Electronic Supplementary Material (ESI) for Dalton Transactions

Trapping $\{BW_{12}\}_2$ tungstoborate: synthesis and crystal structure of hybrid $[\{(H_2BW_{12}O_{42})_2O\}\{Mo_6O_6S_6(OH)_4(H_2O)_2\}]^{14-}$ anion†

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Supporting Information

Spectrophotometric titration data

Table S1 Ratio of the reactants in the preparation of samples for the spectrophotometric titration

	1	2	3	4	5	6	7	8	9	10	11	12	13
V(1[*]), mL	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
V(2[**]), mL	0.4	0.6	0.8	1.0	1.2	1.4	1.7	2.0	2.4	2.8	3.2	4.0	5.0
V(3[***]), mL	9.1	8.9	8.7	8.5	8.3	8.1	7.8	7.5	7.1	6.7	6.3	5.5	4.5
Molar ratio $\{BW_{11}\}/\{Mo_2O_2S_2\}$	0.16	0.24	0.32	0.40	0.48	0.56	0.68	0.79	0.95	1.11	1.27	1.57	1.97

[*] *ca.* 25 mM solution of $\{Mo_2O_2S_2\}$ in water; [**] *ca.* 5 mM solution of $\{BW_{11}\}$ in water; [***] *ca.* 10 mM solution of HCl in water.

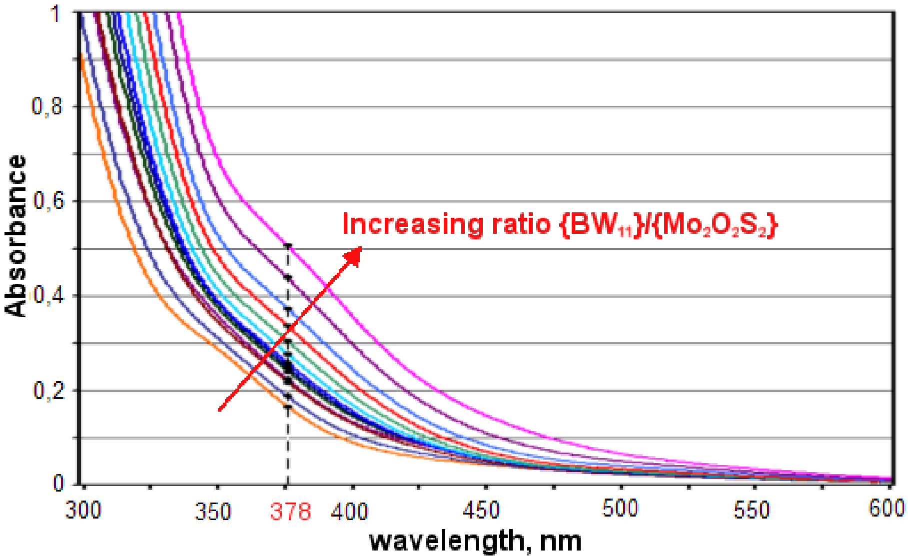

Fig. S1 Evolution of spectra by increasing the ratio $\{BW_{11}\}/\{Mo_2O_2S_2\}$

