Mapping the Synthesis of Low Nuclearity Polyoxometalates From Octamolybdates to Mn-Anderson Clusters

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Experimental

Instrumentation

Microanalysis: Carbon, nitrogen, and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHNS, CE-440 Elemental Analyser;

Single crystal X-ray diffraction

Two different types of X-ray diffractometers were used for single crystal structure determination:

Bruker Apex II Quasar charge-coupled device (CCD) detector (λ ($Mo_{K\alpha}$) = 0.71073Å) at 150(2) K, where the data reduction was performed using the Apex2 software package and structure solution.

Oxford Diffraction Gemini Ultra with an ATLAS charge-coupled device (CCD) detector [(λ ($Cu_{K\alpha}$) = 1.54184 Å] at 150(2) K, where the data reduction was performed using the CrysAlis software package and structure solution.

Independent of the type of X-ray diffractometer, corrections for incident and diffracted beam absorption effects were applied utilising analytical numeric absorption correction with a multifaceted crystal model,[1] or using empirical absorption correction.[2] Refinement was carried out with SHELXS-97[3] and SHELXL-97[3] using WinGX[4] *via* a full matrix least-squares on F2 method. All non-hydrogen atoms were refined anisotropically unless otherwise stated.

Thermogravimetric analysis: Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of 5 °C min^{-1};

NMR Microscopy: All NMR data was recorded on a Bruker Advanced 400 MHz, ^{1}H NMR at 400 MHz with deuterated dimethyl sulfoxide from Goss Scientific;

Electrospray Mass Spectroscopic Measurements: All MS data were collected using a Q-trap, time-of-flight MS (MicrOTOF-Q MS) instrument equipped with an electrospray (ESI) source supplied by Bruker Daltonics Ltd. All analyses were carried out at 180°C in acetonitrile, collected in negative ion mode and the spectrometer was calibrated with the standard tune-mix to give a precision of ca. 1.5 ppm in the region of 500-3000 *m/z*;

Fourier-transform Infrared (FT-IR) Spectroscopy: All spectra were recorded on Shimadzu FTIR 8400S Fourier Transformer Infrared Spectrophotometer. Wavenumbers ($\tilde{\nu}$) are given in cm-1; intensities as denoted as wk = weak, sh = sharp, m = medium, br = broad, s = strong, vs = very strong;

Raman Spectroscopy: Raman spectra were recorded on a Horiba HR800 spectrometer in conjunction with HeNe 20 mW (λ = 514 nm) laser using powdered solid substances. Frequencies are given in cm-1; intensities denoted as w = weak, m = medium, s = strong, vs = very strong, sh = sharp, br = broad.

Synthesis of compound 2: $TEA_3Na_1[\beta\text{-}Mo_8O_{26}]$

Compound **2** was synthesised in the same manner as compound **1**, only tetramethylammonium bromide was substituted with tetraethylammonium bromide (TEA·Br (2.19 g, 10.4 mmol)). The compound, $(TEA)_3Na_1[\beta\text{-}Mo_8O_{26}]$, was obtained as a dry white powder. **Yield** = 3.73 g, 1.93 mmol, 75 % based on Mo; **EA:** Anal. Calcd. for $C_{24}H_{60}Mo_8N_3Na_1O_{26}$ (1597.25 g/mol): C, 18.05; H, 3.79; N, 2.63; **Found:** C, 17.79; H, 3.67; N, 2.64; **IR:** 2986 (w, sh), 2947 (w, br), 1481 (m, sh), 1451 (m, br), 1397 (m, sh), 1304 (w, br), 1173 (m, sh), 1065 (w, br), 1003 (m, sh), 934 (s, sh), 903 (vs, sh), 833 (s, sh), 702 (vs, br), 648 (vs, sh); **Raman:** 962 (s, sh), 939 (m, br), 922 (w, br), 906 (m, br), 893 (w, br); **ESI-MS:** The peak envelopes at m/z 614.16, 721.7 and 1574.6 correspond to $[Mo_4O_{13}Na_1]^{1-}$, $[Mo_4O_{13}(TEA)_1]^{1-}$ and $[Mo_8O_{26}(TEA)_3]^{1-}$, respectively; **TGA:** The loss of 30.02 % corresponds to the loss of the TEA cations (theoretical value 24.46 %). If the weight-dip at about 425 °C is an artefact, then the total loss would be 25.52 %, which corresponds well with the theoretical value.

