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Synthesis, properties and characterization of Dawson-type tungstophosphate heteropoly complexes substituted by titanium and peroxotitanium †

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Twelve new compounds α_2-$M_aH_b[P_2W_{18-n}Ti_nO_{62}]\cdot xH_2O$ and α-1,2,3-$M_aH_b[P_2W_{18-n}(TiO_2)_nO_{62-n}]\cdot xH_2O$ ($M = K^+$, NEt_4^+ or NBu_4^+; $n = 1$, $a + b = 8$; $n = 3$, $a + b = 12$) were synthesized from vacant heteropolytungstate precursors α_2-$[P_2W_{17}O_{61}]^{10-}$ and α-1,2,3-$[P_2W_{15}O_{56}]^{12-}$. The products were characterized by IR, UV spectroscopy, polarography, cyclic voltammetry and X-ray photoelectron spectroscopy. Tungsten-183 NMR studies showed that the titanium atoms or the peroxotitanium group in the anions are at 'polar' sites. The polarographic results indicated that there was a polarographic reduction potential of O_2^{2-} at *ca.* −0.08 V and that of Ti^{4+} at *ca.* −0.20 V. The characteristic charge-transfer absorption band $O_2^{2-}\rightarrow Ti$ at 318 nm occurs in the UV spectra. The peroxotitanium (TiO_2) groups show two additional characteristic bands at *ca.* 870 and *ca.* 490 cm^{-1} in the IR spectra.

Recently we reported the preparation and the characterization of peroxoniobium-containing phosphotungstates and made a comparison between tungstophosphoric heteropoly complexes substituted by niobium and peroxoniobium in respect of their redox properties.[1,2] The results show that the oxidizing power of the heteropolyacid or salt can be modulated by changing substituted atoms. Heteropolyacids or their salts and derivatives with strong acidic properties and oxidizability are good catalysts.[3] Peroxometal substituents have higher catalytic activity and selectivity in the catalysis of allyl epoxidation, alcohol oxydehydrogenation and the conversion of vicinal binary alcohols into carboxylic acids with H_2O_2 as oxidizer.[4] Recently it has been reported that the peroxometal heteropoly complexes exhibit biological activity as a new potent class of anti-HIV agents.[5]

This paper describes the synthesis and characterization of substituted Dawson-type heteropolyanions formed by introducing one or three Ti or TiO_2 groups into the α_2-$[P_2W_{17}O_{61}]^{10-}$ or α-$[P_2W_{15}O_{56}]^{12-}$ anions with K^+ or R_4N^+ counter cations (R = Et or Bu). Their properties and structures were studied by IR, UV, X-ray photoelectron spectroscopy (XPS), polarography, cyclic voltammetry and ^{183}W NMR spectroscopy.

Experimental

Instruments

The following instruments were used: Leeman corporation inductively coupled plasma (ICP) emission spectrograph, PE-3030 atomic absorption spectrometer, 1106-element autoanalyzer, 5DX-FT IR spectrophotometer (Nicolet) with KBr pellets, DU-8B UV spectrophotometer (Beckman), Unity-400 NMR spectrometer, BAS100A electrochemical analyzer.

Starting materials

All reagents were analytical or guaranteed grade. The preparations of α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ and α-$Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ have been described.[6] Their IR spectra and polarography correspond to those already reported.

Preparation of complexes

α_2-$[P_2W_{17}TiO_{62}]^{8-}$. An aqueous solution (5 cm^3) of $Ti(SO_4)_2$ (0.5 g, 0.002 mol) was added dropwise to an aqueous solution (50 cm^3) of α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ (10 g, 0.002 mol). The mixture (pH 1.60) was heated to 60 °C for 40 min. After cooling, it was vigorously stirred and solid KCl (20 g) was added. After 15 min the white crystalline precipitate was filtered off and recrystallized from the minimum volume of warm water (pH 2). Yield: 62%. Substitution of NEt_4Cl or NBu_4Br for KCl gave the corresponding tetraalkylammonium salts. Yield 90%.

