The Tungsten(IV) Aqua Ion; Reduction Studies and Detection of Aquachloro Complexes of $[W_3(\mu_3\text{-O})(\mu_2\text{-O})_3]^{4+}$ by Oxygen-17 and Tungsten-183 NMR Spectroscopy

AYYUB PATEL, MARION R. McMAHON

Department of Chemistry, University of Stirling, Stirling FK9 4LA (U.K.)

and DAVID T. RICHENS*

Department of Chemistry, University of St. Andrews, North Haugh, St. Andrews KY16 9ST (U.K.)

Abstract

Oxygen-17 and tungsten-183 NMR studies on solutions of orange tungsten(IV), prepared in 2 M *p*-toluenesulphonic acid (Hpts) solution via acid catalysed hydrolysis of potassium hexachlorotungstate(IV) in 2 M Hpts followed by treatment with a single DOWEX 50W X2 cation-exchange column, confirm the formation of the species; $[W_3(\mu_3\text{-O})(\mu_2\text{-O})_3(OH_2)_8Cl]^{3+}$ as major product in addition to $[W_3(\mu_3\text{-O})(\mu_2\text{-O})_3(OH_2)_9]^{4+}$ under these conditions in a manner not possible by spectrophotometric means. Further characterisation of the green W(III,III,IV) mixed-valence reduction product has also been carried out with in addition an estimation of the formal reduction potential for the $W(IV)_3/W(III,III,IV)$ redox couple.

Introduction

Successful preparations of the incomplete cuboidal tungsten(IV) aqua ion $[W_3(\mu_3\text{-O})(\mu_2\text{-O})_3(OH_2)_9]^{4+}$ (I) have been reported both by Segawa and Sasaki [1] and more recently by Sykes *et al.* [2]. Both methods involve cation-exchange purification of acidified aqueous solutions of $K_2[WCl_6]$ following heating for 2.5 h at 95 °C under anaerobic conditions. In the former, Segawa and Saskai used a single DOWEX 50W X8 column to purify the aqua ion from solutions heated in 2 M HCl. Sykes *et al.* have since reported an improved preparative method involving heating of $K_2[WCl_6]$ in 2 M Hpts (*p*-toluenesulphonic acid) followed by purification using successive columns of DOWEX 50W X8 and X2 resins. Such a procedure was viewed essential to ensure separation of the aqua ion from chloroaqua complexes. As in the case of molybdenum detection of chloroaqua complexes as distinct from the aqua ion in

mixed solutions is not possible on the basis of spectrophometric measurements. We wish to report here how the use of ^{17}O and ^{183}W NMR has allowed this to be achieved very easily and in doing so has confirmed that the major product of the one column purification step [1] is the monochloro complex $[W_3(\mu_3\text{-O})(\mu_2\text{-O})_3(OH_2)_8Cl]^{3+}$ (Cl opposite $\mu_3\text{-O}$) and not the aqua ion in support of the necessity for two column purification [2]. We also report further characterisation of the W(III,III,IV) mixed-valence aqua ion reduction product [1] as $[W_3(\mu_2\text{-OH})_4]^{6+}$ (aq) following ^{17}O NMR studies along with an estimation of the formal reduction potential for the $W(IV)_3/W(III,III,IV)$ couple.

Experimental

Reagents

Preparation of ^{17}O-enriched Tungsten Samples

Solutions of $[W_3O_4]^{4+}$ (aq) were prepared enriched with between 5–10 at.% of ^{17}O by heating $K_2[WCl_6]$ (4.0 g) at 95 °C for 2.5 h in 2 M Hpts (20 cm^3) prepared in enriched H_2O^{17} (Yeda Isotopes Co. Ltd., Rehovot, Israel). After dilution to 100 cm^3

