Supplementary Information

$(Me_2NH_2)_{10}[H_2$-DODECATUNGSTATE] POLYMORPHS: DODECATUNGSTATE CAGES EMBEDDED IN A VARIABLE DIMETHYLAMMONIUM CATION + WATER OF CRYSTALLIZATION MATRIX

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I. Materials and synthetic methods

Ammonium paratungstate, 40 % aq. dimethylamine solution, chloroform, bromoform, and other analytical reagents were obtained from Deuton-X Ltd., Hungary.
Monoclinic WO_3 precursor was prepared with heating of ammonium paratungstate ($(NH_4)_{10}(H_2W_{12}O_{42})$) at 600 °C (10 °C min^{-1} heating rate) keeping the temperature at 600 °C for 10 min^1. The freshly prepared monoclinic WO_3 (0.8 g) was dissolved in 40 ml of 40 % aq. dimethylamine solution and heated to 50 °C and the mixture was kept at this temperature for 2 h. The initial yellow color of the solution becomes colorless until 1.5 h. The solution was evaporated to 1.5 ml on a water bath, then the product was precipitated out with adding of 5 ml of ethanol. The white powdery material was washed with ethanol until odorless (amine) then dried in open air overnight. The white powder proved to be a single-phase product with the following elemental analysis results: C:H:N:W = 2.13:8.91:1.00:1.19
The reaction was repeated without heating when the solution becomes colorless only in 24 h, and the separation of the product was performed analogously.

II. Instrumental analyses

Elemental analysis

The carbon, hydrogen and nitrogen content were measured by a Fisons CHN101S type elemental analyzer. The tungsten content was determined with atomic emission spectroscopy. A Spectro Genesis ICP-OES (SPECTRO Analytical Instruments GmbH, Kleve, Germany) simultaneous spectrometer with axial plasma observation was used. Standard solutions for ICP (Merck Chemicals GmbH, Darmstadt, Germany) was used for calibration.

Density measurements

Pycnometric density measurements were done in $CHCl_3$:$CHBr_3$ 1:1 (v/v) mixture at 25 °C (the density of the title compound is less than the density of bromoform used, thus the compound 1T did not sink in bromoform) and was found to be 3.0678 g cm^{-3}.

Powder X-ray diffractometry

X-ray powder diffraction measurements were performed using a Philips PW-1050 Bragg-Brentano parafocusing goniometer. It was equipped with a Cu tube operated at 40 kV and 35 mA tube current, a secondary beam graphite monochromator and a proportional counter. Scans were recorded in step mode. Evaluation of the diffraction patterns had been obtained by full profile fitting techniques.

Thermal studies

Thermal data in air were collected using TA Instruments SDT Q600 thermal analyzer coupled to Hiden Analytical HPR-20/QIC mass spectrometer. The decomposition was followed from room temperature to 700 °C at 20 °C min^{-1} heating rate in air as carrier gas (flow rate = 50 cm^3 min^{-1}). Sample holder / reference: alumina crucible / empty alumina crucible. Sample mass ~ 7 mg. Selected ions between m/z = 1–120 were monitored in Multiple Ion Detection Mode (MID).

Simultaneous thermogravimetric, differential scanning calorimetric and mass spectrometric evolved gas analysis (TG-DSC-MS) measurements under inert conditions were performed on a Setaram LabsysEvo thermal analyzer, in high purity helium (6.0) atmosphere, with a flow rate of 90 mL min^{-1}. The measurements were recorded in the 25–700 °C temperature range, with a heating rate of 20 °C min^{-1}, samples were weighed into 100 µL alumina crucibles. The obtained data was baseline corrected and further evaluated by the thermoanalyzer's processing software (Calisto Processing, ver. 2.01). Parallel with the TG-DSC measurement, the analysis of the evolved gases/decomposition products were carried out on a Pfeiffer Vacuum OmniStar™ quadrupole mass spectrometer coupled to the above-described TGA. The gas splitters and transfer lines to the spectrometer were thermostated to 220 °C. The measurements were taken in SEM Bargraph Cycles acquisition mode, in which the total ion current (TIC), the analog bar graph spectra (for structure determination), and the separate ion current of each scanned individual mass (96 masses) was recorded. The scanned mass interval was 5–100 amu, with a scan speed of 20 ms amu-1, and the spectrometer was operated in electron impact mode.

