

A first example of polyoxotungstate-based giant molecule. Synthesis and molecular structure of a tetrapod-shaped Ti–O–Ti bridged anhydride form of Dawson tri-titanium(IV)-substituted polyoxotungstate † ‡

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The preparation and structural characterization of a giant “tetrapod”-shaped inorganic molecule, $[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$, **1a** (abbreviated to $\{TiO_6\}_{12}$; FW ~15700), consisting of four tri-Ti^{IV}-1,2,3-substituted α -Dawson substructures and one encapsulated Cl⁻ ion, are described. A water-soluble, all-inorganic composition compound of the tetrameric Ti–O–Ti bridged anhydride form, $Na_xH_{33-x}K_4[1a] \cdot yH_2O$, **1** ($x = 21-26$, $y = 60-70$), being afforded by a stoichiometric reaction in aqueous solution of tri-lacunary Dawson polyoxotungstate $Na_{12}[B-\alpha-P_2W_{15}O_{56}] \cdot 19H_2O$ with 3 equiv of $Ti(SO_4)_2 \cdot 4H_2O$ in HCl-acidic aqueous solution followed by exchanging the counteraction, was obtained as analytically pure, homogeneous colorless plate crystals. Single-crystal X-ray structure analysis revealed that the polyoxoanion **1a** was an inorganic, giant “tetrapod”-shaped molecule (described as a sphere with a diameter of ~31.2 Å) with approximately T_d symmetry. Characterization of **1** was also accomplished by complete elemental analysis, TG/DTA, FTIR, UV-vis absorption and solution (³¹P and ¹⁸³W) NMR spectroscopy.

Introduction

Inorganic compounds of high nuclearity, symmetry and architectural beauty have been anticipated.¹ The molecular design, synthesis and X-ray crystallography of giant, inorganic molecules that contain many heavy metal atoms are challenging projects in the chemistry of polyoxometalates.²

Polyoxometalate-based giant molecules so far reported have been based on soluble mixed-valence polyoxomolybdates (molybdenum blue). As a matter of fact, Müller and co-workers have reported various kinds of polyoxomolybdate-based giant molecules:³ the Keggin cluster ion encapsulated in the $\{Mo^{VI}_{72}Fe^{III}_{30}\}$ cluster, *i.e.* $[H_3PMo_{12}O_{40} \cdot H_4Mo^{VI}_{72}Fe^{III}_{30}(CH_3COO)_{15}O_{254}(H_2O)_{98}] \cdot ca. 60H_2O$ (FW ~ 17000),^{3a} linked icosahedral, strong molecular magnets $\{Mo^{VI}_{72}Fe^{III}_{30}\}$, *i.e.* $[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}] \cdot ca. 150H_2O$ (FW ~ 15900) and $[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{87}] \cdot ca. 80H_2O$ (FW ~16000),^{3b} $\{Mo_{176}\}$ and $\{Mo_{248}\}$ (FW ~ 37600) clusters,^{3c} Bielefeld giant wheel/nanosize rings $\{Mo_{152}\}$, *i.e.* $Na_{16}[Mo^{VI}_{124}Mo^V_{28}O_{429}(\mu_3-O)_{28}H_{14}(H_2O)_{66.5}] \cdot ca. 300H_2O$ (FW ~ 23474.6),^{3d} a ring-shaped reduced “metal oxide” with the simple composition $[(MoO_3)_{176}(H_2O)_{80}H_{32}]$ (FW ~ 26800).^{3f} Recently reported, other polyoxometalate-based giant molecules, $[Mo^V_{28}Mo^{VI}_{114}O_{432}H_{28}(H_2O)_{58}]^{12-}$ (FW ~ 21608) and $[Mo^V_{28}Mo^{VI}_{126}O_{462}H_{14}(H_2O)_{70}]^{14-}$ (FW ~ 23442),⁴ have also consisted of mixed-valence polyoxomolybdates. On the contrary, the polyoxotungstate-based giant molecule has been scarcely reported so far.[‡]⁵

Site-selective substitution of W^{VI} atoms in polyoxotungstates

with Ti^{IV} atoms is particularly interesting, because of the expected, much higher basicity of the resulting polyoxoanion and, also, of the multicenter active sites formed with corner- or edge-sharing TiO₆ octahedra, *i.e.* molecular modeling of a light-semiconductor TiO₂.⁶ 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 the oligomeric Ti–O–Ti anhydride formation resulting from substitution by several Ti^{IV} atoms.⁷ In fact, the tri-Ti^{IV}-1,2,3-substituted Keggin polyoxotungstates heretofore prepared are the dimeric, Ti–O–Ti bridged anhydride forms, *e.g.* $[\beta, \beta-Si_2W_{18}Ti_6O_{77}]^{14-}$,^{7a} which is formed from two $[A-\beta-SiW_9Ti_3O_{40}]^{10-}$ Keggin units, and $[\alpha, \alpha-Ge_2W_{18}Ti_6O_{77}]^{14-}$,^{7b} which is formed from two $[A-\alpha-GeW_9Ti_3O_{40}]^{10-}$ Keggin fragments, and the very recently found $[\alpha, \alpha-P_2W_{18}Ti_6O_{77}]^{12-}$,^{7c} which is formed from two $[A-\alpha-PW_9Ti_3O_{40}]^{9-}$ Keggin units. The dimeric, Ti–O–Ti bridged anhydride form of the di-Ti^{IV}-1,2-substituted α -Keggin polyoxotungstate, $[\alpha, \alpha-P_2W_{20}Ti_4O_{78}]^{10-}$, is very recently elucidated.^{7d} Mono-titanium(IV)-substituted polyoxotungstate, $[(PTiW_{11}O_{39})_2OH]^{7-}$, also shows a dimeric structure with a Ti–O(H)–Ti bonding between the two Keggin units.^{7e}

The oligomeric Ti–O–Ti anhydride forms are very stable and, therefore, isolation of the monomeric forms from these Ti^{IV}-substituted polyoxotungstates is very difficult. Thus, the ease of oligomerization observed in the Ti^{IV}-substituted polyoxotungstates, in contrast to other d⁰ metal (V^V and Nb^V) substituted polyoxotungstates,⁸ will be extended to the synthesis of polyoxotungstate-based inorganic big molecules with higher nuclearity and higher molecular weights.