and 0.5 M H+ with Hpts and allowing to stand at room temperature for one day under air free conditions the resulting mixture was loaded onto a column (10 cm³ × 1 cm³) of DOWEX 50W X2 resin (200–400 mesh). The column was washed with 0.5 M Hpts (100 cm³) and 1 M Hpts (100 cm³) (to remove lower charged species) prior to elution of orange W(IV) with 2 M Hpts. Elution was also carried out by displacement with a solution of La(pts)₃ (0.25 M) in 1 M Hpts yielding concentrated solutions (up to 0.25 M in W) suitable for the ^{17}O NMR measurements. Enrichment of the bound water ligands of $[W_3O_4]^{4+}$ with ^{17}O following cation-exchange treatment was achieved by addition of further quantities of H_2O^{17} (5–10 at.%) and allowing to stand for one day at 35 °C*. Samples of the green mixed-valence W(III,III,IV) aqua ion enriched with ^{17}O were prepared by amalgamated zinc reduction of fully enriched $[W_3O_4]^{4+}$ (aq) samples directly in the 10 mm NMR tube. Samples of W(III,III,IV) prepared anaerobically in sealed tubes under reduced pressure (10^{-3} mm Hg) in liquid N_2 in the absence of excess Zn/Hg were rapidly oxidised back to W(IV) by H_3O^+ within 10 min on warming to room temperature. For this reason NMR measurements on solutions of W(III,III,IV) had to be performed in open tubes in the presence of excess Zn/Hg.

NMR Spectroscopy

The ^{17}O NMR spectra were recorded as 2 cm³ samples in standard 10 mm tubes at 54.24 MHz on a Bruker AM-400 instrument at 298 (±0.5) K. Approximately 160 000 transients, accumulated over the total spectral width of 83 KHz, were stored and transformed using 4000 data points and a pulse width of 14 μs. The chemical shifts were recorded relative to the bulk water resonance line = 0 ppm. Spline functions were added to correct for the rolling baseline due to acoustic ringing. Integrations were determined by peak area comparison with that of the bulk water line at natural abundance (0.037 at.%). The ^{183}W NMR spectra were recorded in 10 mm tubes at 16.67 MHz using 2 cm³ samples at natural abundance on the AM-400 instrument at 298 (±0.5) K. Approximately 62 000 transients over the total spectral width of 7 KHz were stored and transformed using 8000 data points and a 20 μs pulse width. The chemical shifts were referenced to a 1 M $Na_2[WO_4]$ solution in water = 0 ppm. In this case Spline functions were not added.

Electrochemistry

Cyclic voltammograms were recorded under airfree conditions using a standard three electrode cell design employing hanging mercury drop working (Metrohm), platinum counter and Radiometer saturated calomel reference electrodes connected to a Princeton Applied Research Model 170 Electrochemical system. Triply distilled mercury was used. Potentials are reported relative to the normal hydrogen electrode at 298 K.

Ultraviolet visible spectra were recorded on a Perkin-Elmer Lambda 5 recording spectrophotometer in both 0.1 and 1.0 cm quartz cells.

Results and Discussion

Detection of Chloro Complexes

Figure 1 shows ^{17}O NMR spectra for successive 2 cm³ fractions of the orange W(IV) elutent from a single DOWEX 50 W X2 column following displacement with La(pts)₃ in 1 M Hpts. All the fractions possessed the same UV–Vis spectrum with a peak at 455 nm (ϵ = 125 M^{-1} cm^{-1} per W) as reported previously [1]. Two ^{17}O resonances are observed at 561 and 320 ppm in the first fraction (Fig. 1a) occurring in the expected 3:1 ratio and chemical shift range [4] consistent with assignments to the μ_2- and μ_3-oxo groups in the $[W_3O_4]^{4+}$ core (I). The μ-oxo resonances are more shielded than those observed for the corresponding $[Mo_3O_4]^{4+}$ ion [5] reflecting an increase in the electron density on the oxygens for tungsten**. In the second and third
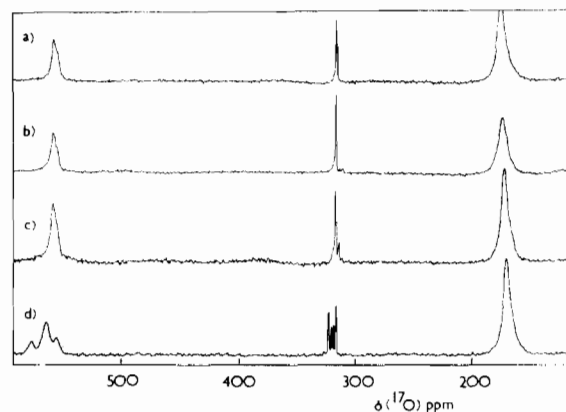

