10.1071/CH19326_AC

Australian Journal of Chemistry 2020, 73(2&3), 137-144

# Supplementary Material

## Incorporation of Vanadium and Molybdenum into Yttrium-Arsenotungstates Supported by Amino Acid Ligands

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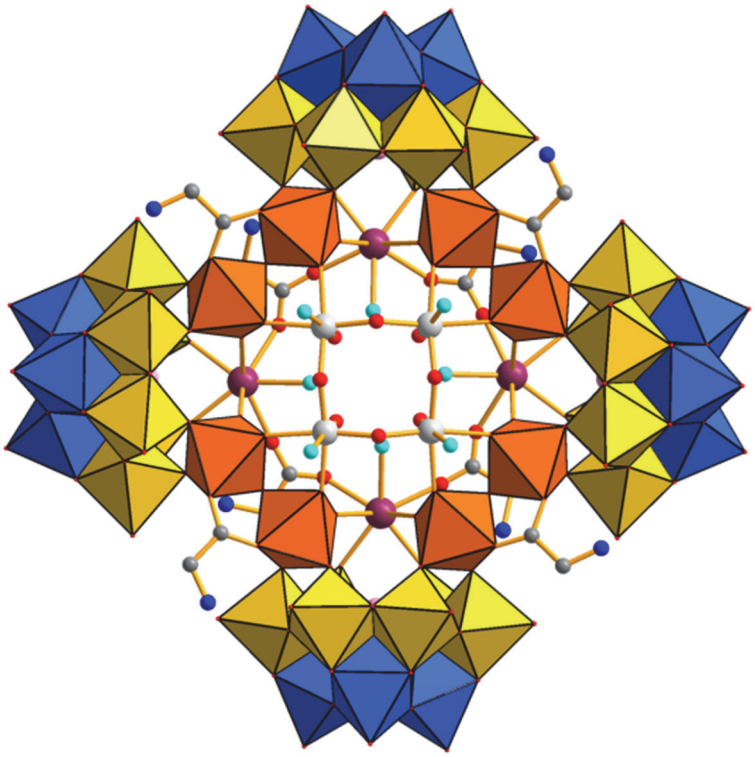

**Fig. S1.** Structural representation of idealised hybrid polyoxometalate $[As_4(M_4)W_{44}Y_4O_{160}(AA)_8(H_2O)_{12}]^{n-}$ indicating the different metal sites: $\{M_4\}$ "core" (grey), $\{Y_4M_8L_8\}$ "ring" (orange), $\{AsM_9\}$ lacunary Keggin "triad" (blue) and $\{AsM_9\}$ lacunary Keggin "belt" (yellow).

**Table S1.** V, Mo and W site occupancies (%) for disordered V/W and V/Mo/W sites and number of V and Mo per POM from crystallography and elemental analysis for **1**·72$H_2O$, **2**·87$H_2O$ and **3**·96$H_2O$.

| | **1**·72$H_2O$ | **2**·87$H_2O$ | **3**·96$H_2O$ |
|---|---|---|---|
| **V occupancies (%)** | | | |
| {$M_4$} core | 43(2), 54(2), 48(2), 55(2) | 50[c] | 50[c] |
| {$Y_4M_8L_8$} ring[b] | 0 | 0 | 0 |
| {$AsM_9$} triad[b] | 0 | 0 | 0 |
| {$AsM_9$} belt[b] | 0 | 0 | 0 |
| **W occupancies (%)** | | | |
| {$M_4$} core | 57(2), 46(2), 52(2), 45(2) | 50[c] | 50[c] |
| {$Y_4M_8L_8$} ring[b] | 100 | 100 | 96(2), 84(1)[c] |
| {$AsM_9$} triad[b] | 100 | 100 | 77(2), 93(2)[c] |
| {$AsM_9$} belt[b] | 100 | 100 | 100 |
| **Mo occupancies (%)** | | | |
| {$M_4$} core | - | - | 0 |
| {$Y_4M_8L_8$} ring[b] | - | - | 4(2), 16(1)[c] |
| {$AsM_9$} triad[b] | - | - | 23(2), 7(2)[c] |
| {$AsM_9$} belt[b] | - | - | 0 |
| **Total V per POM** | | | |
| crystallography (sum of V occupancies) | 2 | 2 | 2 |
| elemental analysis for V (bulk) | 2 | 2 | 2 |
| **Total Mo per POM** | | | |
| crystallography (sum of Mo occupancies) | - | - | 2 |
| elemental analysis for Mo (bulk) | - | - | 2 |

[a] restrained, [b] see Fig. S1; [c] per unit cell.