α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$. An aqueous solution (5 cm^3) of $Ti(SO_4)_2$ (0.5 g, 0.002 mol) was added dropwise to a solution (50 cm^3) of α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ (10 g, 0.002 mol). The mixture (pH 1.60) was heated to 60 °C for 40 min. After cooling, H_2O_2 (1 cm^3, 30%) was added and the mixture stirred for 15 min, then solid KCl (20 g) was added and stirred for 15 min. A yellow crystalline precipitate was filtered off and recrystallized from the minimum volume of warm water (pH 2). Yield: 62%. Substitution of NEt_4Cl or NBu_4Br for KCl gave the corresponding tetraalkylammonium salts. Yield: 90%.

α-1,2,3-$[P_2W_{15}Ti_3O_{62}]^{12-}$. An aqueous solution of α-$Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ (9 g, 2.4 mmol) in 1 mol dm^{-3} LiCl (100 cm^3) and 1 mol dm^{-3} HCl (1 cm^3) was added dropwise to a solution of $Ti(SO_4)_2$ (1.7 g, 7.1 mmol) in water (15 cm^3). The mixture (pH 1.5) was heated to 30 °C for 30 min. After cooling, solid KCl (20 g) was added, a white solid precipitated immediately and the mixture was stirred for 10 min. The precipitate was filtered off and recrystallized from the minimum volume of warm water (pH 2). Yield: 68%. In the synthesis of the corresponding tetraalkylammonium salts 1 mol dm^{-3} $K_{10}H_2[P_2W_{15}Ti_3O_{62}]\cdot 2H_2O$ was added to saturated NEt_4Cl or NBu_4Br solution respectively. The precipitate was filtered off and washed with ethanol and diethyl ether, then air dried for 2 d. Yield: 90%.

α-1,2,3-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$. A solution of α-$Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ (9 g, 2.4 mmol) in 1 mol dm^{-3} LiCl (100 cm^3) and 1 mol dm^{-3} HCl (1 cm^3) was added dropwise to a solution of $Ti(SO_4)_2$ (1.7 g, 7.1 mmol) in water (15 cm^3). The solution (pH 1.5) was heated to 30 °C for 30 min; after cooling, H_2O_2 (30%, 1 cm^3) was added and then the mixture was stirred for 15 min. Finally solid KCl (20 g) was added. A yellow solid precipitated immediately. The product was filtered off and recrystallized. Yield: 68%. The corresponding tetraalkylammonium salts were prepared as above.

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† *Non-SI unit employed*: eV ≈ 1.60 × 10^{-19} J.

Table 1 Analysis data [Found (Calc.)] for the compounds

	Analysis (%)							
Compound	C	H	N	K	W	Ti	H_2O	O_2^{2-}
α_2-$K_8[P_2W_{17}TiO_{62}]\cdot 5H_2O$				6.74 (6.80)				
α_2-$[NEt_4]_6H_2[P_2W_{17}TiO_{62}]\cdot 2H_2O$	11.40 (11.42)	2.35 (2.38)	1.67 (1.66)		61.89 (61.93)	0.92 (0.95)	0.68 (0.71)	
α_2-$[NBu_4]_7H[P_2W_{17}TiO_{62}]$	21.46 (22.70)	4.04 (4.27)	1.56 (1.65)		52.88 (52.74)	0.75 (0.81)		
α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]\cdot 9H_2O$				6.68 (6.63)	66.12 (66.24)	1.05 (1.01)	3.38 (3.43)	0.65 (0.69)
α_2-$[NEt_4]_8[P_2W_{17}(TiO_2)O_{61}]\cdot 2H_2O$	14.15 (14.44)	3.03 (3.08)	2.04 (2.10)		58.70 (58.73)	0.93 (0.90)	0.64 (0.67)	0.56 (0.60)
α_2-$[NBu_4]_8[P_2W_{17}(TiO_2)O_{61}]$	24.90 (24.86)	4.47 (4.66)	1.76 (1.81)		50.76 (50.54)	0.72 (0.77)		0.49 (0.52)
α-$K_{10}H_2[P_2W_{15}Ti_3O_{62}]\cdot 2H_2O$				8.90 (8.92)	62.50 (62.90)	3.20 (3.28)	0.79 (0.82)	
α-$[NEt_4]_9H_3[P_2W_{15}Ti_3O_{62}]\cdot 2H_2O$	16.70 (16.73)	3.45 (3.50)	2.34 (2.44)		53.90 (53.40)	2.69 (2.78)	0.65 (0.70)	
α-$[NBu_4]_9H_3[P_2W_{15}Ti_3O_{62}]$	28.32 (28.15)	5.23 (5.29)	2.02 (2.05)		44.90 (44.92)	2.30 (2.34)		
α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]\cdot 8H_2O$				10.02 (10.16)	59.70 (59.34)	3.02 (3.11)	3.09 (3.12)	1.82 (2.08)
α-$[NEt_4]_{10}H_2[P_2W_{15}(TiO_2)_3O_{59}]\cdot H_2O$	18.00 (18.02)	3.76 (3.79)	2.61 (2.63)		51.72 (51.78)	2.67 (2.70)	0.35 (0.38)	1.66 (1.80)
α-$[NBu_4]_8H_4[P_2W_{15}(TiO_2)_3O_{59}]$	25.71 (25.82)	4.93 (4.91)	1.85 (1.88)		46.25 (46.37)	2.40 (2.42)		1.52 (1.61)

