Electronic Supporting Information

Blurring the line between addenda and heteroatoms in a giant polyoxotungstotellurite

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I. General methods and materials

Reagents were used as purchased without further purification. Na₂WO₄·2H₂O (\geq 98 % purity) was purchased from Merck; Na₂TeO₃ (97 % purity) and anhydrous LiCl (99 % purity) were obtained from Alfa Aesar, and 37.0 % HCl (p. a.) for preparation of 1 M solutions from Chemsolute. Elemental analysis results (ICP-OES and Cl) were obtained from Central Institute for Engineering, Electronics and Analytics (ZEA-3), Forschungszentrum Jülich GmbH (D-52425 Jülich, Germany). TGA/DTA measurements were carried out with a Mettler Toledo TGA/SDTA 851 in dry N₂ (60 mL min⁻¹) at a heating rate of 5 K min⁻¹. FT-IR spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer using KBr pellets. UV-Vis spectra were measured using 10 mm quartz cuvettes on a Shimadzu UV-3600 plus UV-Vis-NIR spectrophotometer.

Synthesis of Na₅₁Li₂₉[H₄Te₄₈W₇₈O₃₇₂]·225H₂O·1.5LiCl (NaLi-1)

Samples of Na₂WO₄·2H₂O (0.90 g, 2.7 mmol) and Na₂TeO₃ (0.09 g, 0.40 mmol) were dissolved in aqueous 1 M LiCl solution (15 mL) acidified with 1 M HCl (1.3 mL) to a final pH of 7.5 (*note*: when more than 2.3 mL of 1 M HCl is added (pH 7.3) only oily products form). The obtained clear colorless solution was heated at 70 °C for 30 min under vigorous stirring and then cooled down to room temperature and filtered. The filtrate was separated into several vials and left for evaporation in air. A white precipitate forming in 3 – 5 days was removed by filtration while continuous evaporation produced colorless block-shaped crystals of **NaLi-1** within 10 – 15 days. The crystals were collected by suction filtration and dried in air. Yield: 0.10 g (37.6 % based on Te). Elemental analysis, calculated for H₄₅₄Cl_{1.5}Li_{30.5}Na₅₁O₅₉₇Te₄₈W₇₈ (found): Cl, 0.17 (0.16); Li, 0.66 (0.68); Na, 3.67 (3.66); Te, 19.2 (19.1); W, 44.94 (45.01) %. FT-IR (KBr pellet), $\nu/$ cm⁻¹: 3410 (s, br); 1635 (m); 931 (s); 877 (s); 735 (s); 698 (s); 595 (s); 484 (s); 456 (s); 410 (s). UV-Vis (H₂O): $\lambda_{max} = 185$ nm, $\varepsilon = 959592$ M⁻¹ cm⁻¹.

II. Single-crystal X-ray diffraction data

Single crystal diffraction data for NaLi-1 were collected at 100 K on a SuperNova (Rigaku) diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). The crystals were mounted in a Hampton cryoloop with Paratone-N oil to prevent water loss. Absorption corrections were applied numerically based on Gaussian integration over a multifaceted crystal model using CrysAlis software.¹ The SHELXTL software package² was used to solve and refine the structure. The positions of tungsten and tellurium centers were found by direct methods, and the remaining atoms were located in an alternating series of least-squares cycles on difference Fourier maps. The hydrogen atoms and Li⁺ positions were not located. All heavy atoms (W, Te and Na) were refined in full-matrix anisotropic approximation. ISOR restrictions had to be applied to get reasonable anisotropic displacement parameters for some Na atoms.

The relative site occupancy factors for disordered W and Te positions (W38/W38A, W39/W39A, Te1/Te1A, Te2/Te2A, Te23/Te23a and Te24/Te24A) of the polyanion as well as for Na18/Na19 and Na20/Na21 were refined using a combination of PART / EADP commands. The relative site occupancy factors for the other sodium counterions as well as O atoms of crystal waters were first refined in an isotropic approximation with $U_{iso} = 0.05$ and then fixed at the obtained values and refined without the thermal parameters restrictions.