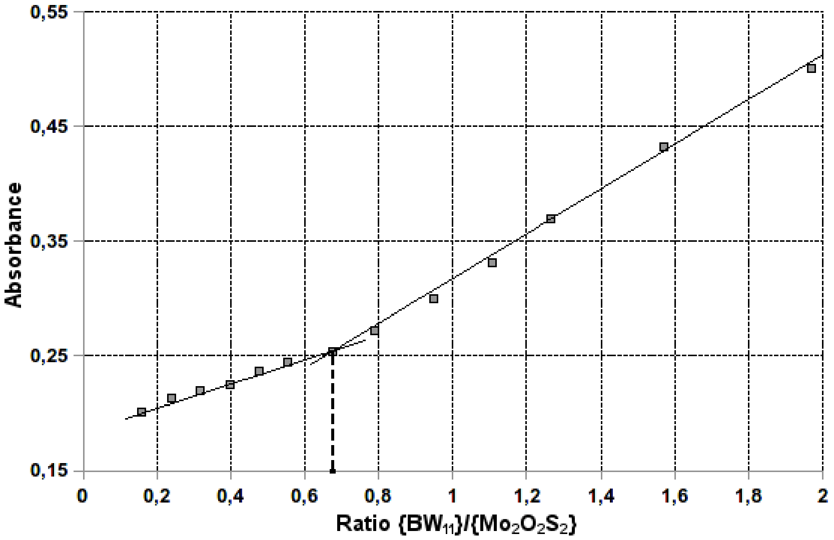

Fig. S2 Absorbance changes at 378 nm as function of the molar ratio $\{BW_{11}\}/\{Mo_2O_2S_2\}$

Electrospray Ionization mass spectrometry (ESI-MS)

A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, U.K.) was used. The temperature of the source block was set to 80 °C and the desolvation temperature to 100 °C. A capillary voltage of 3.3 kV was used in the negative scan mode, and the cone voltage set to low values (U_c = 15 V), to control the extent of fragmentation. Mass calibration was performed using a solution of sodium iodide in isopropyl alcohol/water (50:50) from *m/z* 100 to 2800.ESI time-of-flight mass spectra were acquired in the W-mode at a resolution of ca. 15000 (FWHM) at m/z 2000. Aqueous sample solutions (ca. 1 x 10-3 M) were infused via a syringe pump directly connected to the ESI-MS source at a flow rate of 10 μL/min. The observed isotopic pattern of each species was compared with the theoretical isotopic pattern calculated from their elemental composition using the *MassLynx*4.1 program.