Fig. 1. 54.24 MHz ^{17}O NMR spectra for successive 2 cm³ fractions of $[W_3O_4]^{4+}$ (aq) from the DOWEX 50 W X2 column eluted with La(pts)₃ (0.25 M) in 1 M Hpts: (a), 0.07 M (per W atom); (b) 0.25 M; (c); 0.13 M; (d), (c) following addition of a 20 fold excess of chloride (^{17}O enrichments; 5 at.%).

---

*The use of higher temperatures caused some decomposition of the tungsten(IV) samples during the long timescales involved. Preliminary indications are that water exchange on the coordinated water ligands of $[W_3O_4]^{4+}$ occurs approximately 10 times slower than on the corresponding ion of Mo(IV) [5].

**The greater electron density results from greater overlap with the relativistically expanded 5d orbitals on tungsten [6, 4a].

$$\left[\begin{array}{c} W \\ W \quad W \end{array} \right]^{4+}$$

I
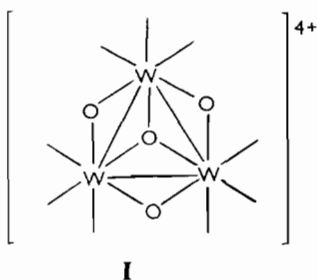
fractions however an additional μ_3-oxo resonance at 316 ppm eventually appears (Fig. 1b and c). This is assigned to the W(IV) aqua ion as will be demonstrated below. The deliberate addition of an excess (20 fold) of chloride to the third fraction produced further μ_3-oxo resonances at $\geqslant 320$ ppm along with additional resonances in the μ_2-oxo region (Fig. 1d) due to the extensive formation of further chloroaqua complexes. Most noteworthy therefore is the remarkable sensitivity of the μ_3-oxo resonance in particular to small changes in the peripheral coordination sphere (Cl^- versus H_2O) of the tungsten ion. When compared to the corresponding resonances observed for $[Mo_3O_4]^{4+}$ (aq) this is seen to be due to the much smaller line width of the μ_3-oxygen for tungsten (50 Hz versus 200 Hz for Mo) an effect most probably due to a smaller electric field gradient component [7]. The μ_3-oxygen is in potentially the most symmetric environment and uniquely coordinated to three tungsten atoms. It is clear from these studies that the aqua ion is only a minor component in this one column preparation.

In further studies it was found that the use of much shorter 95 °C heating times (10 min) for the hydrolysis of $K_2[WCl_6]$ in 2 M Hpts produced larger amounts of the orange W(IV) elutent following single column purification (40% versus 25% using longer heating). Surprisingly ^{17}O NMR studies revealed an increased yield of the aqua ion in the main fraction (Fig. 2). In this case the 320 and 316 ppm (aqua ion) μ_3-oxo resonances appeared in a 2:1 ratio (compare Fig. 1c). In this case, for the purpose of a full integration of the ^{17}O resonances, an equimolar amount (per W) of the bulk water relaxation agent $Mn(pts)_2$ [8] was added in order to allow observation of the bound water region (± 50 ppm). Immediately, two bound water resonances were observed at 24 ppm (H_2O opposite μ_2-oxo) and -10 ppm (H_2O opposite μ_3-oxo) in a ratio of 2.6:1 consistent with a 2:1 mixture of $[W_3O_4(OH_2)_8Cl]^{3+}$ to $[W_3O_4(OH_2)_9]^{4+}$ with location of the chloride in the more inert position *trans* to the μ_3-oxo group (**II**). As additional confirmation, the ^{183}W NMR spectrum of this solu-