FT-IR spectroscopy

FTIR measurements were recorded on a Jasco FT/IR-4600 system, equipped with a Jasco ATR Pro One single reflection diamond ATR accessory (incident angle 45°), and a DLATGS detector in the 4000-400 cm-1 region. A resolution of 4 cm^{-1} and co-addition of 64 individual spectra were applied. Prior to the evaluation, an ATR correction (Jasco Spectra Manager version 2, Spectra analysis module version 2.15.11) was performed on the raw spectra.

Far-IR spectra were recorded on a BioRad-Digilab FTS-60A spectrometer with 6.25 Mylar beamsplitter equipped with Pike GladiATR accessory with diamond ATR crystal for the 700-40 cm^{-1} range in nujol mull.

Raman spectroscopy

The Raman measurements were performed using a Horiba Jobin-Yvon LabRAM-type microspectrometer with an external 532 nm Nd-YAG (~40mW) or 785 diode laser (~50mW) source and an Olympus BX-40 optical microscope. The laser beam was focused by an objective of 20× (NA=0.4). The confocal hole of 1000 µm and grating monochromators of 1800 and 950 groove mm^{-1}, for excitation wavelengths of 532 and 785 nm, respectively, were used in a confocal system and for light dispersion. In the case of 532 nm excitation the spectral range of 100-4000 cm^{-1} was scanned with 3 cm^{-1} resolution with data accumulation time 3 s per point. In the case of 785 nm excitation the corresponding numbers are 100 and 2400 cm^{-1} for the spectral range, 5 cm^{-1} for the resolution and 15 s for the exposure time.

Single crystal diffraction measurements

The diffraction measurement was performed using MoKα radiation. Intensity data were collected on a RIGAKU RAXIS-RAPID diffractometer equipped with graphite monochromator. A numerical absorption correction was applied to the data. The structure was solved by charge flipping method. Non-hydrogen atomic positions have been refined by anisotropic full-matrix least-squares refinement. Hydrogen atomic positions were calculated from assumed geometries. The water hydrogen positions could not be determined. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to. Unusually large residual electron densities were calculated in the proximity of the tungsten atoms. The structures were solved by charge flipping method.

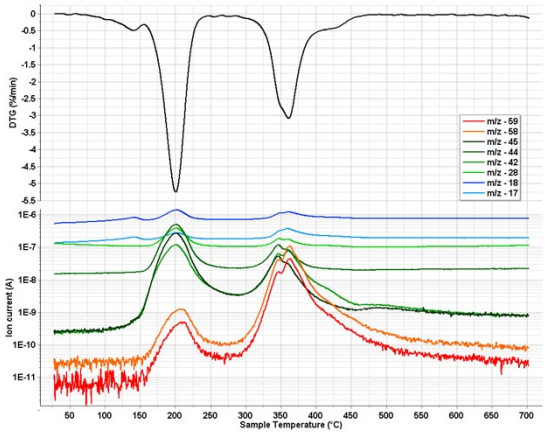
Conductivity measurements

Conductivity measurements were done in bidistilled water as solvent with using a Jenway 4510 instrument and temperature correction.

