular weights have been given 5% error bars, a value that encompasses the maximum experimental error observed in repeat measurements, Table 2. This is true even if the extreme values of partial specific volume from the references are used instead of the average values.

Ultracentrifugation molecular weight measurements in HCl-acidic aqueous solution (pH 1.0); an average MW of 5000 (± 300) for spinning rate/rpm 20000; calcd 5569.5 for $K_{10}[P_2W_{20}Ti_4O_{78}]$ without water and calcd 5178.5 for the anion alone. Ultracentrifugation molecular weight measurements in HCl-acidic aqueous solution (pH 2.2); an average MW of 5200 (± 300) for spinning rate/rpm 20000. Ultracentrifugation molecular weight measurements in water (pH 7.8); an average MW of 2800 (± 100) for spinning rate/rpm 30000 and 2700 (± 100) for spinning rate/rpm 40000; *e.g.* calcd 2878.9 for $K_7[PW_{10}Ti_2O_{40}]$ both without water and calcd 2605.3 for the anion alone.

X-Ray crystallography

A colorless needle crystal of **1** that contained 17 hydrated waters (0.20 × 0.10 × 0.20 mm) was sealed in a glass capillary. Data collection used a Rigaku AFC5S four-circle diffractometer, and the intensity data were collected at 296 K in the range $6 < 2\theta < 55°$. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods followed by subsequent difference Fourier calculation and refined by a full-matrix least-squares procedure using the TEXSAN package.[10] All non-hydrogen atoms, except oxygens, were refined anisotropically. Two potassium atoms which were disordered, were treated isotropically. Crystal data for $K_{10}H_{34}P_2W_{20}Ti_4O_{95}$ **1**, $M = 5875.81$, triclinic, space group $P\bar{1}$ (No. 2), $a = 19.052(2)$, $b = 21.021(2)$, $c = 12.778(2)$ Å, $\alpha = 103.90(1)$, $\beta = 98.18(1)$, $\gamma = 77.220(9)°$, $V = 4823(1)$ Å^3, $Z = 2$, $D_c = 4.05$ g cm^{-3}, μ(Mo-Kα) = 246.3 mm^{-1}. Final $R_{int} = 0.032$, $R1 = 0.065$, $R_w = 0.174$ and GOF = 1.34 (22798 total reflections, 22131 unique reflections of which 22131 with $I > -10.0\sigma(I)$ were used in all calculations). All peaks of large residual density holes were located about 1 Å from the tungsten atoms.

CCDC reference number 186045.

See http://www.rsc.org/suppdata/dt/b2/b204775f/ for crystallographic data in CIF or other electronic format.

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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; (*d*) C. L. Hill, Ed., *Chem. Rev.*, 1998, **98**, 1; (*e*) T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.*, 1996, **41**, 113; (*f*) C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407; (*g*) A series of 34 recent papers in a volume devoted to poloxoanion in catalysis, C. L. Hill, *J. Mol. Catal.*, 1996, **114**, 1; (*h*) R. Neumann, *Prog. Inorg. Chem.*, 1998, **47**,

317; (*i*) M. Pope and A. Muller (Editors), *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*, Kluwer Academic Publishers, Netherlands, 2001.

2 (*a*) S. P. Harmalker, M. A. Leparulo and M. T. Pope, *J. Am. Chem. Soc.*, 1983, **105**, 4286; (*b*) P. J. 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. Takahashi, K. Ohsawa and J. A. Widegren, *J. Chem. Soc., Dalton Trans.*, 2001, 2872.

6 (*a*) C. Rocchiccioli-Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta, Part A*, 1976, **32**, 587; (*b*) C. Rocchiccioli-Deltcheff, M. Fournier and R. Franck, *Inorg. Chem.*, 1983, **22**, 207; (*c*) R. Thouvenot, M. Fournier, R. Franck and C. Rocchiccioli-Deltcheff, *Inorg. Chem.*, 1984, **23**, 598.

7 (*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.

8 (*a*) T. M. Laue, *Methods in Enzymology*, ed. M. L. Johnson and G. K. Ackers, Academic Press, 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. (Totowa, N. J.)*, 1994, **22**, 75; (*d*) T. M. Laue and D. G. Rhodes, *Methods in Enzymology*, ed. M. P. Deutscher, Academic Press, San Diego, 1990, vol. 182, p. 566.

9 A. Teze and G. Herve, *Inorg. Synth.*, 1990, **27**, 85.

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