$$\left[\begin{array}{c} Cl \\ W \\ W \quad W \end{array} \right]^{3+}$$

II

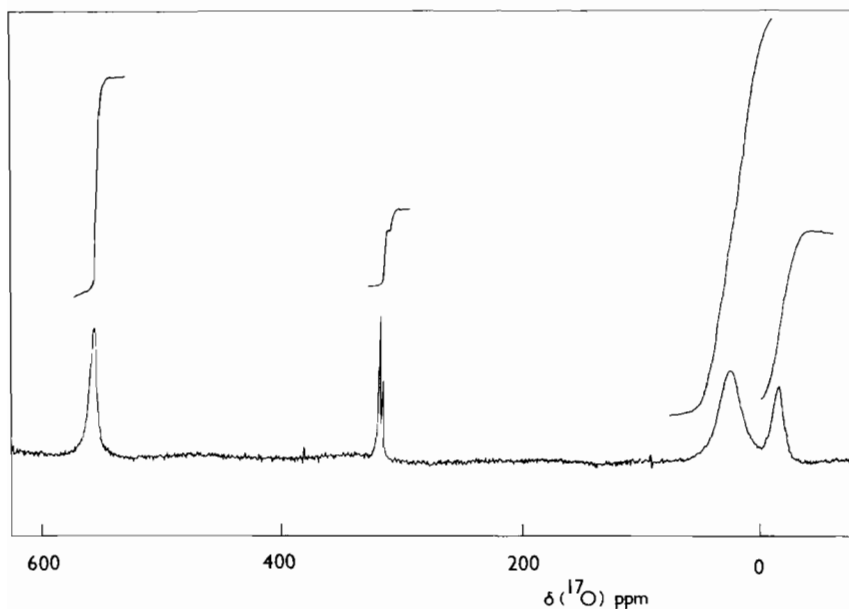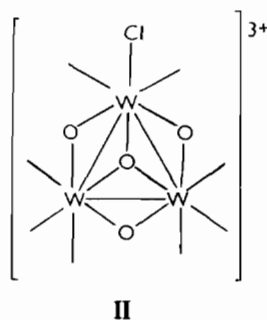Fig. 2. 54.24 MHz ^{17}O NMR spectrum of a solution of $[W_3O_4]^{4+}$ (aq) (main 2 cm^3 fraction, 0.06 M in W) in 2 M Hpts obtained following heating of $K_2[WCl_6]$ in 2 M Hpts at 95 °C for 10 min, aquation in 0.5 M Hpts and cation-exchange treatment as described for Fig. 1. Final ^{17}O enrichments: μ_2- and μ_3-oxo groups 5 at.%, bound water ligands 4 at.% (0.06 M Mn^{2+} added).
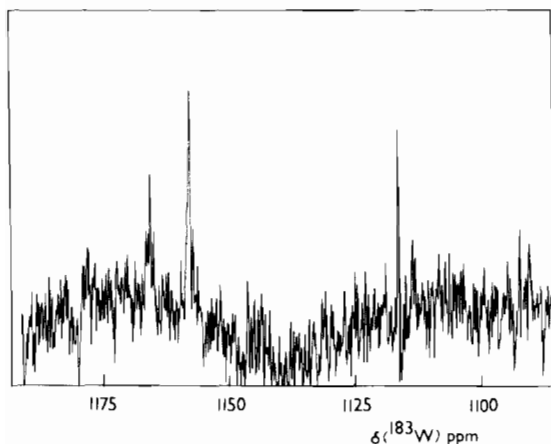
Fig. 3. 16.67 MHz ^{183}W NMR spectrum for the solution as in Fig. 2.