The recently found, two tri-Ti^{IV}-substituted Dawson polyoxotungstates were $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 0.8KCl \cdot 56H_2O$, **2**,[§] obtained as a powder sample and $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot$

§ In the composition of compound **2**, 0.8 KCl as an adduct has been estimated as the best-fitting value to the data of complete elemental analysis.⁹ The present X-ray structure analysis revealed the presence of one encapsulated Cl⁻ ion and, therefore, the true composition of **2** should be considered as an adduct of one KCl.

† Electronic supplementary information (ESI) available: further bond lengths and angles (Table S1) for compound **1**, FTIR (Fig. S1), ¹⁸³W NMR in D₂O (Fig. S2) and ³¹P NMR in D₂O (Fig. S3). See <http://www.rsc.org/suppdata/dt/b3/b304033j>

‡ A related paper of the tetrapod-shaped Dawson polyoxoanion, $K_4(NH_4)_{20}[(P_2W_{15}Ti_3O_{57.5}(OH)_3)_4] \cdot 77H_2O$, reported by German workers is in press.^{5a} We have submitted another paper of the related compound, $Na_xH_{45-x}[1a] \cdot yH_2O$ (**1a** = $[(\alpha-1,2,3-P_2W_{15}Ti_3O_{62})_4(\mu_3-Ti(OH)_3)_4Cl]^{45-}$, $x = 16-19$, $y = 60-70$).^{5b}

46H₂O, **3**, as a crystalline compound derived from **2**. Although the crystals of **3** were not suitable for X-ray structure analysis, the structure has been suggested to have a tetrameric, Ti–O–Ti anhydride form by complete elemental analysis, ultracentrifugation molecular weight measurements and solution (¹⁸³W and ³¹P) NMR spectroscopy.⁹ Although several plausible structures have been proposed as a combination of four [α-1,2,3-P₂W₁₅Ti₃O₆₂]¹²⁻ Dawson units, X-ray structure analysis has not been successful.

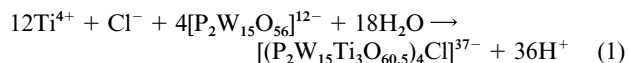
In this work, we were successful in obtaining the water-soluble sodium potassium salts Na_xH_{33-x}K₄[(α-1,2,3-P₂W₁₅Ti₃O_{60.5})₄Cl]³⁷⁻·yH₂O, **1** (x = 21–26, y = 60–70), as crystals suitable for X-ray structure analysis by exchanging the counteraction of compound **2** and in determining the crystal and molecular structures. A molecule of high nuclearity, symmetry, and architectural beauty was realized in an inorganic, giant “tetrapod” molecule composed of four tri-Ti^{IV}-1,2,3-substituted α-Dawson substructures and one encapsulated chloride ion, [(α-1,2,3-P₂W₁₅Ti₃O_{60.5})₄Cl]³⁷⁻, **1a** (abbreviated to {TiO₆}₁₂; FW ~15700).

Herein, we report full details of the synthesis and characterization of **1** and the molecular structure of **1a**.

Results and discussion

Synthesis, isolation, and compositional characterizations of **1**

The water-soluble, sodium potassium salt **1** containing a giant “tetrapod”-shaped inorganic molecule, [(α-1,2,3-P₂W₁₅Ti₃O_{60.5})₄Cl]³⁷⁻ **1a** with approximately T_d symmetry was obtained in 11.9% (0.57 g scale) yield, based on Na₂₆H₇K₄[(P₂W₁₅Ti₃O_{60.5})₄Cl]·70H₂O, by slow evaporation of the crude product in water at room temperature, which was prepared by a stoichiometric reaction, or 1 : 3-ratio reaction of Na₁₂[B–P₂W₁₅O₅₆]·19H₂O with Ti(SO₄)₂·4H₂O in HCl-acidic aqueous solution, followed by precipitating with an excess of KCl, and then by cation-exchanging with NaClO₄. The formation of **1a** can be shown in a charge balanced reaction, eqn. (1).



The tetrameric, Ti–O–Ti bridged anhydride composition for **1a** containing one encapsulated Cl⁻ ion was consistent with X-ray structure analysis, complete elemental analysis, TG/DTA, FTIR, and ³¹P and ¹⁸³W NMR spectroscopy. In the complete elemental analysis performed for compound **1**, dried at room temperature at 10⁻³–10⁻⁴ Torr overnight before analysis, all elements, including oxygen, were observed for **1** (total 101.3%), the data of which were consistent with a composition of Na_xH_{33-x}K₄[(P₂W₁₅Ti₃O_{60.5})₄Cl]³⁷⁻·yH₂O (x = 21–26, y = 30). The weight loss observed during the course of drying before analysis was 4.02% which corresponded to 39–40 water molecules weakly solvated or adsorbed for **1**. TG/DTA measurements performed under atmospheric conditions showed a weight loss of 6.46% with an endothermic point at 68 °C, which corresponded to the presence of 62–63 water molecules due to both intrinsic water of hydration and adsorbed water from the atmosphere. Thus, the number “y” of hydrated water molecules in the title compound is described as 60–70.¶

¶ As for 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 39–40 water molecules plus the analytical results showing 30 water molecules, *i.e.* total 69–70 hydrated water molecules, were inconsistent with the TG/DTA results of 62–63 water molecules) 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 number of hydrated water molecules in the title compound is described as 60–70.

The FTIR spectrum of **1** (1090, 952, 918, 832, 692, 663 cm⁻¹), measured in a KBr disk, showed the characteristic vibrational bands of the Dawson-type “P₂W₁₈O₆₂⁶⁻” polyoxotungstate framework (Fig. S1a in the ESI).[†] The positions of all bands in the polyoxoanion region in **1** were very similar to those of the recently reported, two tetrameric polyoxotungstates, *i.e.* K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·0.8KCl·56H₂O, **2** (Fig. S1b: 1089, 950, 917, 833, 692, 661 cm⁻¹) and K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·46H₂O, **3** (Fig. S1c: 1088, 948, 916, 830, 693, 661 cm⁻¹).