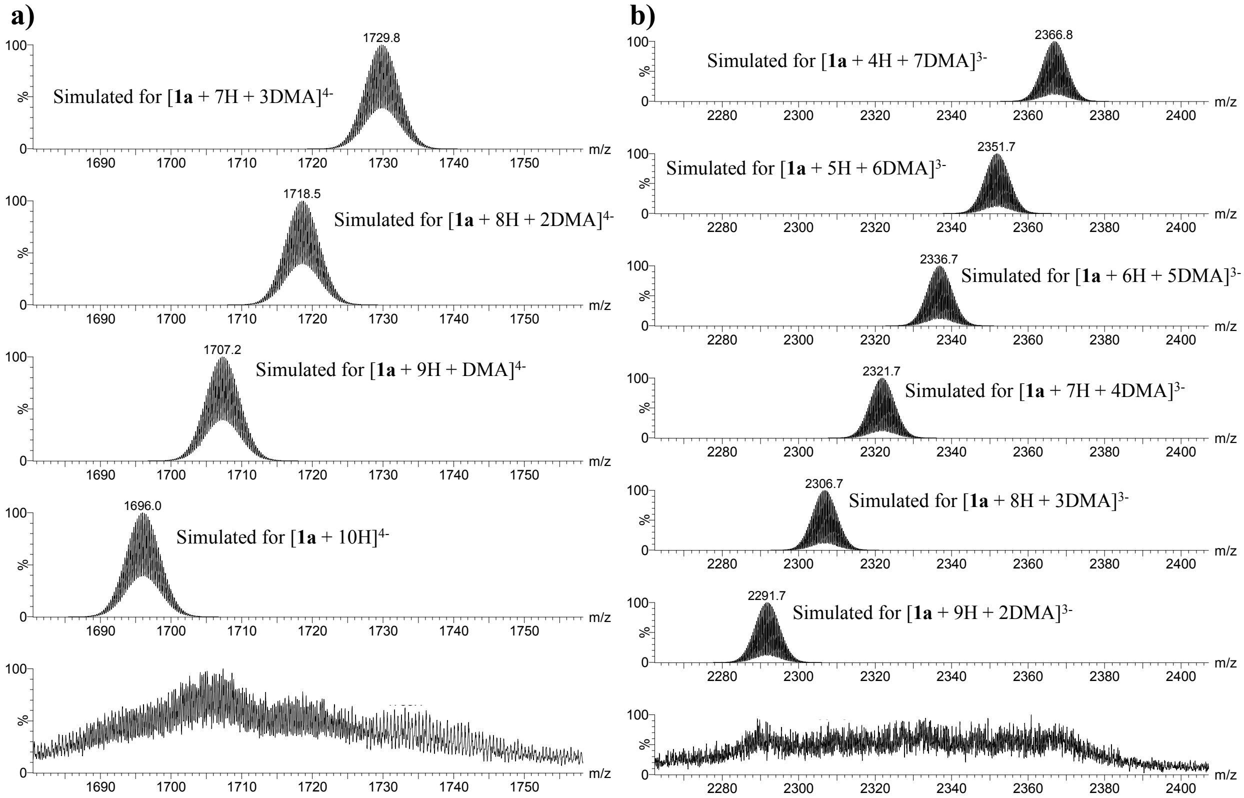

Figure S3. Expanded regions of the high resolution negative ESI mass spectrum of aqueous solutions of **1** recorded at Uc = 15 V, a) in the m/z 1680 to 1760 range where quadruply-charged species are observed (bottom) together with simulated peaks for the different [**1a** + (n-10)H + $nNMe_2H_2$]$^{4-}$(n = 0-3) species; b)in the m/z 2280 to 2400 range where triply-charged species are detected (bottom) together with simulated peaks for the different [**1a** + (n-11)H + $nNMe_2H_2$]$^{3-}$(n = 2-7) species. DMA stands for dimethylammonium.

Additional crystallographic data

Table S2. Experimental crystallographic details

Crystal data	
Chemical formula	$C_{20.60}H_{147}B_2Mo_6N_{10.30}O_{121.45}S_6W_{24}$
M_r	7685.11
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	16.8821 (6), 21.1874 (10), 21.4856 (10)
α, β, γ (°)	84.638 (1), 84.606 (1), 85.998 (1)
V (Å^3)	7603.2 (6)
Z	2
$F(000)$	6897
Radiation type	Mo $K\alpha$
μ (mm^{-1})	18.73
Crystal size (mm)	0.18 × 0.16 × 0.13
Data collection	
Diffractometer	Bruker Nonius X8Apex CCD diffractometer
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.134, 0.195
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	63340, 38102, 29300
R_{int}	0.035
θ values (°)	$\theta_{max} = 28.7$, $\theta_{min} = 1.0$
Range of h, k, l	$-22 \le h \le 12$, $-28 \le k \le 28$, $-29 \le l \le \rightarrow 28$
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.122, 1.05
No. of reflections, parameters, restraints	38102, 1797, 0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 380.7574P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	7.16, -5.66

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS97* (Sheldrick, 1998), *SHELXL97* (Sheldrick, 1998), *SHELXTL* (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

Table S3. Ranges for selected bonds (Å)

Bond type	Bond length
B–μ_2-O(–W)	1.465(27) – 1.558(29)
W=$O_{terminal}$	1.703(11) – 1.750(9)
W–O(H_2)	2.245(8) – 2.271(8)
W–μ_2-O(–W)	1.810(8) – 2.152(8)
W–μ_2-O(–Mo)	1.742(9) – 1.795(9)
W–μ_2-O(–B)	2.309(9) – 2.469(9)
Mo=$O_{terminal}$	1.674(9) – 1.681(11)
Mo–μ_2-O(H)	2.077(10) – 2.121(10)
Mo–μ_2-O(H_2)	2.401(9) – 2.495(9)
Mo–μ_2-O(–W)	2.111(10) – 2.260(9)
Mo–μ_2-S	2.306(3) – 2.335(4)
Mo–Mo	2.8234(17) – 2.8324(17)