III. Determination of the water content

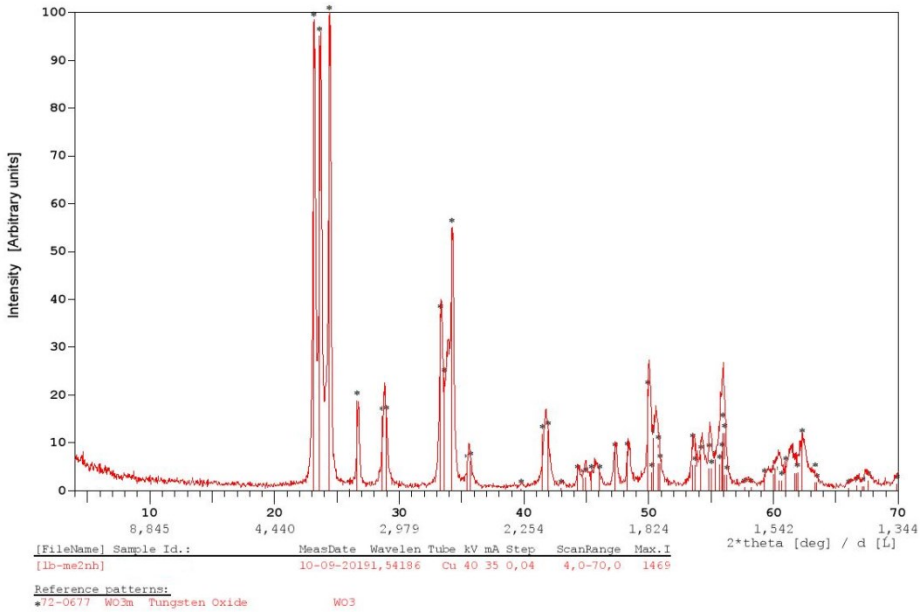
TG method

The TG-MS analysis method, which has been used efficiently for the determination of the amount of crystallization water in other metal polytungstates[2] can be applied when during the heating of the crystals, the crystallization water molecules leave the structure before any other decomposition takes place. Our TG-MS measurements on compound **1T** revealed that this condition is not met, because the amine molecules start to leave before all crystallization water molecules are removed. Therefore, the overall weight loss in this temperature range cannot be separated into contributions from pure H_2O and pure Me_2NH release, and the number of evolved water molecules cannot be calculated. (SI Figure 1).



SI Figure 1. Comparison of water (m/z=18,17) and dimethylamine (m/z=45, 44) and their condensation/oxidation products (m/z=59,58) evolution during thermal decomposition of compound **1T** in air

Then, if the thermal decomposition product definitely does not contain any water, from the total weight loss and the known amount of the other volatile components one can calculate the contribution from crystallization water. To this end we performed the TG-MS analysis for compounds **1T** and **2T** in various atmospheres and identified the intermediates and the final decomposition product by XRD. The thermal decomposition products are tungsten bronzes[3] in inert atmosphere, however, pure WO_3, (with no tungsten bronze formation) was found in air atmosphere which means that all hydrogen- and nitrogen-containing constituents have been removed.



SI Figure 2. XRD of the thermal decomposition product of compound **1T** in air (identified by ICCD-72-0677 card).

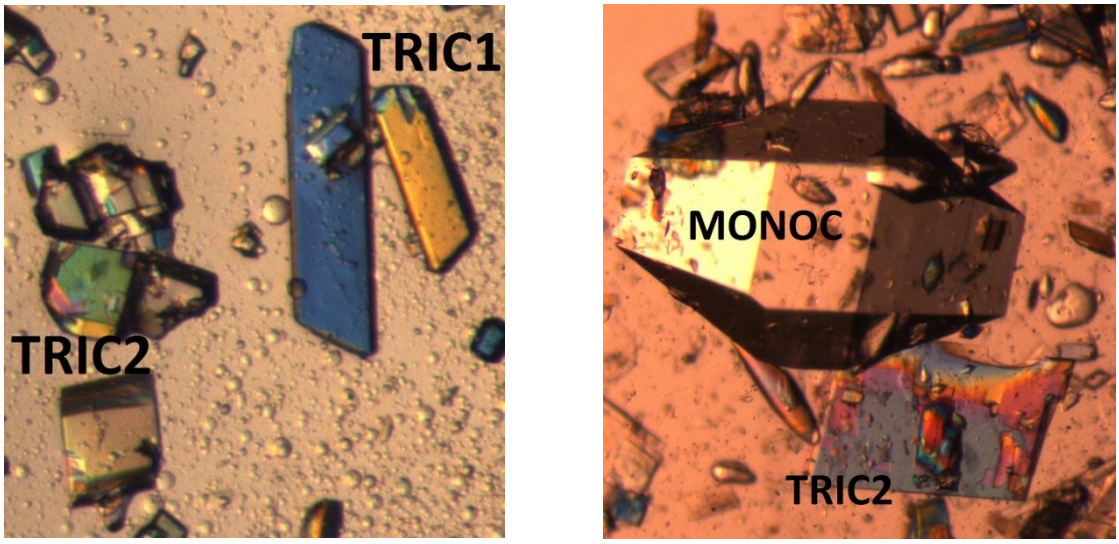
From the formula of the anhydrous salt, $(Me_2NH_2)_{10}[H_2W_{12}O_{42}]$ one can calculate the mass of its volatile constituents as the sum of the masses of 10 Me_2NH as well as the structural H_2O embedded in the dodecatungstate cage (one molecule per dodecatungstate cage). This method gave the presence of 10 and 11 mols of crystallization water for the compounds **1T** and **2T**, respectively. Compound **1M** has too small amount to perform this experiment.