Due to severe disorder of some countercations and solvent molecules involvement of additional analytical techniques was necessary to attest the true composition of the bulk material of **NaLi-1** (which is a common issue of the POM crystallography). Thus, we could only locate 28 Na⁺ cations and 122 co-crystallized H₂O molecules per polyanion from the XRD data, while 51 Na⁺ ion and 225 crystal water molecules are expected to be present from elemental analysis and thermogravimetry. In addition, it was not possible to conclude if there are any Cl⁻ ions (1.5 co-crystallized LiCl molecule per formula unit is found by elemental analysis) present in the structure. On one hand, it is difficult to clearly distinguish O atoms of H₂O from Cl⁻ ions with a low site occupancy factor in the environment expected for this structure. On the other hand, LiCl could be just an impurity isolated with the main product as the synthesis is done in a LiCl medium. For overall consistency, the final formula presented in the CIF file is based on the composition determined by a combination of single crystal X-ray (polyanion part), elemental and thermogravimetric (exact number of cations and solvent molecules in the bulk material) analyses. The remaining electron density in the voids of the structure was treated by a SQUEEZE procedure³ and yielded the number of the diffused electrons

that fits very well with the expected number of non-located solvent H_2O molecules, Na^+ and Li^+ counterions.

Additional crystallographic data are summarized in Table S1. Further details on the crystal structures investigation can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: http://www.ccdc.cam.ac.uk/, e-mail: data_request@ccdc.cam.ac.uk, or fax: +441223 336033 upon quoting CCDC 1908301 depository number.

Empirical formula	$Cl_{1.5}H_{454}Li_{30.5}Na_{51}O_{597}Te_{48}W_{78}$		
Formula weight / g mol ⁻¹	31912.04		
Crystal system	Monoclinic		
Space group	C2/c		
<i>a</i> / Å	58.0985(5)		
<i>b</i> / Å	17.79804(15)		
<i>c</i> / Å	61.6119(6)		
β	115.7502(11)°		
Volume / Å ³	57382.6(10)		
Z	4		
$D_{\rm calc}$ / g cm ⁻³	3.694		
Absorption coefficient / mm ⁻¹	18.132		
F(000)	56704		
Crystal size / mm ³	0.16 imes 0.21 imes 0.29		
Theta range for data collection	3.14° – 25.03°		
Completeness to Θ_{max}	99.8 %		
	-69 < h < 69,		
Index ranges	-21 < k < 21,		
	-73 < <i>l</i> < 73		
Reflections collected	518548		
Independent reflections	50577		
R _{int}	0.1254		
Observed $(I > 2\sigma(I))$	36849		
Absorption correction	Numerical (Gaussian integration)		
T_{\min} / T_{\max}	0.0460 / 0.1920		
Data / restraints / parameters	50577 / 72 / 1743		
Goodness-of-fit on F ²	1.066		
$R_1, wR_2 (I > 2\sigma(I))$	$R_1 = 0.0574, wR_2 = 0.1346$		
R_1 , w R_2 (all data)	$R_1 = 0.0857, wR_2 = 0.1597$		
Largest diff. peak and hole / e Å ⁻³	3.889 / -3.227		

 Table S1. Crystal data and structure refinement for NaLi-1.



Fig. S1. Comparison of the structure of the $\{\text{TeW}_3\text{O}_{15}\}^{8-}$ subunits in **1** (left) and the trilacunary Keggin-type polyanions $[\text{TeW}_9\text{O}_{33}]^{12-}$ (right).⁴ Color code: WO₆ red-violet octahedra; Te rose, O red spheres. The six WO₆ polyhedra of the $[\text{TeW}_9\text{O}_{33}]^{12-}$ polyanion that do not belong to the $\{\text{TeW}_3\}$ moiety of interest are drawn transparent for better visibility.



Fig. S2. Comparison of the structure of the $\{Te_2W_3O_{18}\}^{10-}$ subunits in **1** (left) and the Strandbergtype polyanions $[(PO_4)_2W_5O_{15}]^{6-}$ (right).⁵ Color code: WO₆ cyan-blue and light-blue octahedra; Te cyan-blue, P orange and O red spheres. Te–O bonds are drawn in orange and dark gray to aid visibility.