Table 2 Polarographic data (V)

	Wave				
Compound	1	2	3	4	5
α_2-$K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ [6]			−0.44	−0.59	−0.85
α_2-$K_8[P_2W_{17}TiO_{62}]\cdot 5H_2O$		−0.19	−0.40	−0.63	−0.87
α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]\cdot 9H_2O$	−0.11	−0.20	−0.40	−0.63	−0.88
α-$Na_{12}[P_2W_{15}O_{56}]\cdot 24H_2O$ [6]			−0.52	−0.78	
α-$K_{10}H_2[P_2W_{15}Ti_3O_{62}]\cdot 2H_2O$		−0.17	−0.58	−0.75	−0.95
α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]\cdot 8H_2O$	−0.08	−0.20	−0.52	−0.68	−0.88

Table 3 Cyclic voltammetric data

Compound	Wave	E_{pc}/V	E_{pa}/V	ΔE_p/mV
α_2-$[P_2W_{17}TiO_{62}]^{8-}$	1	−0.325	−0.123	202
	2	−0.504	−0.416	88
	3	−0.737	−0.684	53
	4	−1.002	−0.917	85
α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$	1	−0.334		
	2	−0.505	−0.485	20
	3	−0.763	−0.715	48
	4	−1.041	−0.971	70
α-$[P_2W_{15}Ti_3O_{62}]^{12-}$	1	−0.314		
	2	−0.570	−0.553	17
	3	−0.726	−0.678	48
	4	−0.936	−0.871	65
α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$	1	−0.144		
	2	−0.346	−0.331	15
	3	−0.618	−0.597	21
	4	−0.788	−0.698	90
	5	−1.037	−0.934	103

Results and Discussion

Analyses

The elements were determined by the following methods: potassium by atomic absorption spectrophotometry; tungsten and titanium by an ICP emission spectrograph; O_2^{2-} by I^-–$S_2O_3^{2-}$ titration; carbon, hydrogen and nitrogen by a 1106-element autoanalyzer; water by thermogravimetric analysis. The data are given in Table 1.

Polarography and cyclic voltammetry

Polarography and cyclic voltammetry were performed using Hg/Hg_2Cl_2–Cl^- electrodes with a platinum wire counter electrode and 1 mol dm^{-3} acetic acid–sodium acetate supporting electrolyte at pH 4.7 and 298 K. The half-wave potentials are given in Table 2. Generally, if the substituent atoms are not reduced, the half-wave potentials of the heteropolyanions will be similar to those of their precursors. If the substituent atoms are reduced, the number of reduction waves will be changed. The number of reduction waves of α_2-$[P_2W_{17}TiO_{62}]^{8-}$ is identical to that of the precursor α_2-$[P_2W_{17}O_{61}]^{10-}$ with the addition of a one-electron reduction (−0.19 V); this is the reduction wave of Ti^{4+}. Compared with α_2-$[P_2W_{17}TiO_{62}]^{8-}$, α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$ has an additional two-electron reduction wave at −0.11 V. This is the reduction wave of O_2^{2-}.[7] Cyclic voltam-