Powder XRD-pycnometric method

An indirect way of estimating the number of crystallization water molecules in the comparison of the pycnometric density with the theoretical value obtained from the cell volume. The latter can be determined relatively easily by powder X-ray diffraction. The former refers to the actual mass of the hydrated compound in unit volume, while the density of the unit cell is calculated from the mass of the number of molecules (Z) of the anhydrous salt in the cell volume. (About Z the powder X-ray diffraction does not provide direct information.) From the difference the mass of the crystallization water molecules per volume can be calculated. The measured pycnometric density of the hydrated compound **1T** is d=3.0678 g cm^{-3} at 25 °C. The cell volume determined by powder X-ray diffraction is V=1916±16 $Å^3$ at 25 °C (triclinic, a=11.2081, b=11.3835, c=16.8441 Å, α=96.626, β=103.057 and γ=110.504°. The theoretical density of the anhydrous salt depends on Z. Assuming the reasonable options, Z=1 or 2, one obtains (average) 2.9077 and 5.8154 g cm^{-3}, respectively. Obviously, the former matches the pycnometric density, and from their difference one obtains n=10.21+/-0.82. This value and the n=9.62 obtained by TG-MS bracket the integer n=10. Accordingly, the formula of the hydrated salt is $(Me_2NH_2)_{10}H_2W_{12}O_{42}.10H_2O$.

IV. Single crystal data and characterization

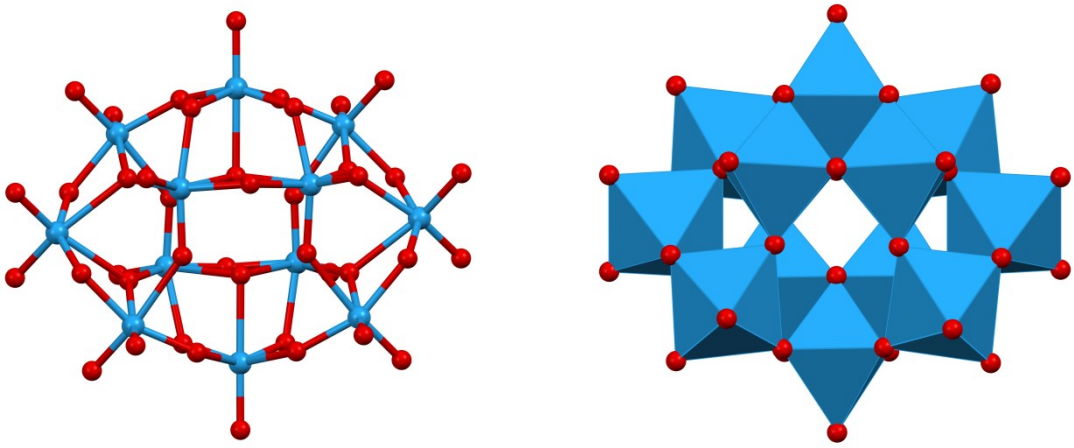
Three crystal forms of decakis(dimethylammonium) dihydrododecatungstate hydrate $[H_2W_{12}O_{42}](NH_2(CH_3)_2)_{10}.xH_2O$ were crystallized from water or ethanol solvents. Different crystal forms were present in the samples (SI Figure 3). The three crystal forms are denoted by TRIC1 **(1T)**, TRIC 2 **(2T)** and MONOC (**1M)**. The crystal properties of the three modifications are listed in SI Table 1.