Fig. S3. Self-assembly of giant polyanions from simple building blocks is frequently considered as a model for a better understanding of the formation of biological nanosystems. In the present case, polyanion **1** with a diameter of ca. 3.5 nm approaching the sizes of small proteins such as haemoglobin (around 5 nm) displays rare overall D_2 symmetry with a subunit arrangement similar to that in haemoglobin. The figure compares the arrangement of the {Te₈W₁₅O₇₃}^{24–} building units in **1** (left) and the organization of the subunits in hemoglobin (right). Color code: atoms of the different {Te₈W₁₅O₇₃}^{24–} units in **1** are alternatively shown as red and blue spheres, the atoms of the {Te₂W₃O₁₈}^{10–} as dark-purple spheres, the atoms of the {TeW₃O₁₅}^{8–} groups are represented as green sticks.

III. Thermal analysis

The thermal stability of **NaLi-1** was investigated in the temperature range from 25 to 900 °C under an N₂ flux. According to the TGA curve (Fig. S4), the release of (crystal) water molecules occurs in three steps. The main step starts already at 25 °C and is completed at 125 °C and corresponds to the loss of 164 H₂O molecules per formula unit (9.35 % obs. *vs.* 9.34 % calc.). The next two mass loss steps occur in the temperature intervals 125 – 300 °C (1.70 %, ~30 H₂O per formula unit) and 300 – 430 °C (1.03 %, ~18 H₂O per formula unit), respectively. The total weight loss of 12.08 % observed until 430 °C is in good agreement with the release of 210 water molecules of crystallization and 2 H₂O molecules associated with the protons of the polyanions (12.16 %). The surprisingly high temperature for the release of some water molecules could be possibly explained by their tight binding to several Na⁺ counterions. Further weight loss (450 – 630 °C, 0.73 %) could be attributed to the release of co-crystallized Cl⁻ ions (0.20 %) and/or O₂ (which can form due to redox processes within the POM skeleton). A further pronounced mass decrease starting at about 720 °C reflects major POM decomposition, which is not completed at 900 °C. The total weight loss at 900 °C amounts to 15.3 %.



Fig. S4. TGA (blue), differential TGA (green) and SDTA (black) curves for NaLi-1 from room temperature to 900 $^{\circ}$ C under N₂ atmosphere.

IV. FT-IR spectrum

A comparison of the FT-IR spectra of **NaLi-1** and Na₂TeO₃ (Fig. S5) suggests that the prominent absorption band at 835 cm⁻¹ as well as the peaks at 1473, 1460 and 1385 cm⁻¹ belong to vibrations of Te–O and O–Te–Na bonds. The band at 931 cm⁻¹ is characteristic for terminal W=O bonds, while the peaks at 877, 698, 595, 484, 456 and 410 cm⁻¹ could be attributed to W–O–W and W–O–Te vibrations.



Fig. S5. FT-IR spectra of NaLi-1 (blue) in comparison with that of Na₂TeO₃ (green)

V. UV-Vis spectra

The UV-Vis spectra of **NaLi-1** in aqueous solution show only one absorption maximum in the UV region at around 185 nm, that corresponds to the ligand to metal charge transitions of the W–O and Te–O bonds (Fig. S6).

The spectrum remains unchanged for at least 15 h (see Fig. S7).



Figure S6. Room temperature UV-Vis spectrum of **NaLi-1** in H₂O (ε values are averaged from the spectra of the solutions with concentrations between 5.85×10^{-7} M and 1.17×10^{-6} M).



Figure S7. Time evolution of room temperature UV-Vis spectra of a 8.15×10^{-7} M NaLi-1 solution in H₂O.

VI. Comparison of the ionic and crystal radii for Te^{IV} and W^{VI} ions

Ion	Coordination number	Ionic radius / Å	Crystal radius / Å
W ^{VI}	6	0.60	0.74
Te ^{IV}	3	0.52	0.66
Te ^{IV}	4	0.66	0.80

Table S2. Ionic and crystal radii for Te^{IV} and W^{VI} according to R. D. Shannon.⁷

VII. Comparison of known Te-containing POMs

Table S3. Summary of the tungstotellurite polyanions and an organotellurium(IV)-containingpolyoxometalates known to date. a