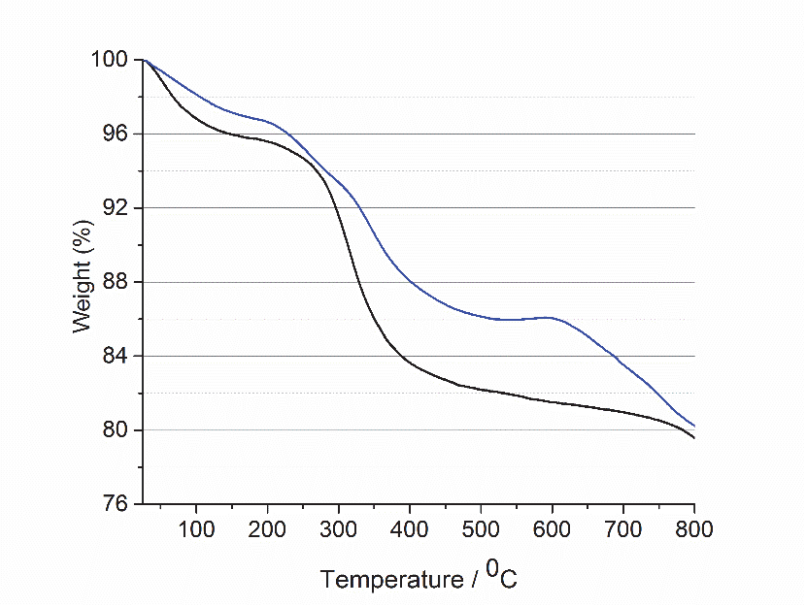


**Fig. S2**. Thermogravimetric analysis data for Gly-containing **1**·25$H_2O$ (blue) and Nle-containing **3**·20$H_2O$ (black). The calculated masses corresponding to loss of all organic cations and ligands are 11 and 15 % for **1** and **3**, respectively.

