

Electronic Supplementary Information

{Mn₁₄W₄₈} aggregate: the perspective of isopolyanions as ligands

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Synthesis of 1a: A 16 g (118 mmol) sample of NaOAc·3H₂O was added to a solution of Na₂WO₄·2H₂O (4.0 g, 0.12 mmol) in 80 mL H₂O. The pH of the solution was adjusted to 2.4 with 2M HCl. Then a sample of Mn₁₂-acetate (1.0 g, 0.49 mmol) was suspended in the solution. The mixture was vigorously stirred at room temperature for 1 hr, refluxed at 100 °C for another 2 hr, and hot filtered. Dimethylamine hydrochloride (4.0 g) was added to the resulting filtrate, and the clear, brown solution was left to crystallize at room temperature. Dark red needle crystals formed after approximately three weeks (yield 0.23 g, 6.3% based on W).

Elemental analysis, calcd. for C₂₈H₂₆₆Mn₁₄N₁₄Na₄O₂₅₅W₄₈: C 2.31, H 1.84, N 1.35, Na 0.63, Mn 5.28, W 60.58%. Found: C 2.56, H 1.90, N 1.51, Mn 5.44, Na 0.67, W 58.9%. IR (KBr pellet, 2000–400 cm⁻¹): $\tilde{\nu}_{\max}$: 1628(m), 1465(m), 1438(w, sh), 1412(w), 1385(w), 1018(w), 950(s), 828(vs, br), 750(s, sh), 686(s), 631(m), 596 (m), 577(m), 485(m), 462(m, sh). TG analysis shows a weight loss of approximately 8.2% between 30 and 240 °C that is associated with the loss of 67 water molecules (both crystalline lattice solvent molecules and coordinated aqua ligands) per molecule of 1a. UV–vis (H₂O, 3.6 × 10⁻⁶ M) displays only a shoulder peak at ca. 275 nm (ϵ_{\max} = 1.1 × 10⁵ M⁻¹ cm⁻¹).

Instruments and physical measurements: Infrared spectra (KBr pellets) were collected with a Brüker Tensor 27 instrument. Elemental analyses are performed by Atlantic Microlab Inc., Norcross, GA (for C, H, and N) and Desert Analytics Laboratory, Tucson, AZ (for Na, Mn, and W). Thermalgravimetric analysis was measured with a TA Instruments thermal analysis system under Ar flow with 10 °C/min heating. UV–vis absorption measurements were performed on a Shimadzu UV-1650PC spectrometer. Quartz cuvettes with optical path lengths of 1 cm were used. Magnetic measurements were made on a polycrystalline sample of 1a (34.44 mg) using a SQUID magnetometer (MPMS-5, Quantum Design). A correction for both diamagnetic and temperature-independent paramagnetic contributions of -3.28 × 10⁻³ emu mol⁻¹ has been applied to the DC susceptibility data.

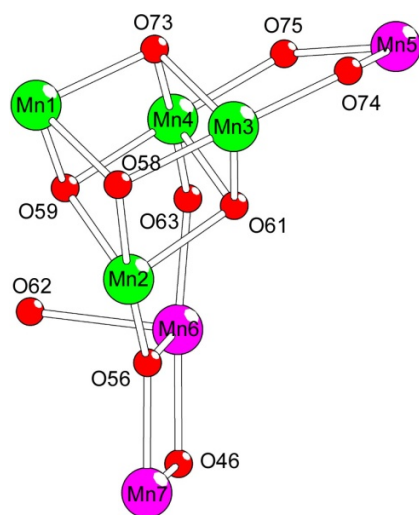
X-ray crystallographic structure determination: Suitable crystals were coated with Paratone-N oil, suspended on a small fiber loop, and placed in a cooled nitrogen stream at 173(2) K on a Brüker SMART 1000 CCD sealed-tube diffractometer with graphite-monochromated Mo K α (0.71073 Å) radiation. A sphere of data was measured using a series of combinations of ϕ and ω scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were all handled using SMART software.¹ Frame integration and final cell refinements were carried out using SAINT software.² The SADABS program was used to carry out absorption corrections.³ The structure was solved using Direct Methods and difference Fourier techniques (SHELXTL, V6.12).⁴ All metal atoms (W and Mn) were refined anisotropically; the rest were isotropically refined. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.⁵ Structure solution, refinement and generation of the crystallographic information file were performed by using SHELXTL, V6.12 software.⁴ Not all of the

counterions (dimethylammonium and Na⁺) and the lattice water molecules could be located due to disorder. Therefore, thermogravimetric and elemental analyses were used to determine the number of water molecules and counteractions, instead.