Fig. 4. Cyclic voltammogram for a solution of $[W_3O_4]^{4+}$ (aq) (0.01 M per W) in 3 M HCl. Scan rate 0.2 V s^{-1}, hanging mercury drop electrode 298 K. - - - -, Simulation of the cathodic peak.

tion was recorded and is shown in Fig. 3. The more deshielded resonances at 1157 and 1165 ppm were in a 2:1 ratio suggesting an assignment to the two different tungsten atoms of $[W_3O_4Cl]^{3+}$ (II), the 1165 ppm resonance assigned to the tungsten atom carrying the chloride. The single resonance at 1116 ppm is assigned to the three equivalent atoms of the pure aqua ion. Piepgrass and Pope [9] reported a ^{183}W chemical shift of 1138 ppm from a solution of the aqua ion in saturated Hpts but no other details were given. It is close to the value obtained here.

The greater retention of coordinated chloride by $[W_3O_4]^{4+}$ versus $[Mo_3O_4]^{4+}$ appears to reflect higher formation constants* for chloro complex formation on tungsten. In this regard, it is noted that equilibrium constants determined from kinetics studies of 1:1 NCS$^-$ complex formation on both $[W_3O_4]^{4+}$ and $[Mo_3O_4]^{4+}$ are three times higher in the case of tungsten**. Attempts to detect the presence of the coordinated chloride in the various fractions directly by standard wet methods failed due to interference from tungsten†.

---

*No detectable decrease in the height of the 320 ppm resonance of $[W_3O_4Cl]^{3+}$ ion was observed in any of the fractions over several weeks at 25 °C. It was thus concluded that either an extremely slow rate of aquation was relevant for $[W_3O_4Cl]^{3+}$ or more likely that the $[W_3O_4]^{4+}$ (aq) solutions were already at equilibrium with free chloride.

**Equilibrium constants for 1:1 NCS$^-$ complex formation on $[Mo_3O_4(OH)]^{3+}$ and $[W_3O_4(OH)]^{3+}$ in μ = 2 M ClO$_4^-$ have the following values at 298 K; Mo, 350 M^{-1}; W, 1132 M^{-1}. The Mo data has been estimated from ref. 10. The W data has been taken from ref. 2.

†The detection of free chloride on the basis of turbidity generated in the presence of silver(I), following oxidation to tungsten(VI) with 6 M HNO$_3$ and filtration of the precipitated tungstic acid, was interfered with by the detection of similar turbidity resulting from solutions of tungsten(VI) generated under identical conditions in the absence of chloride. The formation of insoluble silver tungstates(VI), arising from appreciable levels of soluble tungsten(VI), were assumed responsible.
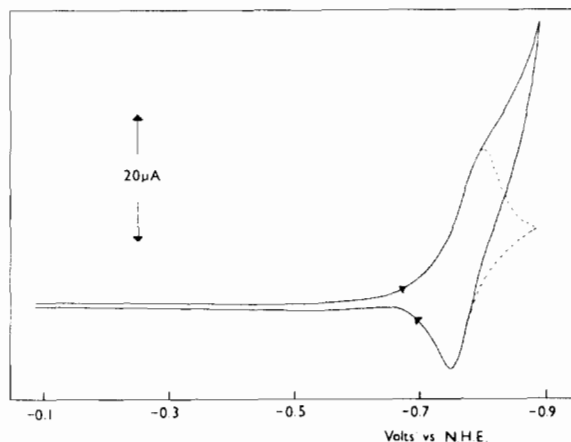
Characterisation of the W(III,III,IV) Aqua Ion

Figure 4 shows a cyclic voltammogram obtained for a 0.01 M solution of $[W_3O_4]^{4+}$ (aq) in 3 M HCl solution employing a hanging mercury drop electrode. HCl was chosen in order to facilitate maximum extension of the cathodic window in these solutions. The reduction process just detectable on the edge of the cathodic limit (H$_3$O$^+$ reduction) is assigned to formation of the W(III,III,IV) ion as a mixture of aquachloro complexes. Estimation of the formal reduction potential for this process is difficult owing to the unresolved cathodic peak. However, simulation (Fig. 4) assuming equal diffusion coefficients for the two forms of the couple gives rise to a value of −0.8 V versus NHE. This value is approximately 0.7 V more negative than the corresponding reduction of $[Mo_3O_4]^{4+}$ (aq) to Mo(III,III,IV) under identical conditions (−0.08 V) [11] reflecting the stronger reducing properties of the tungsten ions. The present value is also more negative than the value reported by Segawa and Sasaki [1] (−0.25 V) following polarographic studies. This previous value would suggest that the Eu^{2+} ion (reduction potential−0.4 V) would be capable of reducing $[W_3O_4]^{4+}$ (aq) to W(III, III,IV). Separate studies from this laboratory have shown this not to be the case. The observed necessity of Zn/Hg as reductant is in support of the more negative reduction potential value observed here. Interestingly as observed with molybdenum there is no evidence of formation of the W(III,IV,IV) mixed-valence intermediate. In contrast to molybdenum however, there is no detectable further reduction (chemically or electrochemically) to a W(III)$_3$ derivative. Indeed no aqua ions of this oxidation state for tungsten have so far been reported.

