Lifting the lid on metatungstate. ^{1}H and ^{183}W NMR study of the six electron reduced anion $[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{34}(OH)_3]^{3-}$

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The distribution of the eleven protons present in a six-electron reduced form of metatungstate, $[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{34}(OH)_3]^{3-}$, in dry CD_3CN is mapped by ^{1}H and ^{183}W NMR, allowing assessment of structural changes which accompany reduction.

The four trinuclear capping units of Keggin polyoxo anions $[X^{n}W^{VI}_{12}O_{40}]^{n-8}$ (T_d point symmetry; see framework in Fig. 1) are linked to define a tetrahedral cavity encapsulating atom X.[1] Six-electron reduction leads, for $X^n = 2H^I, B^{III}, Si^{IV}$, to the 'poly-browns'.[1,2] X-Ray crystallographic and aqueous solution NMR data suggest effective C_{3v} point symmetry for these species, consistent with localisation of the added electrons in a single trinuclear cap whose terminal oxo ligands are protonated to aqua ligands.[3–6]

$$(W^{VI}{=}O)_3 + 6\ e^- + 6\ H^+ \rightarrow (W^{IV} \leftarrow OH_2)_3$$

The salt $(NH_4)_4[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{35}(OH)_2]$ **I** was synthesised by controlled potential electrolysis in aqueous HCl and converted to $(NBu_4)_3[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{34}(OH)_3]$ **II** by phase transfer.[7] In D_2O, **I** exhibits a single ^{1}H NMR resonance (two equivalent internal hydrogen atoms) and three ^{183}W resonances (3 : 3 : 6) consistent with effective C_{3v} point symmetry.[2–4,8] However, in dry CD_3CN, **II** exhibits five ^{1}H resonances (a–e) integrating for eleven protons and seven ^{183}W resonances (A–G) integrating for three W^{IV} and nine W^{VI} centres (Fig. 2, Table 1).

The intensities of the ^{1}H (4 : 2 : 1 : 2 : 2) and ^{183}W (1 : 2 : 2 : 2 : 2 : 2 : 1) resonances imply the presence of a mirror plane consistent with effective C_s point symmetry. It is apparent that proton exchange rates are reduced significantly in dry CD_3CN, allowing detection of surface-bound protons and differentiation of inequivalent tungsten sites. What is the driving force responsible for the effective change from T_d to C_s symmetry that accompanies the six electron reduction process?

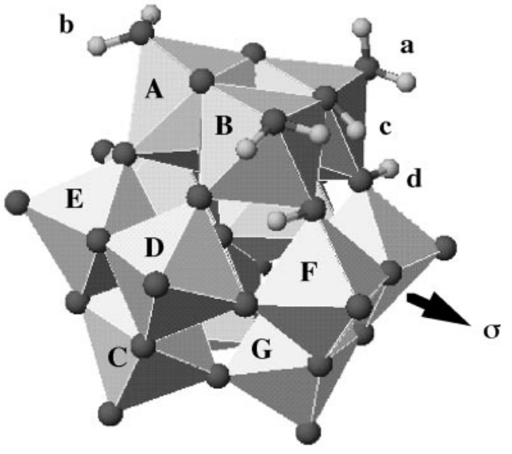

Fig. 1 Polyhedral representation of $[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{34}(OH)_3]^{3-}$. W atoms are centred in each 'octahedron' of O atoms.