SI Figure 3. Crystal habits of the different crystal forms of $[H_2W_{12}O_{42}](NH_2(CH_3)_2)_{10}.xH_2O$

SI Table 1. Characteristics of the three different crystal forms **TRIC1**, **TRIC2**, and **MONOC**

Form	**Habit**	**Colour**	**Solvent**	**Water cont.**
TRIC1	needle	colourless	96 % ethanol	10
TRIC2	platelet	colourless	water	11
MONOC	prism	colourless	96 % ethanol	10



SI Figure 4. Molecular structure of $[H_2W_{12}O_{42}]^{10-}$ polyanion in compoiund 1T, 2T and 1M, ball and stick and polyhedral representations (tungsten: light blue, oxygen: red).

Crystal structure of 1T[4]

Colourless single crystals of **1T** were grown from 96 % ethanol solvent by slow evaporation. A single crystal with the size of 0.2 x 0.4 x 0.5 mm has been mounted on a loop and measured by single crystal X-ray diffraction method at -123 °C using MoK_α radiation. A numerical absorption correction was applied to the data. The structure was solved by charge flipping method. The non-hydrogen atomic positions have been refined by anisotropic full-matrix least-squares refinement except the N1, N5 and N6 atomic positions which have been refined by isotropic full-matrix least-squares refinement. Hydrogen atomic positions of the dimethylammonium cations were calculated from assumed geometries. Hydrogens could not be generated in the cases of the water molecules and the disordered ammonium ions. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. Unusually large residual electron densities were calculated in the proximity of the tungsten atoms. The final R factor is 8.11 %. Crystal data and details of structure determination and refinement are listed in Table 2, atomic coordinates and equivalent isotropic displacement parameters in Table 3, hydrogen coordinates and equivalent isotropic displacement parameters in Table 4, anisotropic displacement parameters in Table 5, bond lengths and angles, respectively in Table 6 and 7, as well the intermolecular interactions are listed in Table 8 and 9.

SI Table 2. Crystal data and structure refinement of **1T**

Label	**1T**
Empirical formula	C20 H64 N10 O52 W12
Formula weight	3483.01
Temperature	150(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å
Crystal system	triclinic
Space group	*P* -1
Unit cell dimensions	*a* =11.4037(5)Å
	b =13.7428(7)Å
	c =13.9665(8)Å
	α =63.686(4)°
	β =79.005(6)°
	γ =69.227(5)°
Volume	1832.99(18)Å^3
Z	1
Density (calculated)	3.155 Mg/m^3
Absorption coefficient, μ	18.841 mm^{-1}
F(000)	1558
Crystal colour	colorless
Crystal description	needle
Crystal size	0.51 x 0.42 x 0.21 mm
Absorption correction	numerical
Max. and min. transmission	0.0150.207
θ–range for data collection	2.999 ≤ θ ≤ 30.507°
Index ranges	-16 ≤ *h* ≤16;-19≤ *k* ≤19;-19 ≤ *l* ≤19
Reflections collected	77800
Completeness to 2θ	0.998
Independent reflections	11156 [*R*(int) =0.1174]
Reflections *I*>2σ(*I*)	10975
Refinement method	full-matrix least-squares on *F*2
Data / restraints / parameters	11156 /355 /441
Goodness-of-fit on *F*2	1.392
Final *R* indices [*I*>2σ(*I*)]	*R*1 =0.0813, *wR*2 =0.1724
R indices (all data)	*R*1 =0.0832, *wR*2 =0.1732
Max. and mean shift/esd	0.001;0.000
Largest diff. peak and hole	6.140;-5.441 e.Å^{-3}

SI Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3). *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor of **1T**