Further characterisation of the W(III,III,IV) ion has been achieved using ^{17}O NMR spectroscopy.
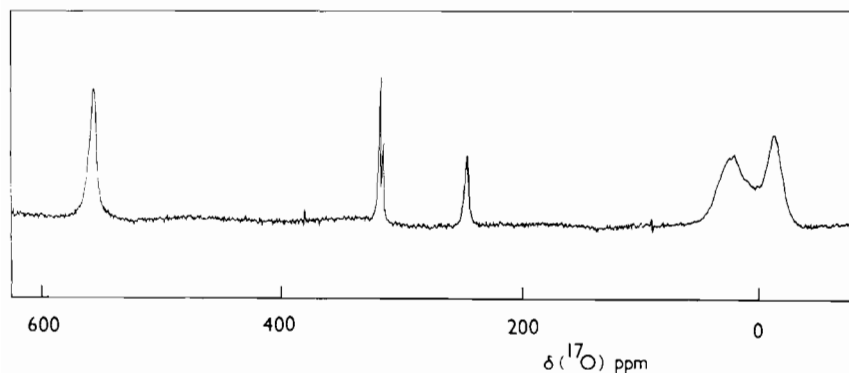
Fig. 5. 54.24 MHz ^{17}O NMR spectrum of the solution as in Fig. 2 (2 cm^3) following 1 h treatment with amalgamated zinc (2 g) directly in the NMR tube.

Figure 5 shows a ^{17}O NMR spectrum recorded for a solution of W(III,III,IV) generated from the fully ^{17}O-enriched solution of $[W_3O_4]^{4+}$ as in Fig. 2 following treatment with an excess of Zn/Hg for one hour (Mn^{2+} added). In addition to W(III,III,IV), an appreciable amount of $[W_3O_4]^{4+}$ (aq) is present owing to the spontaneous reoxidation of W(III,III,IV) by H$_3$O$^+$. A new μ-oxo resonance is observed for the reduced ion along with changes to the appearance of the bound water region (growth of a new resonance around -10 ppm). The highly shielded position (252 ppm) of the new resonance suggests an assignment to a μ_2-hydroxo-group* indicating that protonation accompanies reduction. Since only one resonance is observed an assignment to equivalent μ_2-hydroxo-groups on the NMR timescale is relevant implying conversion of the μ_3-oxo ligand upon protonation into a μ_2-bridging group and suggesting **III**

III
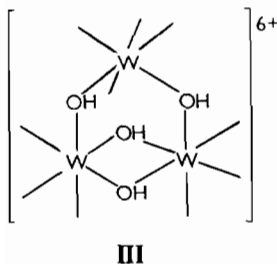
as a likely structure for the W(III,III,IV) ion. Corresponding studies on the Mo(III,III,IV) ion** are also consistent with structure **III** (single μ_2-hydroxo resonance at 403 ppm observed here). The green W(III,III,IV) and orange–brown Mo(III,III,IV) ions

have similar electronic spectra with absorption maxima respectively at 678 nm ($\epsilon = 200$ M^{-1} cm^{-1} per W^2) and 1050 nm ($\epsilon = 100$ M^{-1} cm^{-1} per Mo [11]) suggesting an assignment to an intervalence transition [12]. The higher energy and more intense band observed for tungsten is consistent with greater delocalisation resulting from the greater overlap of the relativistically expanded 5d orbitals [6]. These observations suggest that both of these mixed-valence ions are valence delocalised on the NMR timescale (equivalent μ_2-hydroxo groups) but are essentially localised (class II behaviour) with respect to the much faster electronic timescale.