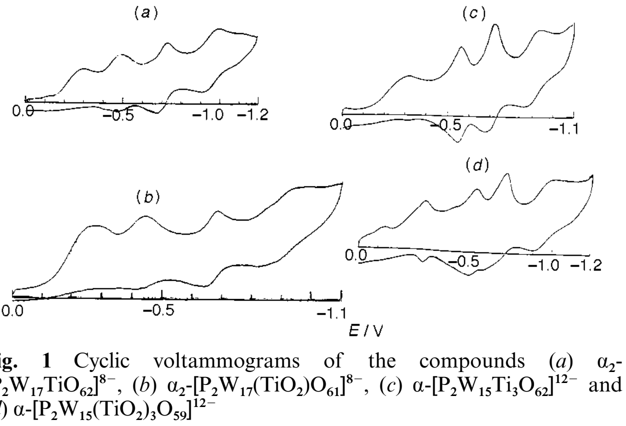

Fig. 1 Cyclic voltammograms of the compounds (*a*) α_2-$[P_2W_{17}TiO_{62}]^{8-}$, (*b*) α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$, (*c*) α-$[P_2W_{15}Ti_3O_{62}]^{12-}$ and (*d*) α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$

Table 4 The main IR bands (cm^{-1})

Compound	A	B		C	D	E	F
α_2-$K_8[P_2W_{17}TiO_{62}]$	953	1090	1017	915	787		
α_2-$[NEt_4]_6H_2[P_2W_{17}TiO_{62}]$	955	1091	1016	917	789		
α_2-$[NBu_4]_7H[P_2W_{17}TiO_{62}]$	954	1090	1017	912	785		
α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]$	951	1090	1017	916	782	878	484
α_2-$[NEt_4][P_2W_{17}(TiO_2)O_{61}]$	955	1089	1020	917	787	880	487
α_2-$[NBu_4][P_2W_{17}(TiO_2)O_{61}]$	950	1091	1018	915	789	876	485
α-$K_{10}H_2[P_2W_{15}Ti_3O_{62}]$	947	1087	1009	913	781		
α-$[NEt_4]_9H_3[P_2W_{15}Ti_3O_{62}]$	949	1087	1010	907	780		
α-$[NBu_4]_9H_3[P_2W_{15}Ti_3O_{62}]$	948	1086	1010	909	785		
α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]$	945	1087	1011	912	775	876	487
α-$[NEt_4]_{10}H_2[P_2W_{15}(TiO_2)_3O_{59}]$	951	1088	1011	914	769	878	485
α-$[NBu_4]_8H_4[P_2W_{15}(TiO_2)_3O_{54}]$	950	1088	1010	912	787	879	489

A, ν_{asym} (W–O$_d$); B, γ_{asym} (P–O$_a$); C, γ_{asym} (W–O$_b$–W); D, γ_{asym} (W–O$_c$–W); E, γ (–O–O–); F, γ_{asym} $\overline{\text{Ti(–O–O}}$).

Table 5 Binding energies (eV)

Compound	P_{2p}	$Ti_{2p\frac{3}{2}}$	$W_{4f\frac{7}{2}}$	K_{2p}	$O_{1s\frac{1}{2}}$	
					O^{2-}	O_2^{2-}
α_2-$K_8[P_2W_{17}TiO_{62}]$	133.4	458.6	35.4	293.5	530.6	
α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]$	133.5	458.7	35.7	293.7	530.7	532.0
α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]$	134.0	458.6	35.4	292.8	530.4	532.0