Polyanion		pH of the synth. medium	Te : W ratio	Reference	
	Homometallic derivatives				
[H ₄ Te ₄₈ W ₇₈ O	372] ^{80–}	7.5	1 : 1.625	this work	
$[Te_{10}W_{28}O_{118}]$]28–	7.0	1:2.8	8	
[Te ₉ W ₂₈ O ₁₁₅]	26-	7.0	1:3.1	8	
$[Te_8W_{28}O_{112}]$	24	7.0	1:3.5	8	
$[H_2Te_4W_{20}O_8$	0]22-	7.5	1:5	9	
$[Te_3W_{21}O_{75}]^{11}$	2–	4.6	1:7	10	
$[Te_8W_{64}O_{224}]$	32-	4.6	1:8	10	
$[Te_2W_{16}O_{58}(C$	DH) ₂] ^{14–}	5.7	1:8	11	
$[Te_2W_{17}O_{61}]^{11}$	2–	5.7	1:8.5	11	
$[Te_2W_{18}O_{62}(0)]$	DH) ₂] ^{10–}	5.7	1:9	11	
[TeW ₉ O ₃₃] ⁸⁻		?	1:9	4	
[NaTeW ₁₅ O ₅₄]13-	7.5	1:15	9	
$[H_4P_4Te_4W_{64}$	O ₂₂₄] ³²⁻	4.0	1:16	12	
[H ₃ TeW ₁₈ O ₆₀]5-	?	1:18	13	
		Heterometallic derivatives ^b			
$[Pd^{II}_{6}Te_{19}W_{42}$	O ₁₉₀] ^{40–}	5.6	1:2.2(1)	14	
$[\mathrm{Cu}^{\mathrm{II}}_{14}\mathrm{Te}^{\mathrm{IV}}_{10}\mathrm{C}$	$O_{28}(B-\alpha-{ m SiW}_9{ m O}_{34})_4]^{28-1}$	8	1:3.6	15	
$[Ln^{III}_{2}(H_{2}O)_{4}(H_$	$[L_{2}W_{2}O_{5}][(Ln(H_{2}O)W_{2}(HL W_{8}O_{30}H_{2})_{2}]_{2}^{4-}]$ We, Nd, Sm, Eu; HL = 2-	4.5	1 : 9.5	16	
$\{ [Sn^{IV}(CH_3)V \\ TeW_8O_{31}]Ln(Ce^{III}, Pr^{III}, Nd) \} \}$	$V_2O_4(\text{isonicotinate})][(B-\alpha-H_2O)(OAc)]_2\}_2^{20}(Ln = 10^{\text{III}}, \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}})$	4.5	1 : 10	17	
$[\{M^{II}L(H_2O)\}]$ (L = 1H-imi Mn, Co)	$a_2(WO_2)_2(\overline{B-\beta}-TeW_9O_{33})_2]^{n-1}$ dazole-4-carboxylate, M =	4.75	1 : 10	18	
$[Te_2W_{20}O_{70}]$	$Re(CO)_{3}_{2}]^{10-}$	2.94	1:10	19	

$[\{(TeO_3)W_{10}O_{34}\}_8\{Ce^{III}_8(H_2O)_{20}\}-(WO_2)_4(W_4O_{12})]^{48-}$	5.0	1:11	20	
$[Ce^{III}_{10}Te_8W_{88}O_{298}(OH)_{12}(H_2O)_{40}]^{18-}$	4.5	1:11	21	
$[Ln^{III}_{2}(OH)(B-\alpha-TeW_{7}O_{28})Sn_{2}(CH_{3})_{4}^{-}$ (W ₅ O ₁₈)] ₂ ¹⁴⁻ (Ln = Er, Yb, Ho, Y)	6.5	1:12	22	
$[H_{10}Ag_{18}Cl(Te_3W_{38}O_{134})_2]^{29-}$	4-4.5	1 : 12.6(6)	23	
$[H_{13}Ag_{18}Cl(Te_3W_{38}O_{134})_2]^{26-}$	4-4.5	1 : 12.6(6)	23	
${[[H_{15}Ag_{18}Cl(Te_{3}W_{38}O_{134})_{2}]}_{n}^{24n-}$	4-4.5	1 : 12.6(6)	23	
	Organotellurium(IV) derivative			
$[(C_4H_8Te^{IV})_3(XW_9O_{33})_2]^{12-}$ (X = As ^{III} , Sb ^{III})	7.5	1:6	24	

^{*a*} Sorted with decreasing Te : W ratio

^{*b*} The {TeW₉O₃₃} complexes of the { $M_x(TeW_9)_y$ } type with various heterometals are not included.