Synthesis of compound 3: $TPA_2Na_2[\beta\text{-}Mo_8O_{26}]$

Compound **3** was synthesised in the same manner as compound **1**, only tetramethylammonium bromide was substituted with tetrapropylammonium bromide (TPA·Br (2.77 g, 10.4 mmol)). The compound, $(TPA)_2Na_2[\beta\text{-}Mo_8O_{26}]$, was obtained as a white powder. **Yield** = 3.63 g, 2.26 mmol, 87 % based on Mo; **EA:** Anal. Calcd. for $C_{24}H_{56}Mo_8N_2Na_2O_{26}$ (1602.2 g/mol): C, 17.99; H, 3.52; N, 1.75, Na 2.87; Found: C, 17.81; H, 3.45; N, 1.78, Na, 2.77; **IR:** 2970 (w, br), 2886 (w, br), 1682 (w, br), 1466 (m, br), 1381 (w, br), 1319 (w, br), 1258 (w, br), 1157 (w, br), 1042 (w, br), 934 (s, sh), 903 (vs, sh), 841 (s, sh), 702 (vs, sh), 656 (vs, sh); **Raman:** 963 (s, sh), 944 (m, br), 916 (w, br), 905 (w, br); **ESI-MS:** The peak envelopes at m/z 614.16 and 778.3 correspond to $[Mo_4O_{13}Na_1]1-$ and $[Mo_4O_{13}(TPA)_1]1-$ respectively; **TGA:** The loss of 25.52 % corresponds to the loss of the TPA cations (theoretical value 23.26 %). If the weight-dip at about 425 °C is an artefact, then the total loss would be 24.17 %, which corresponds well with the theoretical value.

Comment on Sodium composition: The sodium composition of the compounds **1-3** has been studied by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Flame photometry (FP). Nevertheless, due to the poor reliability of the results, those are not presented here.

Synthesis of compound 5: $TEA_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$

Compound **2** (0.498 g, $0.31\text{x}10^{-3}$ mol) was dissolved in 60 mL of DMF at room temperature (30 min). $Mn(OAc)_3\cdot 2H_2O$ (0.127 g, $0.47\text{x}10^{-3}$ mol) and TRIS-base (0.131 g, $1.08\text{x}10^{-3}$ mol) were added and the resulting solution was heated up to 80°C for 20 hrs. The reaction is then cooled down to room temperature and the clear orange solution was set up of crystallisation at 4°C by ether diffusion. This crystallisation led to de formation of crystals and a precipitate both made of compound **5**. Compound **5** is obtained pure by redissolving separately the crystals and the precipitate in DMF and recrystallised by ether diffusion at 4 °C. **Yield** = 27 % based on Mo; **EA:** Anal. Calcd for $C_{32}H_{76}Mn_1Mo_6N_5O_{24}$ (1545.54 g/mol): C, 24.87; H, 4.96; N, 4.53; Found: C, 24.16; H, 4.73; N, 4.42; **IR:** 3277 (w, sh), 2982 (w, br), 2932 (w, br), 2900 (w, sh), 2857 (w, sh), 1655 (w, br), 1614 (w, sh), 1481 (w, br), 1454 (w, sh), 1439 (w, sh), 1395 (w, sh), 1304 (w, br), 1242 (w, br), 1173 (m, sh), 1132 (w, sh), 1042 (m, sh), 999 (m, sh), 935 (s, sh), 916 (s, sh), 895 (vs, sh), 646 (vs, br); **^{1}H NMR ($(CD_3)_2SO$, 400**

MHz): δ 65.00-58.00 (br, m, CH_2,12H), 3.60 (br, s, NH_2, 4H), 3.28-3.12 (m, CH_2, 24H), 1.26-1.00 (m, CH_3, 36H); **ESI-MS:** The peak envelope at m/z 1414.8 corresponds to $[(TEA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$.