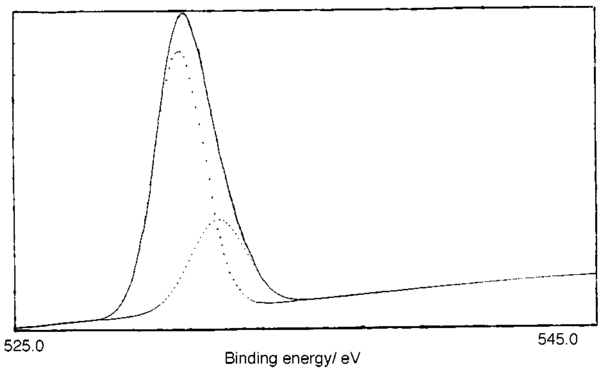

Fig. 2 Sum (—) of the binding energies of O^{2-} (· · ·) and O_2^{2-} (···)

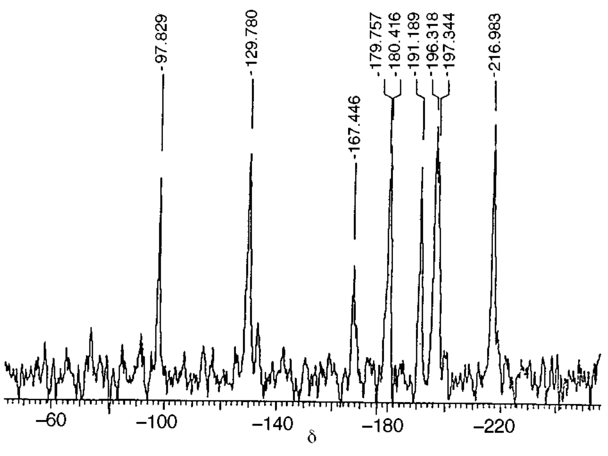

Fig. 3 The ^{183}W NMR spectrum of α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]\cdot 9H_2O$

mograms of the compounds at a sweep rate of 100 mV s^{-1} are given in Fig. 1 (data in Table 3). We can only find four reduction waves for α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$; those of Ti^{4+} and O_2^{2-} may be overlapped. Controlled-potential electrolysis at −0.3 V showed that the first reduction wave of α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$ is a three-electron process. Compared with α-$[P_2W_{15}O_{56}]^{12-}$, α-$[P_2W_{15}Ti_3O_{62}]^{12-}$ has two additional reduction waves; that at −0.17 V is due to reduction of Ti^{4+}, and the other wave is one of the disintegration waves of the first four-electron wave (−0.52 V) of α-$[P_2W_{15}O_{56}]^{12-}$ owing to atom (Ti) substitution.[8] The number of reduction waves of α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$ is identical to that of α-$[P_2W_{15}Ti_3O_{62}]^{12-}$ with the addition of a two-electron O_2^{2-} reduction (−0.08 V). The polarography data show that the relative oxidizing power is α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$ > α_2-$[P_2W_{17}TiO_{62}]^{8-}$, α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$ > α-$[P_2W_{15}Ti_3O_{62}]^{12-}$; α_2-$[P_2W_{17}TiO_{62}]^{8-}$ < α-$[P_2W_{15}Ti_3O_{62}]^{12-}$ and α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$ < α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$. Cyclic voltammetry shows that the reduction wave of O_2^{2-} is irreversible.

IR spectra

The main bands of the heteropolyanions with the Dawson structure are given in Table 4. However, the IR spectra of two anions, α_2-$[P_2W_{17}(TiO_2)O_{61}]^{8-}$ and α-$[P_2W_{15}(TiO_2)_3O_{59}]^{12-}$, show two additional bands at 870 and 490 cm^{-1} respectively. The characteristic band at 870 cm^{-1} suggests O_2^{2-} (ref. 4) and that at 490 cm^{-1} TiO_2.