In conclusion, our present findings provide support for the preparative method for $[W_3O_4]^{4+}$ (aq) as reported by Sykes and co-workers [2] employing two successive columns of DOWEX 50W X8 and X2 resins with washing of the X8 column with 2M Hpts (removal of chloroaqua complexes) prior to elution from the second column. Use of the single DOWEX 50 W column as reported by Segawa and Sasaki is insufficient as demonstrated here for producing pure solutions of the aqua ion. The major product under these conditions is the monochloro complex; $[W_3O_4(OH_2)_8Cl]^{3+}$. In this work the use of ^{17}O and ^{183}W NMR has allowed clear identification of this product not possible using UV–Vis spectrophotometry.

Reduction of $[W_3O_4]^{4+}$ (aq) leads to a mixed-valence W(III,III,IV) ion with probable structure **III** having equivalent μ_2-hydroxo groups and valence delocalised behaviour on the NMR timescale. The reduction potential value for the W(IV)$_3$/W(III,III,IV) couple is -0.8 V versus NHE in 3 M HCl at 25 °C.

*Electrochemical measurements [11] on Mo(III,III,IV) (aq) support the $[Mo_3(\mu_2\text{-}OH)_4]^{6+}$ formulation. The more shielded μ-oxo resonance for W(III,III,IV) (aq) (252 ppm) vs. Mo(III,III,IV) (aq) (403 ppm) supports the presence of similar protonated μ-oxo groups on the tungsten ion.

**Solvent shifts in the 1050 nm band maximum of Mo-(III,III,IV) (aq) have recently been observed in support of the intervalence assignment and localised class II behaviour on the electronic timescale [12].

References

1 M. Segawa and Y. Sasaki, *J. Am. Chem. Soc.*, *107* (1985) 5565.

2 B.-L. Ooi, A. Petrou and A. G. Sykes, *Inorg. Chem.*, *27* (1988) 3626.

3 C. D. Kennedy and R. D. Peacock, *J. Chem. Soc.*, (1963) 3392.

4 (a) R. I. Maksimovskaya and K. G. Burtseva, *Polyhedron*, *4* (1985) 1559; (b) L. P. Kazanskii, M. A. Fedotov and V. I. Spitzyn, *Dokl. Akad. Nauk. SSSR*, *234* (1977) 1376; (c) M. A. Fedotov, L. P. Kazanskii and V. I. Spitzyn, *Dokl. Akad. Nauk. SSSR*, *272* (1983) 1179.

5 D. T. Richens, L. Helm, P.-A. Pittet, A. E. Merbach, F. Nicolo and G. Chapuis, *Inorg. Chem.*, *28* (1989) 1394; D. T. Richens, L. Helm, P.-A. Pittet and A. E. Merbach, *Inorg. Chim. Acta*, *132* (1987) 85.

6 P. Pykko and J. P. Desclaux, *Acc. Chem. Res.*, *12* (1979) 276.

7 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Pitman, London, 1983.

8 D. Hugi-Cleary, L. Helm and A. E. Merbach, *J. Am. Chem. Soc.*, *109* (1987) 4444.

9 K. Piepgrass and M. T. Pope, *J. Am. Chem. Soc.*, *109* (1987) 1586.

10 P. Kathirgamanathan, A. B. Soares, D. T. Richens and A. G. Sykes, *Inorg. Chem.*, *24* (1985) 2950.

11 D. T. Richens and A. G. Sykes, *Inorg. Chim. Acta*, *54* (1981) L3; *Inorg. Chem.*, *21* (1982) 418.

12 D. T. Richens and C. Guille-Photin, *J. Chem. Soc., Dalton Trans.*, (1989) in press.