Synthesis of compound 6 and 7:

Compound **3** (0.500 g, 0.31x10^{-3} mol) was dissolved in 60 mL of DMF at room temperature (30 min). $Mn(OAc)_3{\cdot}2H_2O$ (0.127 g, 0.47x10^{-3} mol) and TRIS-base (0.131 g, 1.08x10^{-3} mol) were added and the resulting solution was heated up to 80°C for 20 hrs. The reaction was then cooled to room temperature and the resulting clear orange solution was set up of crystallisation at 4°C by ether diffusion. This crystallisation led to de formation of crystals and a precipitate. The crystalline material is compound **7**, whilst compound **6** is obtained by redissolving the precipitate in DMF and crystallised by ether diffusion at 4 °C.

Compound 6 $TPA_2Na_1[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$: **Yield** = 16 % based on Mo (0.103 g); **EA:** Anal. Calcd. for $C_{32}H_{72}Mn_1Mo_6N_4Na_1O_{24}$ (1550.49 g/mol): C, 24.79; H, 4.68; N, 3.61; Found: C, 24.87; H, 4.77; N, 3.91; **IR:** 2972 (w, br), 2936 (w, br), 2902 (w, br), 2880 (w, br), 1657 (m, sh), 1605 (w, br), 1460 (w, br), 1393 (w, sh), 1308 (w, br), 1240 (m, br), 1184 (w, br), 1134 (w, br), 1111 (m, br), 1034 (m, sh), 984 (w, br), 9936 (s, sh), 912 (sm sh), 897 (vs, sh), 754 (w, ah), 648 (vs, br); **^{1}H NMR ($(CD_3)_2SO$, 400 MHz):** δ 63.00-59.00 (br, m, CH_2, 12H), 3.60 (br, s, NH_2, 4H), 3.19-3.06 (m, CH_2, 24H), 1.70-1.53 (m, CH_2, 24H), 0.94-0.83 (m, CH_3, 36H); **ESI-MS:** The peak envelope at m/z 1527.8 corresponds to $[(TPA)_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$.

Compound 7 $Na_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$: Yield: 17% based on Mo; **EA:** Anal. Calcd for $C_8H_{16}Mn_1Mo_6N_2Na_3O_{24}$ $\cdot(DMF)_3$ (1443.04 g/mol): C, 14.15; H, 2.58; N, 4.85; Found: C, 15.55; H, 2.24; N, 4.37; **IR:** 3480 (w, br), 3437 (w, br), 3356 (w, sh), 3293 (w, br), 2932 (w, br), 1661 (s, sh), 1443 (m, sh), 1412 (w, sh), 1393 (m, sh), 1306 (m, sh), 1233 (vs, sh), 1182 (m, sh), 1123 (s, sh), 1105 (s, sh), 1061 (m, sh), 1021 (s, sh), 1001 (m, sh), 984 (s, sh), 937 (sm sh), 640 (vs, br); **^{1}H NMR ($(CD_3)_2SO$, 400 MHz):** δ 64.00-58.00 (br, m, 12H), 3.60 (br, s, NH_2); **ESI-MS:** The peak envelope at *m/z* 1201.4 corresponds to $[Na_2[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]]^{1-}$.

TGA

TGA: The formula for compound **1** is $(TMA)_2Na_2[\beta\text{-}Mo_8O_{26}]$. The first loss is of 3.94 %, with a second loss at about 250 °C of 13.94 %. The theoretical value for the loss of the TMA cations is 10.76 %. If the weight-dip at about 450 °C is an artefact, then the second loss would be 12.36 %, which corresponds well with the theoretical value.