The ¹⁸³W NMR of **1** measured in D₂O at 19.7 °C showed a three-line spectrum of –148.3, –185.8 and –211.2 ppm with integrated intensities 1 : 2 : 2 (Fig. S2a) in accord with the presence of two tungsten belts consisting of six WO₆ octahedra and a tungsten cap of three WO₆ octahedra (W₃ cap). Thus, the three Ti^{IV} octahedra are edge-shared within the α-Dawson polyoxoanion to form the Ti₃ cap site. The ³¹P NMR spectrum of **1** in D₂O at 20.5 °C showed a clean two-line spectrum at –7.59 and –13.97 ppm, confirming its purity and single-product nature (Fig. S3a). The downfield resonance is assigned to the phosphorus closest to the Ti₃ cap, whereas the upfield resonance is due to the phosphorus closer to the W₃ cap. These ¹⁸³W and ³¹P NMR spectra are consistent with the X-ray structure and, also, can be compared with those of the recently reported, tetrameric Ti^{IV}-substituted Dawson polyoxotungstates; K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·0.8KCl·56H₂O, **2** (¹⁸³W NMR in D₂O at 25 °C (Fig. S2b): –147.6(3W × 4), –183.5(6W × 4), –210.8(6W × 4); ³¹P NMR in D₂O at 25 °C (Fig. S3b): –7.7, –14.0 ppm) and K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·46H₂O, **3** (¹⁸³W NMR in D₂O at 25 °C (Fig. S2c): –149.1(3W × 4), –183.9(6W × 4), –213.4(6W × 4); ³¹P NMR in D₂O at 25 °C (Fig. S3c): –7.4, –13.9 ppm).

The UV-vis absorption spectrum (Fig. 1a) of **1** in water showed an absorption maximum at 269 nm (ε = 4.28 × 10⁵ mol⁻¹ dm³ cm⁻¹) based on the formula weight with x = 26, y = 70) due to a ligand-to-metal charge transfer (LMCT) transition. This absorption band is compared with those of the recently reported, K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·0.8KCl·56H₂O, **2**, in pH 4.0 water: 271 nm (ε = 4.28 × 10⁵ mol⁻¹ dm³ cm⁻¹) (Fig. 1b) and K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·46H₂O, **3**, in pH 4.0 water: 271 nm (ε = 4.28 × 10⁵ mol⁻¹ dm³ cm⁻¹).

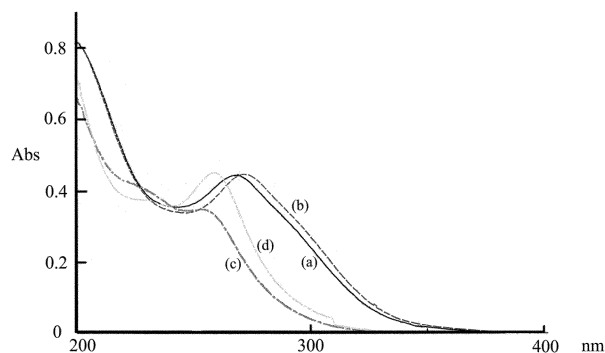


Fig. 1 UV-vis spectra at 22 °C of (a) Na₂₆H₇K₄[(P₂W₁₅Ti₃O_{60.5})₄Cl]·70H₂O, **1**, in H₂O (1.04 × 10⁻⁶ M); (b) K₂₈H₈[P₂W₁₅Ti₃O_{60.5}]₄·0.8KCl·56H₂O, **2**, in pH 4.0 water (1.00 × 10⁻⁶ M); (c) K₁₀H₂[(α-PW₉Ti₃O₃₇)₂O₃]·17H₂O in H₂O (3.11 × 10⁻⁶ M); and (d) K₁₀[(α-PW₁₀Ti₂O₃₈)₂O₂]·12H₂O in H₂O (3.04 × 10⁻⁶ M).

[Note: The UV-vis absorption spectrum (λ_{max} and ε) of **2** was identical with that of **3**.] The absorption bands at 269, 271 and 271 nm, respectively, are much more intense in the products with their three edge-sharing Ti^{IV} atoms incorporated into the Dawson structure, compared with the unsubstituted polyoxotungstate, K₆[α-P₂W₁₈O₆₂]·12H₂O (λ_{max} ca. 300 and ca. 250 nm). The UV-vis absorption spectrum of **1** is also compared with those of Keggin-type dimeric Ti–O–Ti anhydride forms (see Figs. 1c and 1d): K₁₀H₂[(α-PW₉Ti₃O₃₇)₂O₃]·17H₂O, which

contains the three Ti–O–Ti bonds between the two Keggin units and the three corner-sharing Ti–O–Ti bonds within the Keggin unit (Fig. 1c: λ_{max} 257 nm, $\epsilon = 1.11 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), and $\text{K}_{10}[(\alpha\text{-PW}_{10}\text{Ti}_2\text{O}_{38})_2\text{O}_2] \cdot 12\text{H}_2\text{O}$, which contains the two Ti–O–Ti bonds between the two Keggin units and the two corner-sharing Ti–O–Ti bonds within the Keggin unit (Fig. 1d: λ_{max} 259 nm, $\epsilon = 1.48 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). The absorption band at 269 nm of **1** was longer than those of Keggin di- and tri-Ti(IV)-substituted polyoxotungstates.

The two giant polyoxoanions (compounds **2** and **3**) with and without an encapsulated chloride ion, have been found to be tetrameric in aqueous solution by solution MW measurements.⁹ The solution (¹⁸³W and ³¹P) NMR data are consistent with the tetrapod-shaped tetrameric structures. UV-vis absorption spectra of the two giant tetrapod-shaped polyoxoanions were identical. Thus, the present cluster is stable in aqueous solution and the giant tetrapod-shaped polyoxoanion is kept in aqueous solution.