Crystallographic data for **1a**: C₂₈H₂₆₆Mn₁₄N₁₄Na₄O₂₅₅W₄₈, M = 14566.47 g mol⁻¹, space group P $\bar{1}$, a = 13.222(1), b = 22.045(2), c = 22.708(2) Å, α = 84.881(2), β = 80.521(2), γ = 79.599(2), V = 6409.1(10) Å³, T = 173(2) K, Z = 1, D_c = 3.774 Mg m⁻³, F(000) = 6518, μ (Mo-K α) = 22.228 mm⁻¹. 75196 reflections measured, 28895 unique (R_{int} = 0.0964). The refinement converges to R1 = 0.0662, wR2 = 0.1296 and GOF = 1.022 for 16304 reflections with I > 2 σ (I). CCDC 781988.

Bond valence sum calculations: For determination of the oxidation states of metal centers and the protonation states of oxygen sites, bond valence sum (BVS) calculations were carried out using the method of I. D. Brown (See, Brown, I. D.; Altermatt, D. *Acta Crystallogr. Sect. B* **1985**, *41*, 244). The R₀ values were taken from the literature for calculations performed on Mn⁶ and O⁶⁻⁸ sites.

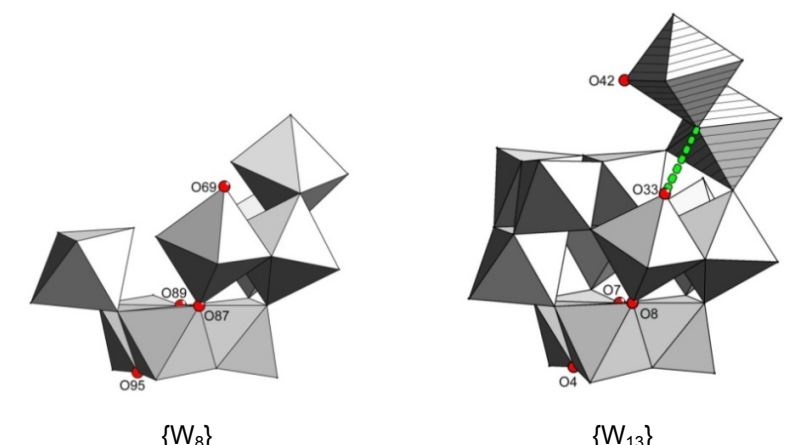
- (1) SMART Version 5.628, 2003, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- (2) SAINT Version 6.36A, 2002, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- (3) SADABS Version 2.08, 2003, George Sheldrick, University of Göttingen.
- (4) SHELXTL 6.12, 2002, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- (5) Wilson, A. J. C., Ed.; *International Tables for X-ray Crystallography, Volume III*. Academic Publishers: Dordrecht, 1992, Tables 6.61.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222).
- (6) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.
- (7) Roulhac, P. L.; Palenik, G. J. *Inorg. Chem.* **2003**, *42*, 118.
- (8) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr. Sect. B* **1991**, *47*, 192.



	BVS ⁶		
	Mn(II)	Mn(III)	Mn(IV)
Mn1	4.47	4.09	4.29
Mn2	4.21	3.85	4.04
Mn3	4.19	3.83	4.02
Mn4	3.93	3.60	3.78
Mn5	3.25	2.98	3.12
Mn6	3.22	2.95	3.09
Mn7	3.34	3.06	3.21

Oxygen atoms	BVS ⁶⁻⁸	Assigned oxidation state
O46	1.22	OH
O56	2.05	O
O58	1.97	O
O59	1.93	O
O61	1.84	O
O62	0.27	H₂O
O63	2.07	O
O73	1.98	O
O74	1.29	OH
O75	1.69	O

Figure S1/ Table S1. Bond valence sum (BVS) calculations for Mn centers and selected oxygen sites of the Mn₇ cores in **1**. The assigned oxidation states and protonated states are highlighted in bold and shaded.



	Oxygen atoms	BVS ⁶⁻⁸	Assigned oxidation state
{W ₈ }	O69	1.71	O
	O87	1.84	O
	O89	1.29	OH
	O95	1.07	OH
{W ₁₃ }	O4	1.88	O
	O7	1.32	OH
	O8	2.05	O
	O33	0.93	OH
	O42	0.33	H₂O

Figure S2/Table S2. Bond valence sum (BVS) calculations for selected oxygen sites of the isopolyanion ligands {W₈} and {W₁₃} in **1**. The assigned protonated states are highlighted in bold and shaded.