VIII. References

- 1. CrysAlisPro, Agilent Technologies, 1.171.36.28 (release 01-02-2013 CrysAlis171 .NET).
- 2. G. M. Sheldrick, Acta Cryst. 2008, A64, 112–122.
- 3. A. L. Spek, Acta Cryst. 2015, C71, 9–18.
- 4. A. J. Gaunt, I. May, R. Copping, A. I. Bhatt, D. Collison, O. D. Fox, K. T. Holman, M. T. Pope, *Dalton Trans.* **2003**, 3009–3014.
- 5. R. Strandberg, Acta Chem. Scand. 1973, 27, 1004–1018.
- 6. A. Müller, P. Gouzerh, Chem. Soc. Rev. 2012, 41, 7431-7463.
- 7. R. D. Shannon, Acta Cryst. 1976, A32, 751-767.
- J. Gao, J. Yan, S. G. Mitchell, H. N. Miras, A. G. Boulay, D.-L. Long, L. Cronin, *Chem. Sci.* 2011, 2, 1502–1508.
- 9. A. H. Ismail, N. H. Nsouli, M. H. Dickman, J. Knez, U. Kortz, J. Clust. Sci. 2009, 20, 453-465.
- 10. J. Gao, J. Yan, S. Beeg, D.-L. Long, L. Cronin, Angew. Chem. Int. Ed. 2012, 51, 3373-3376.
- 11. C. Ritchie, K. G. Alley, C. Boskovic, Dalton Trans. 2010, 39, 8872-8874.
- Q. Zheng, L. Vilà-Nadal, Z. Lang, J.-J. Chen, D.-L. Long, J. S. Mathieson, J. M. Poblet, L. Cronin, J. Am. Chem. Soc. 2018, 140, 2595–2601
- 13. J. Yan, D.-L. Long, E. F. Wilson, L. Cronin, Angew. Chem. Int. Ed. 2009, 48, 4376-4380.
- 14. J. M. Cameron, J. Gao, D.-L. Long, L. Cronin, Inorg. Chem. Front. 2014, 1, 178-185.
- W.-C. Chen, S.-T. Wu, C. Qin, X.-L. Wang, K.-Z. Shao, Z.-M. Su, E.-B. Wang, *Dalton Trans*.
 2018, 47, 16403–16407.
- 16. Q. Han, Y. Wen, J.-C. Liu, W. Zhang, L.-J. Chen, J.-W. Zhao, *Inorg. Chem.* 2017, 56, 13228–13240.
- 17. Q. Han, J.-C. Liu, Y. Wen, L.-J. Chen, J.-W. Zhao, G.-Y. Yang, *Inorg. Chem.* 2017, 56, 7257–7269.
- B. Artetxe, S. Reinoso, L. San Felices, P. Vitoria, A. Pache, J. Martín-Caballero, J. M. Gutiérrez-Zorrilla, *Inorg. Chem.* 2015, 54, 241–252.
- 19. J. Lu, X. Ma, P. Wang, J. Feng, P. Ma, J. Niu, J. Wang, Dalton Trans. 2019, 48, 628-634.
- W.-C. Chen, H.-L. Li, X.-L. Wang, K.-Z. Shao, Z.-M. Su, E.-B. Wang, *Chem. Eur. J.* 2013, 19, 11007 11015
- 21. W.-C. Chen, C. Qin, X.-L. Wang, Y.-G. Li, H.-Y. Zang, K.-Z. Shao, Z.-M. Su, E.-B. Wang,

Dalton Trans. 2015, 44, 11290–11293.

- 22. J.-L. Liu, M.-T. Jin, L.-J. Chen, J.-W. Zhao, Inorg. Chem. 2018, 57, 12509–12520.
- C. Zhan, J. M. Cameron, J. Gao, J. W. Purcell, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* 2014, *53*, 10362–10366.
- 24. B. Kandasamy, B. S. Bassil, A. Haider, J. Beckmann, B. Chen, N. S. Dalal, U. Kortz, J. Organomet. Chem. 2015, 796, 33–38.