	x	*y*	*z*	*U*(eq)
W1	10705.8(5)	580.2(5)	1471.1(5)	12(1)
W2	11785.8(5)	1988.3(5)	-987.1(5)	12(1)
W3	8196.2(6)	-804.8(5)	2896.3(5)	15(1)
W4	7329.0(6)	2015.4(5)	1973.4(5)	16(1)
W5	8472.8(5)	3307.7(5)	-430.2(5)	15(1)
W6	12651.8(5)	-857.1(5)	45.7(5)	11(1)
O1	9932(10)	-504(9)	1948(8)	13(1)
O2	10979(10)	652(10)	2607(9)	18(2)
O3	9196(10)	1823(9)	1003(9)	14(1)
O4	11532(9)	1800(9)	430(9)	13(1)
O5	9992(10)	2895(9)	-1180(9)	15(1)
O6	12490(10)	3053(9)	-1572(10)	17(2)
O7	11546(10)	1812(9)	-2239(9)	14(1)
O8	13133(9)	673(9)	-678(9)	13(1)
O9	10895(9)	558(8)	-197(8)	11(1)
O10	12317(9)	-451(8)	1289(8)	12(1)
O11	8107(10)	1906(9)	-664(9)	16(2)
O12	14223(10)	-1627(10)	299(10)	21(2)
O13	7478(10)	634(9)	1371(9)	15(1)
O14	9128(11)	-1761(10)	3979(10)	22(2)
O15	6677(11)	-782(10)	3442(10)	20(2)
O16	8170(10)	582(9)	3000(9)	15(1)
O17	5764(11)	2116(11)	2411(11)	24(2)
O18	7711(11)	2831(10)	2470(10)	20(2)
O19	7014(10)	3080(9)	523(9)	16(1)
O20	8812(11)	4154(9)	31(10)	18(2)
O21	7523(10)	4316(9)	-1509(10)	18(2)
N5	4980(60)	-420(50)	5420(50)	75(8)a
C9	5710(40)	610(30)	5040(30)	75(8)
C10	9360(30)	990(20)	4840(30)	58(6)
N1	5478(15)	400(13)	8299(13)	26(3)
C1	5783(18)	-643(15)	8078(15)	26(3)
C2	5260(20)	1460(17)	7342(18)	34(4)
N2	1041(19)	6848(15)	3114(16)	39(4)
C3	780(20)	5780(20)	3757(19)	44(5)
C4	2220(20)	6924(19)	3300(20)	45(6)
N3	4995(17)	6110(15)	923(14)	32(3)
C5	5500(20)	5445(18)	1967(17)	33(3)
C6	5960(20)	5980(20)	30(18)	38(4)
N4	84(17)	3399(15)	1960(20)	45(5)
C7	-630(30)	4410(20)	2130(20)	56(8)
C8	1350(20)	3290(20)	1560(30)	47(6)
O1W	3580(15)	3518(13)	3001(11)	40(4)
O2W	4420(20)	3720(20)	4690(18)	72(7)
O3W	2676(18)	4459(15)	6114(13)	48(4)
O4W	6935(16)	3508(15)	4204(13)	44(4)
O5W	2040(70)	2110(40)	4000(20)	240(30)

Site occupation factors:
a: 0.5

SI Table 4 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) of **1T**

	x	*y*	*z*	*U*(iso)
H1A	4797	435	8733	31
H1B	6110	328	8639	31
H1C	5085	-596	7753	39
H1D	5949	-1312	8737	39
H1E	6511	-683	7603	39
H2A	5943	1392	6831	51
H2B	5202	2072	7524	51
H2C	4491	1615	7040	51
H2D	412	7401	3226	46
H2E	1043	6982	2429	46
H3C	1237	5235	3455	66
H3D	-100	5894	3771	66
H3E	1042	5490	4472	66
H4C	2237	6792	4033	67
H4D	2294	7670	2844	67
H4E	2917	6360	3143	67
H3A	4699	6842	816	38
H3B	4355	5897	895	38
H5A	5841	4656	2081	50
H5B	4848	5527	2498	50
H5C	6154	5705	2021	50
H6A	6647	6221	50	58
H6B	5573	6451	-648	58
H6C	6261	5200	127	58
H4A	94	2800	2579	54
H4B	-326	3351	1508	54
H7A	-1033	4194	2833	83
H7B	-1260	4876	1605	83
H7C	-85	4825	2075	83
H8A	1365	3919	876	71
H8B	1714	2588	1476	71
H8C	1824	3307	2049	71