Molecular structure of **1a**

The crystal of **1** contained four discrete Dawson-polyoxoanion units, one encapsulated chloride ion, sodium and 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 molecular 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.^{7,11}

Structure analysis revealed that the molecular structure of $[(\alpha\text{-}1,2,3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{60.5})_4\text{Cl}]^{37-}$, **1a**, was composed of the four Dawson units, which are linked through Ti–O–Ti bonds and arranged in approximately T_d symmetry (Fig. 2a). The partial structure containing one Dawson unit to which other Dawson units are linked is depicted in Fig. 2b.

The molecular structure of **1a** was composed of one encapsulated Cl^- ion and four “ $\text{P}_2\text{W}_{15}\text{Ti}_3\text{O}_{62}$ ” Dawson-polyoxoanion units (designated as A, B, C and D), each Dawson unit of which had the same α -Dawson structure $[\alpha\text{-}1,2,3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{62}]^{12-}$. As expected, the three TiO_6 octahedra (Ti_3 cap) in each “ $\text{P}_2\text{W}_{15}\text{Ti}_3$ ” Dawson unit substituted the three edge-sharing WO_6 octahedra (W_3 cap) of $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$. The three terminal oxygen atoms of the Ti_3 cap were linked to three different Dawson units through Ti–O–Ti bonds, *i.e.* Dawson unit A was connected to other Dawson units (B, C and D).

In the T_d structure of $[(\text{P}_2\text{W}_{15}\text{Ti}_3\text{O}_{59})_4(\text{O})_6\text{Cl}]^{37-}$, the four Ti_3O_6 faces (Ti_3 cap) of “ $\text{P}_2\text{W}_{15}\text{Ti}_3$ ” occupied four alternate faces of an octahedron (Fig. 2d) and the one Cl^- ion was encapsulated in the central octahedral cavity. The three Ti atoms and fifteen W atoms for each Dawson unit all exhibited conventional octahedral coordination polyhedra. The polyhedral representation of **1a** is shown in Fig. 2c. The T_d molecular structure containing six Ti–O–Ti bonds for **1a** has been anticipated as one of most plausible structures by solution molecular weight measurements with ultracentrifugation and solution ³¹P and ¹⁸³W NMR spectra.⁹ The giant “tetrapod”-shaped molecule **1a** with approximately T_d symmetry may be described as a sphere with a diameter of $\sim 31.2 \text{ \AA}$ (a longitudinal distance of one Dawson unit $\sim 12.7 \text{ \AA}$). Selected bond distances and angles around the titanium(IV) centers (Table 1), and average bond distances and angles (Table 2) for the Dawson-polyoxoanion unit A in **1a** are given (other bond distances and angles are provided in Table S1 in the ESI†).

With respect to the Dawson unit A (Fig. 2b, Table 2), in the W_3 cap (W13, W14, W15), the W–Ot (Ot: terminal oxygen) [1.716(19)–1.72(2) \AA], W–Oe (Oe: edge-sharing oxygen) [1.908(18)–1.966(18) \AA], W–Oc (W belt) (Oc: corner sharing

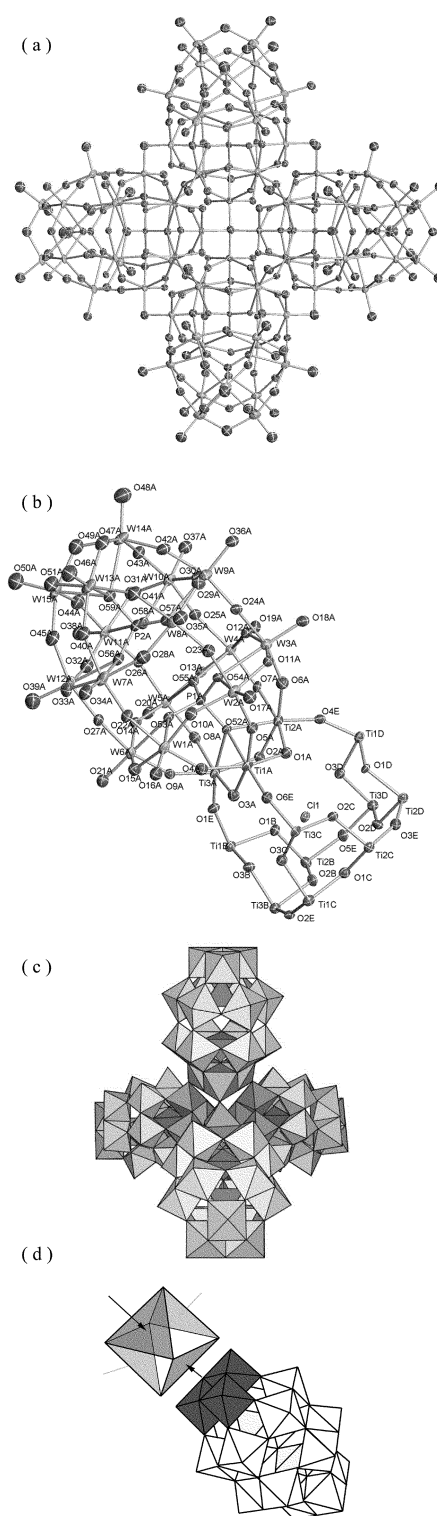


Fig. 2 (a) Molecular structure with 50% probability ellipsoids of the tetrameric Ti–O–Ti bridged anhydride form **1a** containing an encapsulated Cl^- ion in the central cavity, (b) the partial structure of **1a**; Dawson unit A and the atom numbering, and the linkage of Dawson unit A with other units (B, C and D) through Ti–O–Ti bonds, (c) polyhedral representation of **1a** with approximately T_d symmetry, and (d) another polyhedral representation showing that the four Ti_3O_6 faces of $\text{P}_2\text{W}_{15}\text{Ti}_3$ unit occupy four alternate faces of an octahedron resulting in the formation of the maximum number of Ti–O–Ti anhydride bonds (six).