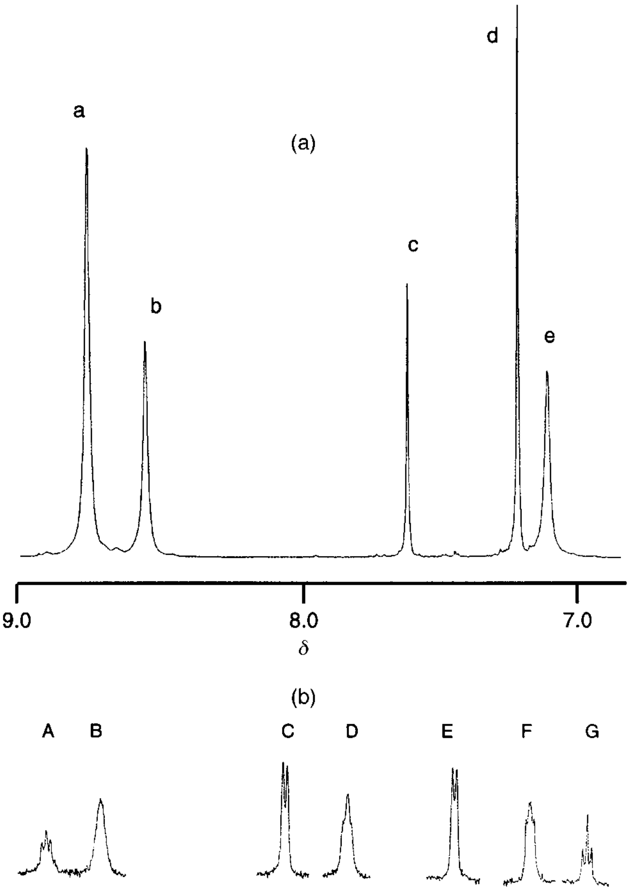

Fig. 2 NMR spectra of **II** (0.15 M) in CD_3CN (anion resonances only) (a) ^{1}H, (b) ^{183}W (99 atom% ^{183}W).

H_2O addition experiments assign resonance e to the slowly exchanging internal protons H_e and indicate that the protons H_a and H_b are in chemically similar sites.[10] Their relative intensities a : b = 4 : 2 allow assignment to the W^{IV}–aqua ligand protons. Tungsten resonances A and G of intensity 1 must be assigned to the unique W^{IV} and W^{VI} atoms lying on the mirror plane. The five resonances B–F of intensity 2 are due to five pairs of W atoms related by the mirror plane. B must be assigned to W^{IV} and so the fragments $W_AO(H_b)_2$ and $\{W_BO(H_a)_2\}_2$ are identified (Fig. 1).

A sample of II was enriched to 99 atom% ^{183}W. Its ^{183}W NMR spectrum featured resolved fine structure (13–18 Hz) assigned as $^{2}J_{WOW}$ coupling characteristic of corner-sharing WOW bridges [Fig. 2(b)].[11] Assigned resonances A and G are triplets consistent with corner-sharing to two equivalent W

Table 1 NMR data for $(NBu_4)_3[(H)_2\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{34}(OH)_3]$ **II** (0.15 M, CD_3CN)

Nucleus	Resonance	δ	$W_{1/2}{}^a$/Hz	Relative intensity
^1H	H_a	8.76	7.7	3.9
	H_b	8.55	7.3	2.0
	H_c	7.61	2.5	1.0
	H_d	7.22	2.4	2.0
	H_e	7.11	8.6	2.1
^{183}W	W_A	1413.2	4.4	1
	W_B	1402.7	5.7	2
	W_C	−42.6	5.7	2
	W_D	−64.5	7.1	2
	W_E	−128.7	4.5	2
	W_F	−171.0	3.4	2
	W_G	−187.4	5.2	1

^{a} For natural abundance samples.

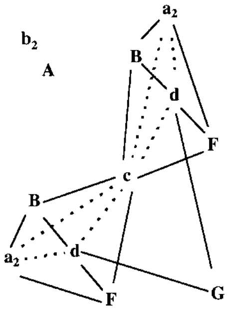

Fig. 3 Map of dipolar HH (----) and scalar WH (——) connectivities to protons H_a–H_d in **II**. Longer range interactions bd and Ad are are also observed but are omitted for clarity.

atoms (Fig. 1). On the other hand, C and E are doublets. A COSY experiment displayed a $W^{VI}W^{VI}$ cross-peak CG which allows assignment of C to the pair of tungsten atoms corner-sharing to unique atom W_G and E to the pair of tungsten atoms corner-sharing with unique atom W_A (Fig. 1). The only other $W^{VI}W^{VI}$ COSY crosspeak detected was DF and tungsten atoms W_D and W_F were assigned on the basis of multiple WOW corner-sharing interactions [Figs. 1, 2(b); *vide infra*: ref. 12].

Assignment and location of the three protons H_c and H_d were addressed initially by a HH ROESY experiment. Cross peaks ac, ad, bd and cd were detected. These dipolar interactions are mapped in Fig. 3. No interactions were observed between internal protons H_e and any of the external protons H_a–H_d.