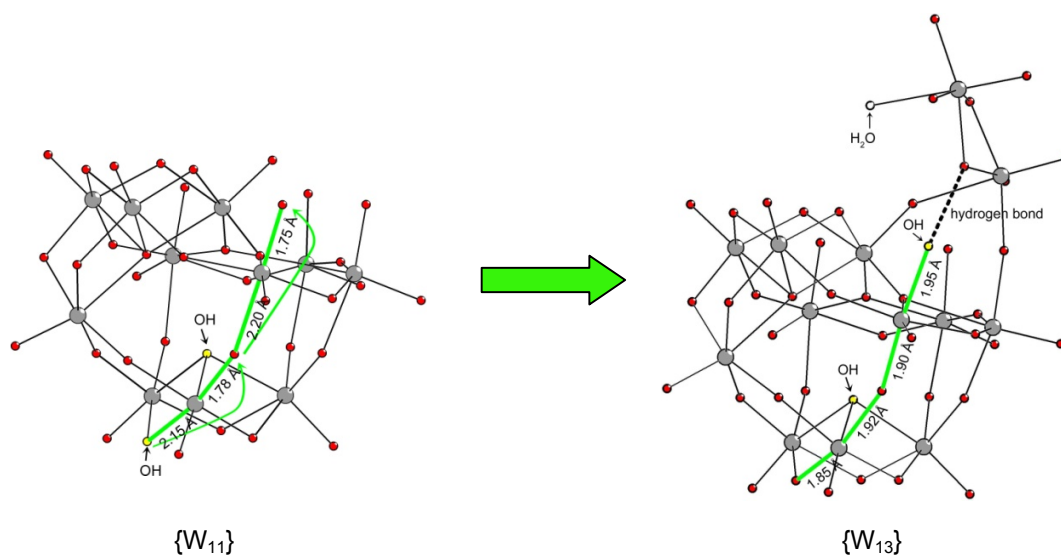


Figure S3. Side-by-side comparison of the crystal structures of the {W₁₁} species (see: Lehmann, T.; Fuchs, J. Z. *Naturforsch. B* 1988, 43, 89.) and the {W₁₃} unit in compound **1a**. It illustrates the tautomeric migration of a proton from a bridging μ_2 -OH to a terminal oxygen atom that is hydrogen-bonded to the newly added {W₂} fragment in {W₁₃}. The relevant W–O bond lengths are shown. W, gray; oxo, red; OH, yellow; H₂O, white sphere.

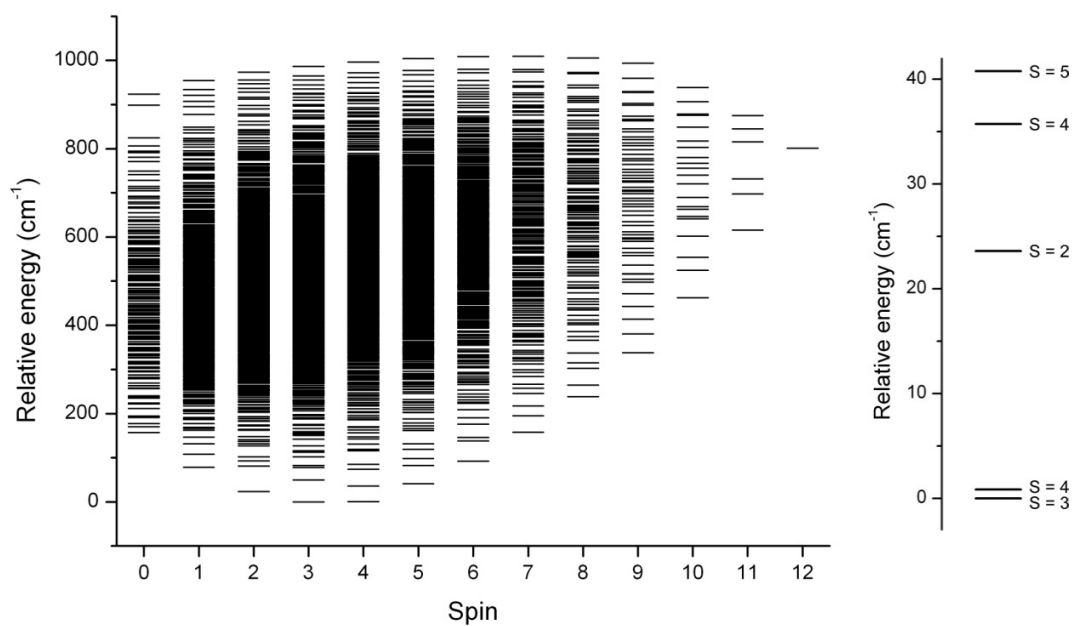


Figure S4. Spin state energy spectrum calculated for each Mn_7 cluster in **1a** using MAGPACK (J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.* 2001, 22, 985). Shown on the right is the relative energy of the ground state and nearby excited states.