oxygen) [1.871(17)–1.902(17) \AA] and W–Oa (Oa: oxygen coordinated to P atom) [2.365(15)–2.366(15) \AA] distances were in the normal range.^{2b} In the belt W(1–6), the W–O distances were W–Ot [1.688(16)–1.737(16) \AA], W–Oe [1.907(14)–1.945(15) \AA], W–Oc (M cap) [1.818(15)–1.856(14) \AA], W–Oc in the same belt [1.898(15)–1.922(16) \AA], W–Oc between the belts [1.946(15)–

Table 1 Selected bond distances (Å) and angles (°) around the titanium(IV) centers for the Dawson-polyoxoanion unit A in **1a**

Ti–O–Ti distances (within Dawson units)		Ti–O–W distances (within Dawson units)			
Ti1A–O1A	1.888(15)	Ti1A–O4A	1.975(16)	W1A–O4A	1.833(15)
Ti2A–O1A	1.935(16)	Ti1A–O5A	1.937(15)	W2A–O5A	1.856(14)
Ti2A–O2A	1.955(14)	Ti2A–O6A	1.939(15)	W3A–O6A	1.825(15)
Ti3A–O2A	1.951(15)	Ti2A–O7A	1.969(15)	W4A–O7A	1.833(14)
Ti3A–O3A	1.923(16)	Ti3A–O8A	1.982(16)	W5A–O8A	1.818(15)
Ti1A–O3A	1.954(17)	Ti3A–O9A	1.953(15)	W6A–O9A	1.831(14)
Ti–Oa distances		Ti–O–Ti distances (between Dawson units)			
Ti1A–O52A	2.242(15)	Ti1A–O6E	1.845(15)		
Ti2A–O52A	2.252(14)	Ti2A–O4E	1.809(15)		
Ti3A–O52A	2.307(14)	Ti3A–O1E	1.815(15)		
Angles					
Ti1A–O1A–Ti2A	114.6(8)	Ti2A–O7A–W4A	149.8(8)		
Ti2A–O2A–Ti3A	115.6(7)	Ti3A–O8A–W5A	150.3(9)		
Ti3A–O3A–Ti1A	114.6(8)	Ti3A–O9A–W6A	151.2(8)		
Ti1A–O4A–W1A	149.5(9)	Ti1A–O6E–Ti3C	151.5(9)		
Ti1A–O5A–W2A	150.4(9)	Ti2A–O4E–Ti1D	154.4(9)		
Ti2A–O6A–W3A	152.5(10)	Ti3A–O1E–Ti1B	155.1(10)		

Table 2 Average bond distances (Å) and angles (°) [range] for the Dawson-polyoxoanion unit A in **1a**

	Cap W(13, 14, 15)	Cap Ti(1, 2, 3)
M–O(terminal)	1.719 (20) [1.716(19)–1.72(2)]	1.823(15) [1.809(15)–1.845(15)]
M–O(M cap)	1.940 (18) [1.908(18)–1.966(18)]	1.934(15) [1.888(15)–1.955(14)]
M–O(W belt)	1.891(19) [1.871(17)–1.902(17)]	1.959(15) [1.937(15)–1.982(16)]
M–O(P)	2.366(17) [2.365(15)–2.366(15)]	2.267(14) [2.242(15)–2.307(14)]
	Tetrahedral P(2A)O ₄	Tetrahedral P(1A)O ₄
P–O	1.550(16) [1.520(16)–1.598(15)]	1.551(15) [1.533(15)–1.592(14)]
O–P–O angles	109.4(9) [106.6(9)–114.4(9)]	109.4(8) [106.9(8)–112.2(8)]
	Belt W(1–6)	Belt W(7–12)
W–O(terminal)	1.712(16) [1.688(16)–1.737(16)]	1.720(17) [1.701(17)–1.749(18)]
W–O(M cap)	1.833(15) [1.818(15)–1.856(14)]	1.957(16) [1.941(17)–1.968(17)]
W–O(W belt) ^a	1.932(15) [1.907(14)–1.945(15)]	1.912(16) [1.891(16)–1.927(16)]
W–O(W belt) ^b	1.910(15) [1.898(15)–1.922(16)]	1.896(17) [1.862(17)–1.931(17)]
W–O(W belt) ^c	1.970(15) [1.946(15)–1.982(15)]	1.851(15) [1.839(15)–1.870(15)]
W–O(P)	2.352(14) [2.338(14)–2.363(15)]	2.357(15) [2.330(16)–2.406(15)]

^a Edge sharing, between octahedra. ^b Corner sharing, same belt. ^c Corner sharing, between belts.

1.982(15) Å] and W–Oa [2.338(14)–2.363(15) Å]. In the belt W(7–12), the W–O distances were W–Ot [1.701(17)–1.749(18) Å], W–Oe [1.891(16)–1.927(16) Å], W–Oc (M cap) [1.941(17)–1.968(17) Å], W–Oc in the same belt [1.862(17)–1.931(17) Å], W–Oc between the belts [1.839(15)–1.870(15) Å] and W–Oa [2.330(16)–2.406(15) Å].

In the Ti₃ cap (Ti 1, Ti2, Ti3), the Ti–O distances were Ti–Ot [1.809(15)–1.845(15) Å], Ti–Oe [1.888(15)–1.955(14) Å], Ti–Oc (W belt) [1.937(15)–1.982(16) Å] and Ti–Oa [2.242(15)–2.307(14) Å]. The Ti–O–Ti bond lengths and angles between the three terminal oxygens (O1E, O4E, O6E) of the Ti₃ cap of Dawson unit A and the Ti atoms of the other Dawson units (B, C and D) were Ti3A–O1E–Ti1B (1.815(15), 1.823(15) Å), 155.1(10)°; Ti2A–O4E–Ti1D (1.809(15), 1.807(15) Å), 154.4(9)°; Ti1A–O6E–Ti3C (1.845(15), 1.785(15) Å), 151.5(9)°, respectively. Dawson unit A contained two central P atoms in an almost regular tetrahedral environment of PO₄: the PO₄ closest to the Ti₃ cap [P–O distances 1.533(15)–1.592(14) Å; O–P–O angles 106.9(8)–112.2(8)°] and the PO₄ closer to the W₃ cap [P–O distances 1.520(16)–1.598(15) Å; O–P–O angles 106.6(9)–114.4(9)°]. The encapsulated Cl[–] atom was placed in the center of the central octahedral cavity.