UV spectra

Generally there are two absorption bands of the 18-heteropolytungstophosphoric anion at 210 and 325 nm.[9] The band at higher energy has been attributed to a $O_b(O_c)\rightarrow W$ charge-transfer band. Another band at lower energy has been assigned to the $O_d\rightarrow W$ charge-transfer band. Bands at 199 and 285 nm for α_2-$K_8[P_2W_{17}TiO_{62}]$, at 199 and 267 nm for α-$K_{12}[P_2W_{15}Ti_3O_{62}]$, at 201, 290 and 317 nm for α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]$ and at 197, 260 and 318 nm for α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]$ were observed. The difference in energy between the lowest unoccupied orbital of W and the highest occupied orbital of O is increased because of the substitution of Ti or TiO_2. So the characteristic band at 325 nm moves to shorter wavelength. The absorption bands of heteropoly complexes substituted by peroxotitanium at 317 or 318 nm have been assigned to the $O_2^{2-}\rightarrow Ti$ charge-transfer band.[10]

X-Ray photoelectron spectra

The inner-shell electron-binding energies of the compounds are given in Table 5. The oxygen bands in complexes substituted by TiO_2 groups are unsymmetrical (Fig. 2). This illustrates that there are two types of O atoms. By dividing the band, we find that the binding energy of O_2^{2-} is at *ca.* 532 eV and that of O^{2-} at *ca.* 530 eV.

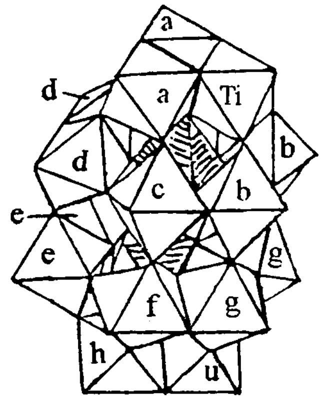

Fig. 4 Tungsten atom sites in the Dawson structure

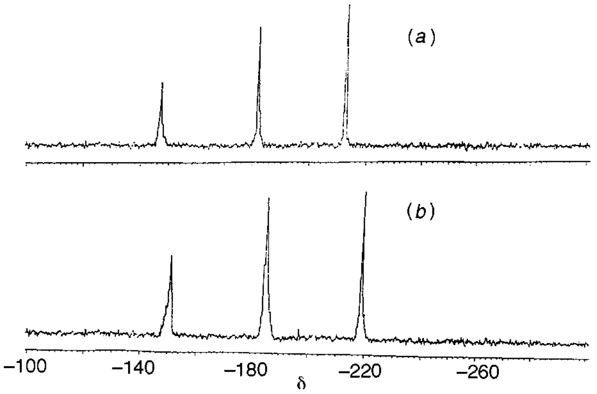

Fig. 5 The ^{183}W NMR spectra of (*a*) α-$K_{12}[P_2W_{15}Ti_3O_{62}]$ and (*b*) α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]$

^{183}W NMR spectra

The ^{183}W NMR spectrum of α_2-$K_8[P_2W_{17}(TiO_2)O_{61}]\cdot 9H_2O$ is shown in Fig. 3. It has a sharp nine-line spectrum with chemical shifts δ −97.8, −129.8, −167.4, −179.7, −180.4, −191.2, −196.3, −197.3 and −216.9 and relative intensities of 2:2:1:2:2:2:2:2:2. This result strongly suggests that the position of the TiO_2 group is at a 'polar' site. By following the broad shift patterns proposed in ref. 11 and in particular the comparatively low shifts of 'polar' sites, we suggest the following assignments, using the labels as in Fig. 4: −167.4, u; −97.8, a; −197.3, g; −191.2, d; −180.4, c; −129.8, h; −216.9, e; −196.3, f; 179.7, b. The ^{183}W NMR spectra of α-$K_{12}[P_2W_{15}Ti_3O_{62}]$ and α-$K_{12}[P_2W_{15}(TiO_2)_3O_{59}]$ are shown in Fig. 5: the former has a sharp three-line spectrum with chemical shifts δ −147.7 (3W), −182.5 (6W) and −213.0 (6W) and relative intensities of 1:2:2; the latter has peaks at δ −151.1 (3W), −183.6 (6W) and −219.4 (6W) with relative intensities of 1:2:2. The studies[11] argue that the 3W atoms on the 'polar' sites are at δ −147.7 and −151.1, the 6W atoms far from the substituted 'polar' sites are at δ −182.5 and −183.6 and that the other 6W atoms are at δ −213 and −219.4.

Acknowledgements

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