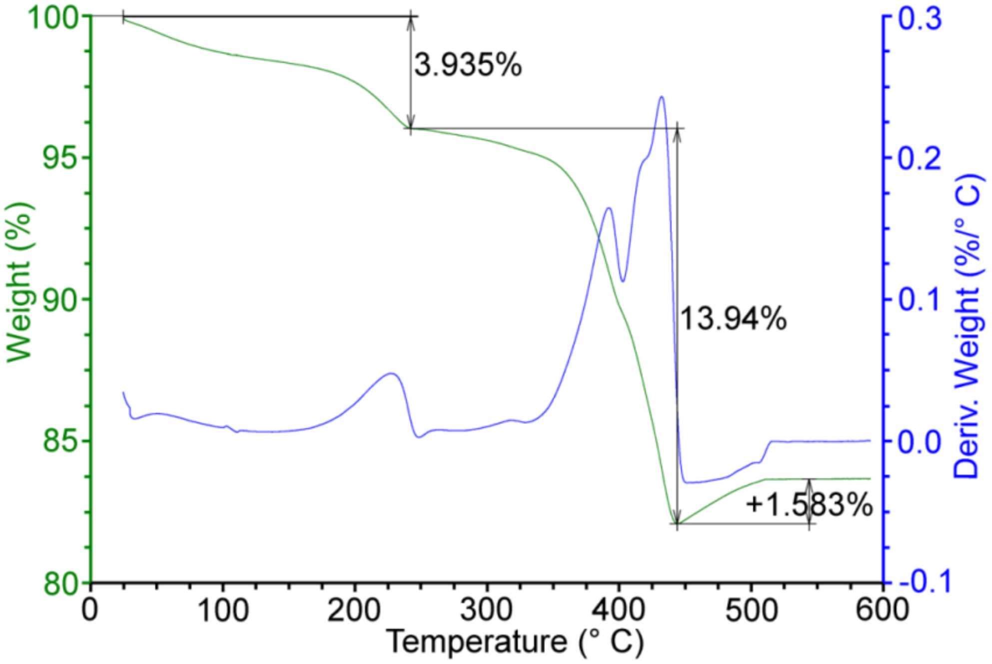

Figure S1: TGA of compound **1**.

TGA: The formula for compound **2** is $(TEA)_3Na_1[\beta\text{-}Mo_8O_{26}]$, and the loss of 30.02 % corresponds to the loss of the TEA cations (theoretical value 24.46 %). If the weight-dip at about 425 °C is an artefact, then the total loss would be 25.52 %, which corresponds well with the theoretical value.

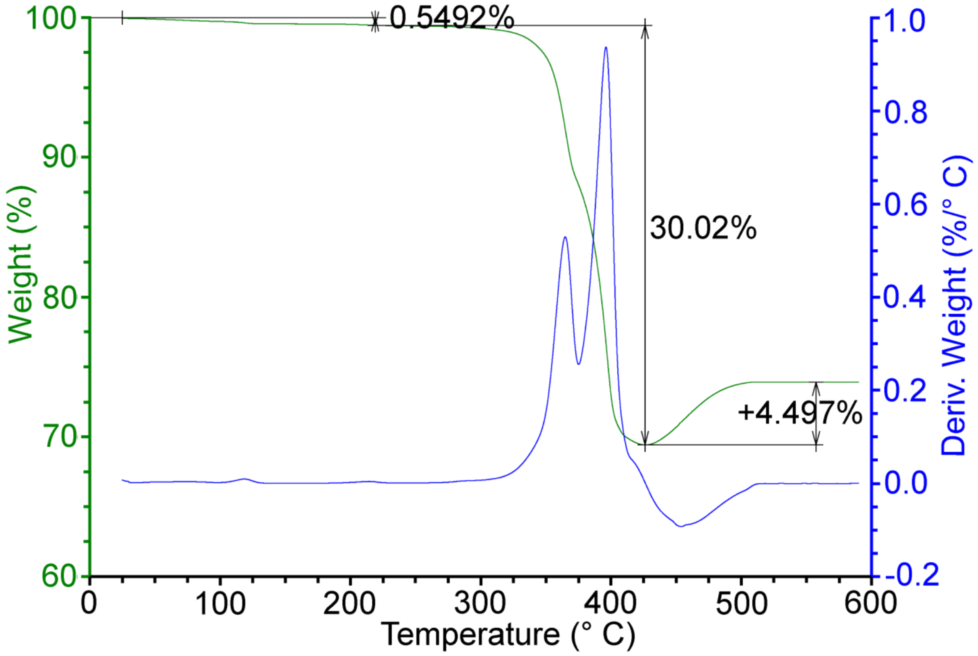

Figure S2: TGA of compound **2**.

TGA: The formula for compound **3** is $(TPA)_2Na_2[\beta\text{-}Mo_8O_{26}]$ and the loss of 25.52 % corresponds to the loss of the TPA cations (theoretical value 23.26 %). If the weight-dip at about 425 °C is an artefact, then the total loss would be 24.17 %, which corresponds well with the theoretical value.