The bond valence sums (BVS),¹² calculated based on observed bond lengths for Dawson unit A, were in the range of 3.898–3.964 for the three Ti atoms, 5.839–6.336 for the fifteen W atoms and 4.832–4.853 for the two P atoms, which reasonably correspond to formal valences of Ti⁴⁺, W⁶⁺ and P⁵⁺, respectively. The BVS for Dawson unit B were in the range of 3.937–3.961 for the three Ti atoms, 5.856–6.391 for the fifteen W atoms and 4.967–4.995 for the two P atoms, those of Dawson unit C were in the range of 3.993–4.071 for the three Ti atoms, 5.660–6.366 for the fifteen W atoms and 4.829–4.919 for the two P atoms, and those for Dawson unit D were in the range of 3.955–4.050 for the three Ti atoms, 5.825–6.242 for the fifteen W atoms and 4.809–4.878 for the two P atoms.

Bonding nature of TiO₆ octahedra incorporated in **1a**

Titanium dioxide (rutile, anatase and brookite) and perovskite SrTiO₃ have attracted much attention because of their efficient properties for various catalytic photoreactions.⁶ Numerous studies on the correlations between the structures of active titanium sites and the catalytic activities have been reported; however, the mechanisms for catalytic photoreactions on

titanium oxide and SrTiO₃ still remain as a significant matter of discussion for the development of new catalysts.^{6b-d}

TiO₂ (rutile, anatase and brookite) contain edge-sharing TiO₆ octahedra,^{6a} whereas SrTiO₃ consists of corner-shared TiO₆ octahedra.^{6c} The bonding nature of TiO₆ octahedra substituted in the Keggin polyoxotungstates resembles that of TiO₆ octahedra in the perovskite SrTiO₃, rather than in the TiO₂. In fact, there are six corner-sharing TiO₆ octahedra, ($\{TiO_6\}_6$), in the dimeric, Ti–O–Ti bridged anhydride forms of the tri-Ti^{IV}-substituted Keggin polyoxotungstates, e.g. $[(\beta-SiW_9Ti_3O_{37})_2O_3]^{14-}$,^{7a} $[(\alpha-GeW_9Ti_3O_{37})_2O_3]^{14-}$,^{7b} and $[(\alpha-PW_9Ti_3O_{37})_2O_3]^{12-}$.^{7c} The dimeric di-Ti^{IV}-1,2-substituted α -Keggin polyoxotungstate, $[(\alpha-PW_{10}Ti_2O_{38})_2O_2]^{10-}$ has four corner-sharing TiO₆ octahedra.^{7d} Edge-sharing TiO₆ octahedra contained in Keggin polyoxotungstates have not hitherto been found.

In contrast, the general feature of the Dawson units in **1a** is, overall, similar to those of the reported polyoxotungstates $[(\alpha-1,2,3-P_2W_{15}Nb_3O_{62})]^{9-8d}$ and $[(\alpha-1,2-P_2W_{16}Ti_2O_{62})(Ti(ox)_2)_2]^{20-}$, which contain two edge-sharing TiO₆ octahedra and two bridging Ti(ox)₂ groups (ox = oxalato).¹³ The edge-sharing TiO₆ octahedra in **1a** might be called soluble analogs of titanium(IV) oxide and would be used as a model catalyst of titanium(IV) oxide for homogeneous photoreactions.

Conclusion

A first example of the Dawson polyoxotungstate-based, giant “tetrapod”-shaped molecule described as a sphere with diameter of ~ 31.2 Å, $[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$, **1a** (FW ~ 15700), is presented. A single crystal of the water-soluble, sodium potassium salt, $Na_xH_{33-x}K_4[1a] \cdot yH_2O$, **1** ($x = 21-26$, $y = 60-70$), was successfully derived from the recently reported, powder compound $K_{28}H_8[P_2W_{15}Ti_3O_{60.5}]_4 \cdot 0.8KCl \cdot 56H_2O$, **2**, the polyoxoanion of which has been proposed as the tetrameric Ti–O–Ti anhydride form by solution molecular weight measurements and ³¹P and ¹⁸³W NMR spectroscopy.⁹

Characterization of **1** was accomplished by X-ray structure analysis, complete elemental analyses, TG/DTA, FTIR and solution (³¹P and ¹⁸³W) NMR spectroscopy. The linkage of TiO₆ octahedra substituted in **1a** resembled that in titanium(IV) oxide rather than in the perovskite such as SrTiO₃. Thus, the polyoxotungstate **1a** will be of interest as a soluble analog of titanium(IV) oxide. Studies in this direction are in progress and the data will be reported in due course.

Experimental

Materials

The following were used as received: Na₂WO₄·2H₂O, 85% H₃PO₄, KCl, NaClO₄, 12 M aqueous HCl solution (quantitative analysis grade) (all from Wako); Ti(SO₄)₂·4H₂O (Junsei); D₂O (Isotec). Na₁₂[B- α -P₂W₁₅O₅₆]₄·19H₂O was prepared according to the literature.¹⁴

Instrumentation/analytical procedures

Complete 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 FT-IR 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. UV-visible absorption spectra were recorded on a Jasco V-560 spectrophotometer.

³¹P NMR (161.70 MHz) spectra in D₂O solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and a JEOL EX-400 NMR data-

processing system. ³¹P NMR spectra were referenced to an external standard of 25% H₃PO₄ in H₂O in a sealed capillary. Chemical shifts were reported on the δ scale with resonances upfield of H₃PO₄ (δ 0) as negative. ¹⁸³W 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. ¹⁸³W NMR spectra measured in D₂O were referenced to an external standard of saturated Na₂WO₄-D₂O solution. Chemical shifts were reported as negative for resonances upfield of Na₂WO₄ (δ 0).