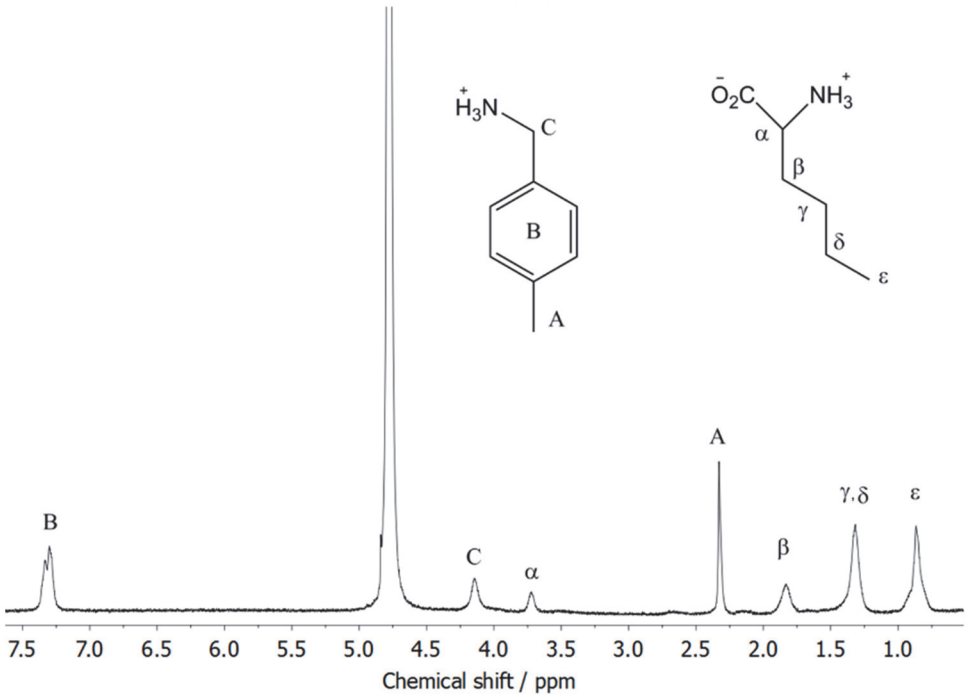


**Fig. S3.** Solution $^1$H NMR spectrum of **3** in $D_2O$ with assignments.

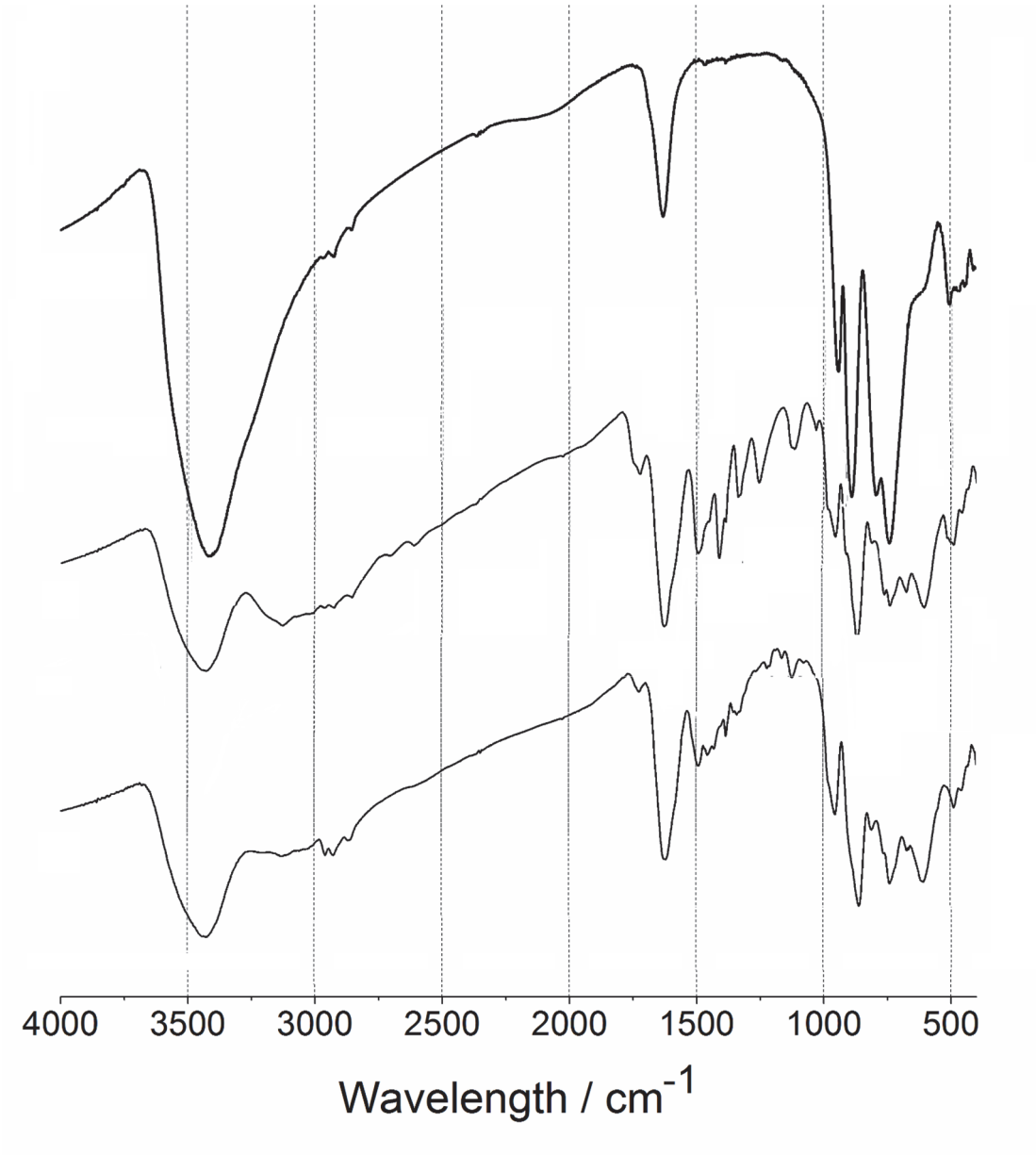


**Fig. S4.** Infrared spectra (KBr) of (from top to bottom): $K_{14}[As_2W_{19}O_{67}(H_2O)]$ precursor, **1**·25$H_2O$ and **3**·20$H_2O$.