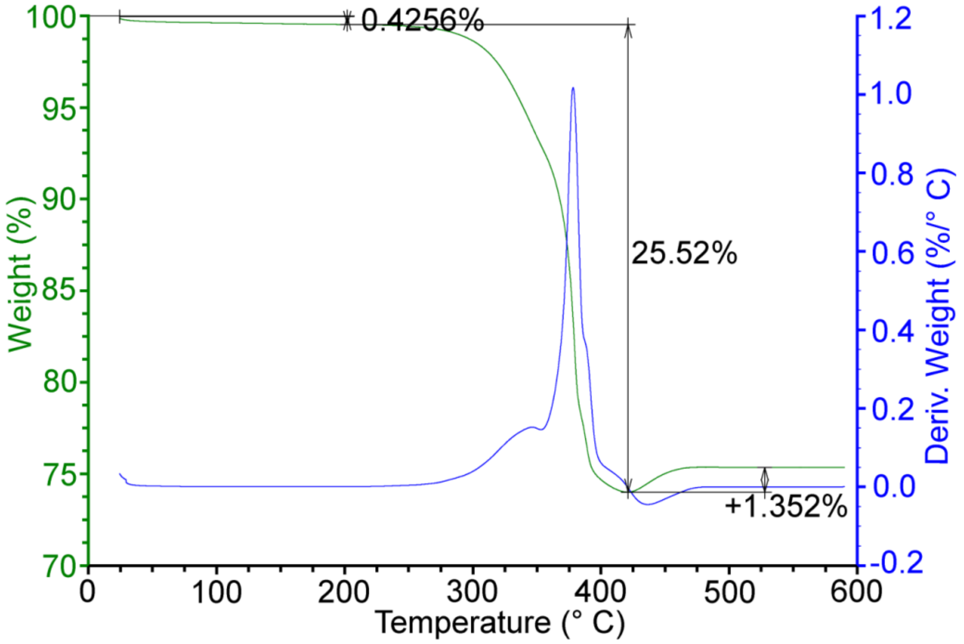

Figure S3: TGA of compound **3**.

^{1}H NMR

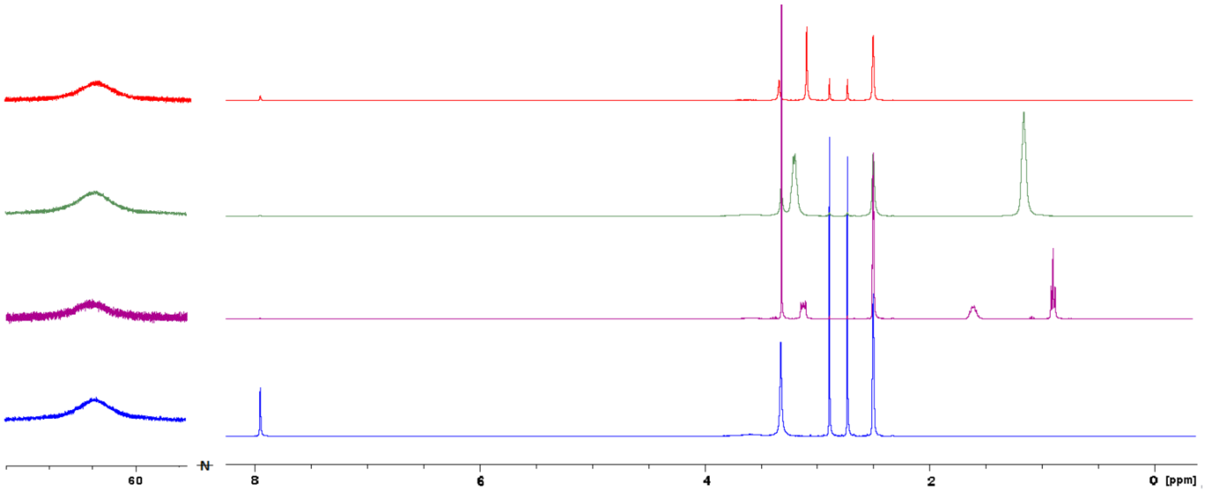

Figure S4: ^{1}H NMR obtained in DMSO for compounds **4** (red), **5** (green), **6** (purple) and **7** (blue).

Due to the paramagnetic nature of the Mn^{III} central heteroatom the 12 protons situated closest to the paramagnetic centre are shifted to 65-60 ppm. A broad peak can be observed in this region for all the four TRIS Mn-Anderson compounds.

References

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