Synthesis

$Na_xH_{33-x}K_4[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot yH_2O$ ($x = 21-26$, $y = 60-70$), **1**. To 2.2 g (7.05 mmol) of Ti(SO₄)₂·4H₂O dissolved in 20 mL water by warming was added 60 mL water and then 2.8 mL of 6 M aqueous HCl solution. To the vigorously stirred, clear colorless solution 10.0 g (2.30 mmol) of solid Na₁₂[B- α -P₂W₁₅O₅₆]₄·19H₂O was added for more than 15 min. The clear colorless solution was stirred for 10 min, followed by adding 16.0 g (0.22 mol) of KCl. After stirring for 15 min, a white powder formed was collected on a glass filter (G4). At this stage, the crude product of the potassium salt was obtained in ca. 7.5 g yield. To 7.0 g of the white powder dissolved in 50 mL water was added 3.0 g (0.025 mol) of NaClO₄. The white powder of KClO₄ formed during 2 h-stirring in an ice-cooled bath was filtered off through a folded filter paper (Whatman #2). The colorless filtrate was evaporated to ca. 20 mL volume by a rotary evaporator at 40 °C. The crystals of KClO₄ formed was filtered off through a folded filter paper (Whatman #2) and the filtrate was added dropwise to 500 mL of ice-cooled acetone. After stirring for 30 min in an ice bath, white powder was collected on a membrane filter (JG 0.2 μ m), washed with EtOH (50 mL \times 2) and diethyl ether (100 mL \times 2), and then dried *in vacuo* for 3 h. A white powder of the crude product was obtained in ca. 5 g yield.

Crystallization and characterization of 1. 5.0 g of the crude product was dissolved in 5 mL water by warming on a water-bath at 90 °C. The clear pale yellow solution was evaporated to ca. 3 mL volume on a water-bath at 90 °C. The solution was divided to two portions and slow evaporation for both at room temperature was performed.

After two days, clear colorless hexagonal plate crystals formed; one portion was used for X-ray diffraction measurements and the other portion for another characterization described below. The crystals of one portion (1.5 mL) was obtained in 11.9% yield (0.57 g scale) based on $Na_xH_{33-x}K_4[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot yH_2O$ ($x = 26$, $y = 70$).

[Note: compound **1** was readily reduced by metalware such as a spatula to form blue materials or a heteropoly blue.] Compound **1** was hygroscopic and highly soluble in water, but insoluble in diethyl ether, acetone and EtOH {Found: H, 0.38; Na, 3.26; K, 1.02; P, 1.45; W, 65.5; Ti, 3.57; O, 26.0; Cl, 0.12; total 101.3%. Calculated values were fitted within allowed errors for all $x = 21-26$ in $Na_xH_{33-x}K_4[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot 30H_2O$. Calc. for $x = 21$ or H₇₂Na₂₁K₄P₈W₆₀Ti₁₂O₂₇₂Cl: H, 0.43; Na, 2.85; K, 0.92; P, 1.46; W, 65.1; Ti, 3.39; O, 25.7, Cl, 0.21% and calc. for $x = 26$ or H₆₇Na₂₆K₄P₈W₆₀Ti₁₂O₂₇₂Cl: H, 0.40; Na, 3.50; K, 0.92; P, 1.45; W, 64.7; Ti, 3.37; O, 25.5, Cl, 0.21%.} A weight loss of 4.02% was observed during the course of drying at room temperature at 10⁻³–10⁻⁴ Torr overnight before analysis, suggesting the presence of 39–40 waters, weakly solvated or adsorbed. TG/DTA under atmospheric conditions: a weight loss of 6.46% was observed below 443 °C with an endothermic point at 68 °C; calc. 6.43% for $y = 63$ in $Na_{26}K_4H_7[(\alpha-1,2,3-P_2W_{15}Ti_3O_{60.5})_4Cl] \cdot yH_2O$. IR (KBr disk) (polyoxometalate region): 1090vs, 1014w, 952vs, 918s, 832vs, 663vs, 564m, 527m cm⁻¹. ³¹P NMR (20.5 °C, D₂O): δ -7.59, -13.97. ¹⁸³W NMR (19.7 °C, D₂O): δ -148.3 (3W \times 4), -185.8

(6 W × 4), -211.2 (6 W × 4). UV-vis absorption (water): λ_{\max} 269 nm (ϵ $4.28 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ based on the formula weight with $x = 26$, $y = 70$).

X-ray crystallography

A colorless hexagonal plate crystal of **1** ($0.29 \times 0.14 \times 0.08 \text{ mm}$) was surrounded by liquid paraffin to prevent its degradation. Data collection was done by Bruker SMART APEX CCD diffractometer at 90 K in the range of $4.74 < 2\theta^\circ < 49.42$. The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (program SHELXS-97)^{15a} followed by subsequent difference Fourier calculation and refined by full-matrix, least-square procedure (program SHELXL-97).^{15b}

Crystal data for $\text{H}_{147.5}\text{ClK}_4\text{Na}_{24}\text{O}_{312}\text{P}_8\text{Ti}_{12}\text{W}_{60}$: $M = 17737.85$, triclinic, space group $P\bar{1}$, $a = 29.297(2)$, $b = 29.5965(18)$, $c = 29.6362(18) \text{ \AA}$, $\alpha = 119.4640(10)$, $\beta = 90.6870(10)$, $\gamma = 115.478(2)^\circ$, $V = 19363(2) \text{ \AA}^3$, $Z = 2$, $D_c = 3.042 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 18.175 \text{ mm}^{-1}$. $R_{\text{int}} = 0.0532$, $R_1 = 0.0696$, $wR_2 = 0.1977$, $\text{GOF} = 1.029$ (120930 total reflections, 64449 unique reflections where $I > 2\sigma(I)$). The maximum and minimum residual density (6.854 and $-4.621 \text{ e \AA}^{-3}$) holes were located at 0.80 \AA from W15D and 0.08 \AA from K4, respectively.