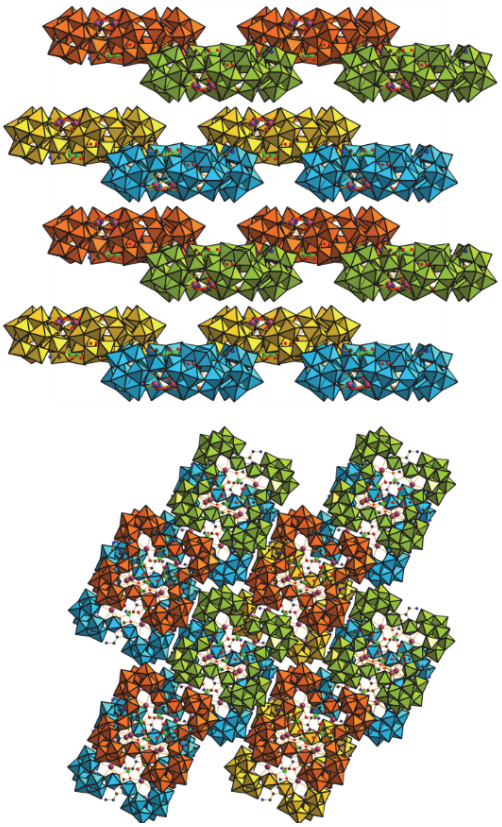

**Fig. S5**. Crystal packing diagram for **1**·72$H_2O$ looking down the: (top) crystallographic *b* axis, and (bottom) crystallographic *a* axis. Color code as per Fig. 1 except $WO_6$ octahedra, yellow and blue is one double layer and green and orange in the other.

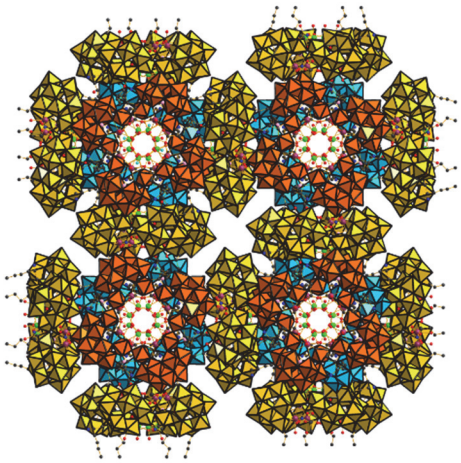

**Fig. S6.** Crystal packing diagram for **2**·87$H_2O$ and **3**·96$H_2O$ illustrating how the disk-shaped POMs are arranged on the six faces of the "cubic" cavities. Color code as per Fig. 1 except $WO_6$ octahedra, orange for the POM on the "front" of the cubic cavities.

**Table S2**. XPS Binding Energies (eV) for **1**·25$H_2O$ and **3**·20$H_2O$ obtained from spectral deconvolution.

| Compound | W(VI) | | V(IV) |
|---|---|---|---|
| | $4f_{7/2}$ | $4f_{5/2}$ | $2p_{3/2}$ |
| **1** | 35.9 | 37.9 | 516.4 |
| **3** | 35.7 | 37.7 | 516.3 |

**Table S3**. Spin Hamiltonian parameters obtained from simulating the 130 K X-band powder EPR spectra of **1**·25$H_2O$ and **3**·20$H_2O$, assuming for three and two V(IV) environments, respectively

| compound | $g_x$ | $g_y$ | $g_z$ | $A_x$[a] | $A_y$[a] | $A_z$[a] | environment | ratio |
|---|---|---|---|---|---|---|---|---|
| **1** | 1.972 | 1.972 | 1.884 | 162 | 162 | 495 | I | 4 |
| | 1.972 | 1.972 | 1.942 | 162 | 162 | 520 | II | 2 |
| | 1.972 | 1.972 | 1.915 | 162 | 162 | 530 | III | 1 |
| **3** | 1.972 | 1.972 | 1.888 | 162 | 162 | 490 | I | 1 |
| | 1.972 | 1.972 | 1.900 | 162 | 162 | 510 | II | 1 |

[a] Hyperfine parameters are × $10^{-4}$ $cm^{-1}$