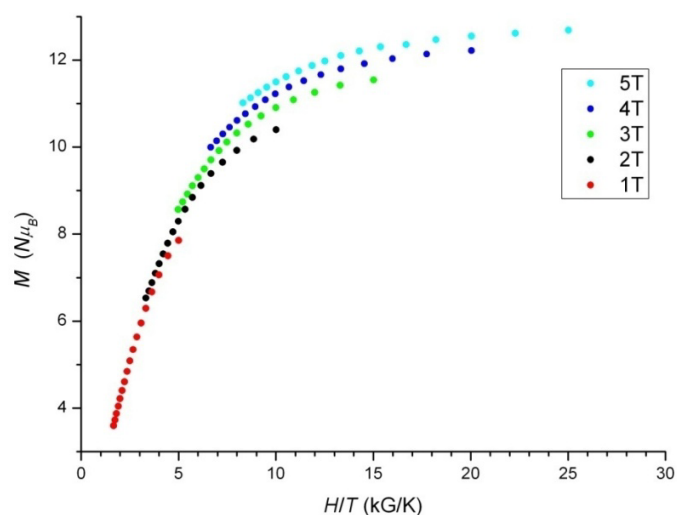


Figure S5. Plot of reduced magnetization vs H/T for **1a** at 5, 4, 3, 2, and 1 T in the temperature range 2–6 K.

A list of structurally characterized isopolytungstate species:

- [W₄O₁₆]⁸⁻, A. Hüllen, *Naturwiss.*, 1964, **51**, 508; A. Hüllen, *Berich. Bunsen Gesell.*, 1966, **70**, 598;
[HW₅O₁₉]⁷⁻, J. Fuchs, R. Palm and H. Hartl, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2651;
[W₆O₁₉]²⁻, J. Fuchs, W. Freiwald and H. Hartl, *Acta Crystallogr. Sect. B*, 1978, **34**, 1764; R. Bhattacharyya, S. Biswas, J. Armstrong and E. M. Holt, *Inorg. Chem.*, 1989, **28**, 4297;
[H₃W₆O₂₂]⁵⁻, H. Hartl, R. Palm and J. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1492;
[W₇O₂₄]⁶⁻, K. G. Burtseva, T. S. Chernaya and M. I. Sirota, *Dokl. Akad. Nauk*, 1978, **243**, 104; J. Fuchs and E. P. Flindt, *Z. Naturforsch. B*, 1979, **34**, 412;
[W₁₀O₃₂]⁴⁻, Y. Sasaki, T. Yamase, Y. Ohashi and Y. Sasada, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 4285;
[H₄W₁₁O₃₈]⁶⁻, T. Lehmann and J. Z. Fuchs, *Z. Naturforsch. B*, 1988, **43**, 89;
[H_xW₁₂O₄₀]^{(8+x)-}, R. Singer and H. Gross, *Helvetica Chim. Acta.*, 1934, **17**, 1076;
[H₂W₁₂O₄₂]¹⁰⁻, R. Allmann, *Acta Crystallogr. Sect. B*, 1971, **27**, 1393; A. Chrissafidou, J. Fuchs, H. Hartl and R. Palm, *Z. Naturforsch. B*, 1995, **50**, 217;
[H₄W₁₉O₆₂]⁶⁻, D.-L. Long, P. Kögerler, A. D. C. Parenty, J. Fielden and L. Cronin, *Angew. Chem., Int. Ed.*; 2005, **45**, 4798;
[H₄W₂₂O₇₄]¹²⁻, H. N. Miras, J. Yan, D.-L. Long and L. Cronin, *Angew. Chem., Int. Ed.*, 2008, **47**, 8420;
[W₂₄O₈₄]²⁴⁻, I. Brüdgam, J. Fuchs, H. Hartl and R. Palm, *Angew. Chem., Int. Ed.*; 1998, **37**, 2668;
[H₁₀W₃₄O₁₁₆]¹⁸⁻, H. N. Miras, J. Yan, D.-L. Long and L. Cronin, *Angew. Chem., Int. Ed.*, 2008, **47**, 8420;
[H₁₂W₃₆O₁₂₀]¹²⁻, D.-L. Long, H. Abbas, P. Kögerler and L. Cronin, *J. Am. Chem. Soc.* 2004, **126**, 13880.