CCDC reference number 208175.

See <http://www.rsc.org/suppdata/dt/b3/b304033j/> for crystallographic data in CIF or other electronic format.

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References

- 1 K. L. Taft and S. J. Lippard, *J. Am. Chem. Soc.*, 1990, **112**, 9629.
- 2 (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 poloxoanions in catalysis, ed. C. L. Hill, *J. Mol. Catal.*, 1996, **114**, 1; (h) R. Neumann, *Prog. Inorg. Chem.*, 1998, **47**, 317; (i) *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*, Kluwer Academic Publishers, Netherlands, ed. M. T. Pope and A. Müller, 2001; (j) *Polyoxometalate Chemistry for Nano-Composite Design*, Kluwer Academic Publishers, Netherlands, ed. T. Yamase and M. T. Pope, 2002.
- 3 Two recent books: refs. 2i and j; (a) A. Müller, S. K. Das, P. Kogerler, H. Bögge, M. Schmidtman, A. X. Trautwein, V. Schunemann, E. Krickemeyer and W. Preetz, *Angew. Chem., Int. Ed.*, 2000, **39**, 3414; (b) A. Müller, E. Krickemeyer, S. K. Das, P. Kogerler, S. Sarkar, H. Bögge, M. Schmidtman and S. Sarkar, *Angew. Chem., Int. Ed.*, 2000, **39**, 1612; (c) A. Müller, S. Q. N. Shah, H. Bögge and M. Schmidtman, *Nature*, 1999, **397**, 48; (d) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, C. Beugholt, S. K. Das and F. Peters, *Chem. Eur. J.*, 1999, **5**, 1496; (e) A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtman, S. Sarkar, P. Kogerler, B. Hauptfleisch, A. X. Trautwein and V. Schunemann, *Angew. Chem., Int. Ed.*, 1999, **38**, 3238; (f) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, C. Beugholt, P. Kogerler and C. Lu, *Angew. Chem., Int. Ed.*, 1998, **37**, 1220; (g) L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtman, H. Bögge, P. Kogerler, T. K. K. Luong and A. Müller, *Angew. Chem., Int. Ed.*, 2002, **41**, 2805; (h) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, S. Roy and A. Berkle, *Angew. Chem., Int. Ed.*, 2002, **41**, 3604; (i) A. Müller, E. Beckmann, H. Bögge, M. Schmidtman and A. Dress, *Angew. Chem., Int. Ed.*, 2002, **41**, 1162; (j) A. Müller, S. K. Das, M. O. Talismanova, H. Bögge, P. Kogerler, M. Schmidtman, S. S. Talismanova, M. Luban and E. Krickemeyer, *Angew. Chem., Int. Ed.*, 2002, **41**, 579; (k) A. Müller, S. K. Das, C. Kuhlmann, H. Bögge, M. Schmidtman, E. Diemann, E. Krickemeyer, J. Hormes, H. Modrow and M. Schindler, *Chem. Commun.*, 2001, 655.
- 4 T. Yamase and P. V. Prokop, *Angew. Chem., Int. Ed.*, 2002, **41**, 466.
- 5 (a) U. Kortz, S. S. Hamzeh and A. Nasser, *Chem. Eur. J.*, 2003, **9**, 2945; (b) Y. Sakai, K. Yoza, C. N. Kato and K. Nomiya, *Chem. Eur. J.*, 2003, in press.
- 6 (a) U. Müller, *Inorganic Structural Chemistry*, Wiley, New York, 1993, p. 37; (b) A. L. Linsenbigler, G. Lu and J. T. Yates, Jr., *Chem. Rev.*, 1995, **95**, 735; (c) N. Erdman, K. R. Poepelmeier, M. Asta, O. Warschkow, D. E. Ellis and L. D. Marks, *Nature*, 2002, **419**, 55; (d) T. Kawahara, Y. Konishi, H. Tada, N. Tohge, J. Nishii and S. Ito, *Angew. Chem., Int. Ed.*, 2002, **41**, 2811.
- 7 (a) Y. Lin, T. J. R. Weakley, B. Rapko and R. G. Finke, *Inorg. Chem.*, 1993, **32**, 5095; (b) T. Yamase, T. Ozeki, H. Sakamoto, S. Nishiya and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 103; (c) K. Nomiya, M. Takahashi, K. Ohsawa and J. A. Widegren, *J. Chem. Soc., Dalton Trans.*, 2001, 2872; (d) K. Nomiya, M. Takahashi, J. A. Widegren, T. Aizawa, Y. Sakai and N. C. Kasuga, *J. Chem. Soc., Dalton Trans.*, 2002, 3679; (e) 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.
- 8 (a) R. G. Finke, B. Rapko, R. J. Saxton and P. J. Domaille, *J. Am. Chem. Soc.*, 1986, **108**, 2947; (b) K. Nomiya, M. Pohl, N. Mizuno, D. K. Lyon and R. G. Finke, *Inorg. Synth.*, 1997, **31**, 186; (c) H. Weiner, J. D. Aiken III and R. G. Finke, *Inorg. Chem.*, 1996, **35**, 7905; (d) R. G. Finke, D. K. Lyon, K. Nomiya and T. J. R. Weakley, *Acta Crystallogr., Sect. C*, 1990, **46**, 1592.
- 9 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.
- 10 C. Rocchiccioli-Deltcheff and R. Thouvenot, *Spectrosc. Lett.*, 1979, **12**, 127.
- 11 T. J. R. Weakley and R. G. Finke, *Inorg. Chem.*, 1990, **29**, 1235.
- 12 (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.
- 13 N. J. Carno, R. C. Chambers, V. M. Lynch and M. A. Fox, *J. Mol. Catal. A*, 1996, **114**, 65.
- 14 W. J. Randall, M. W. Droegge, N. Mizuno, K. Nomiya, T. J. R. Weakley and R. G. Finke, *Inorg. Synth.*, 1997, **31**, 167.
- 15 (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (b) G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.