Mapping of scalar interactions utilised WH HMQC experiments. ^{183}W–^1H coupling was not detected in the 1D spectra (*cf.* Fig. 2) implying that $^2J_{WOH} < W_{1/2} = 2$–9 Hz, allowing constraints to be set on mixing times. A spectrum is shown in Fig. 4 and the scalar connectivities are included in Fig. 3.[12]

The mapping indicates that resonances c and d may be assigned to three hydroxyl protons associated with the reduced $W^{IV}_3(AB_2)$ and unique $W^{VI}_3(GF_2)$ caps (Figs. 1, 3). Hydrogen oxide ligands $H_3O_2{}^-$ ligands which bridge pairs of metal atoms have been identified previously,[13] but similar stereochemistry does not appear possible here.

The C_s point symmetry of II is imposed by the positions of the three hydroxyl protons H_c and H_d (Fig. 1). The electronic feature which drives this localisation of protons is the localisation of the six added electrons in the reduced cap AB_2. In six-electron reduced $K_5[B^{III}\{W^{IV}_3(OH_2)_3\}W^{VI}_9O_{37}]\cdot 13.5H_2O$, the W^{IV}–W^{IV} bond lengths [mean 2.543(3) Å] in the reduced cap are *ca.* 0.77 Å shorter than the $W^{VI}\cdots W^{I}$ separations in the oxidised caps.[6] The resulting mismatch in dimensions causes the boron atom to move *ca.* 0.4 Å within the internal BO_4 unit and away from the reduced cap but C_{3v} symmetry is retained. The internal cavity in **II** features two hydrogen atoms only and this anion accommodates the mismatch in a different way: three WOW links are converted to longer W(OH)W links [Fig. 1]. Ongoing work will provide more details.

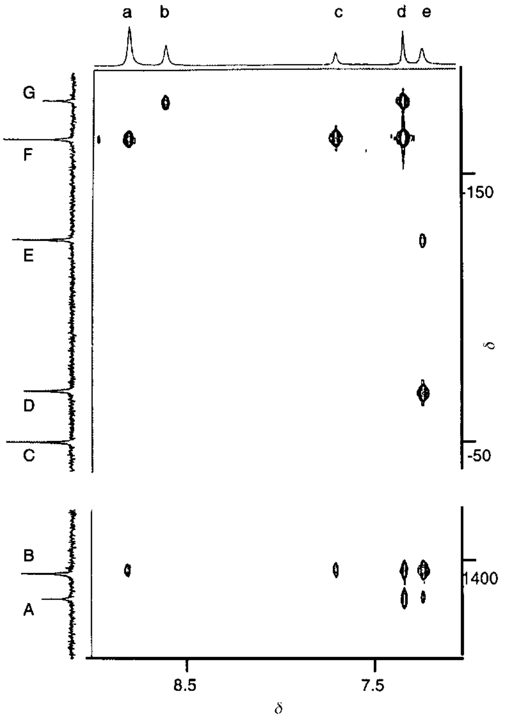

Fig. 4 ^{183}W–^1H HMQC spectrum of **II** (0.15 M, natural abundance) in CD_3CN (t_m = 60 ms; 128 × 4 K, 256 transients per increment; 25 °C).

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Notes and references

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7 A solution of ammonium metatungstate in HCl was reduced to the $6e^-$ level.[3] The ammonium salt was isolated after volume reduction and precipitation with MeOH. Phase transfer[4] mediated *via* a solution of NBu_4Br in CH_2Cl_2 led to the NBu_4Br salt.

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9 ^{183}W spectra were acquired on a Bruker DRX500 spectrometer equipped with a broadband probe at 30 °C. Spectra were acquired at 20.837 MHz using a 60° pulse of 26 μs. Spectra were processed with a line broadening of 1 Hz. COSY 90 spectra were acquired using a 90° pulse of 39 μs. Experiments over the W^{VI} and W^{IV} chemical shift regions were acquired separately owing to their large separation. Gradient non-phase sensitive HMQC experiments were acquired on a Bruker DRX400 spectrometer equipped with an inverse probe at 25 °C. The probe was tuned to 400.130 MHz for ^1H and 16.671 MHz for ^{183}W. 90° pulses of 13.5, 15.3 and 25.7 μs for ^1H and 44 μs for ^{183}W were employed.

10 H_e shifts by < 0.1 ppm ($W_{1/2}$, 5–9 Hz) in the range 0–100 equiv. added H_2O. Resonances H_a, H_b and H_c, H_d broaden beyond detectability at ≈ 100 and 25 equiv. added H_2O, respectively.

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