SI Table 5. Anisotropic displacement parameters (Å^2 x 10^3) of **1T**. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	10(1)	13(1)	15(1)	-9(1)	0(1)	-3(1)
W2	10(1)	12(1)	17(1)	-8(1)	1(1)	-3(1)
W3	17(1)	18(1)	14(1)	-9(1)	3(1)	-8(1)
W4	13(1)	19(1)	23(1)	-15(1)	4(1)	-4(1)
W5	10(1)	11(1)	24(1)	-10(1)	0(1)	-1(1)
W6	8(1)	11(1)	16(1)	-8(1)	-1(1)	-1(1)
O1	11(1)	14(1)	15(2)	-8(1)	0(1)	-3(1)
O2	12(4)	31(5)	19(2)	-17(3)	2(2)	-8(3)
O3	11(1)	14(1)	18(1)	-9(1)	2(1)	-2(1)
O4	11(2)	13(1)	19(1)	-10(1)	-1(1)	-4(1)
O5	11(1)	12(1)	20(1)	-7(1)	0(1)	-1(1)
O6	16(3)	15(2)	25(3)	-11(3)	4(4)	-8(2)
O7	11(2)	13(2)	16(1)	-7(1)	0(1)	-3(2)
O8	10(1)	13(1)	17(2)	-8(1)	0(1)	-3(1)
O9	8(2)	11(2)	15(2)	-8(2)	-1(2)	-2(1)
O10	10(1)	13(1)	15(1)	-8(1)	-1(1)	-2(1)
O11	13(4)	15(3)	22(4)	-11(3)	0(3)	-3(3)
O12	12(3)	16(3)	27(6)	-11(4)	-1(3)	6(3)
O13	13(3)	14(2)	22(3)	-11(1)	-5(3)	0(2)
O14	21(4)	21(2)	18(3)	-3(3)	2(2)	-7(3)
O15	17(3)	27(5)	27(4)	-19(4)	6(3)	-12(3)
O16	16(1)	19(1)	18(1)	-13(1)	4(1)	-8(1)
O17	14(2)	32(5)	31(4)	-22(3)	9(2)	-6(2)
O18	24(5)	19(3)	22(4)	-15(3)	4(3)	-8(4)
O19	11(1)	15(1)	24(1)	-12(1)	1(1)	-3(1)
O20	17(4)	17(3)	26(5)	-12(3)	3(3)	-7(3)
O21	8(3)	15(3)	27(2)	-6(2)	-1(2)	-3(2)
N5	75(8)	75(8)	75(8)	-31(3)	-3(2)	-23(3)
C9	75(8)	75(8)	75(8)	-31(4)	-2(2)	-23(3)
N6	73(15)	49(12)	71(15)	-31(12)	-20(13)	-26(11)
C10	74(15)	49(12)	72(15)	-31(12)	-20(13)	-26(11)
N1	25(3)	27(3)	25(3)	-13(2)	1(2)	-6(2)
C1	25(8)	26(5)	26(8)	-12(6)	-2(7)	-5(7)
C2	30(9)	26(5)	40(8)	-7(4)	-8(8)	-7(7)
N2	43(9)	31(8)	38(10)	-2(7)	-20(8)	-13(7)
C3	42(12)	45(11)	36(11)	-3(9)	2(10)	-24(9)
C4	40(11)	29(10)	53(14)	2(10)	-24(10)	-11(8)
N3	32(3)	31(3)	33(3)	-13(2)	-2(2)	-9(2)
C5	32(5)	31(5)	34(3)	-12(3)	-2(3)	-8(3)
C6	38(5)	40(5)	36(4)	-18(4)	-1(3)	-6(3)
N4	28(7)	27(8)	78(15)	-16(9)	-9(8)	-10(7)
C7	54(12)	73(15)	79(18)	-61(15)	47(14)	-49(11)
C8	36(9)	42(12)	90(10)	-46(13)	5(10)	-19(9)
O1W	41(8)	36(8)	18(6)	-5(6)	0(6)	6(7)
O2W	71(14)	109(19)	54(13)	-56(14)	4(11)	-21(14)
O3W	56(11)	47(9)	26(8)	-9(7)	-6(7)	-6(8)
O4W	43(9)	49(9)	37(9)	-27(8)	-5(7)	1(7)
O5W	5800(10)	180(30)	58(18)	-80(10)	150(30)	-260(60)

SI Table 6. Bond lengths (Å) and angles (°) of **1T**

W1-O2	1.72(1)	W1-O1	1.81(1)
W1-O3	1.91(1)	W1-O10	1.93(1)
W1-O4	2.06(1)	W1-O9	2.31(1)
W2-O6	1.73(1)	W2-O8	1.85(1)
W2-O4	1.86(1)	W2-O7	1.95(1)
W2-O5	1.98(1)	W2-O9	2.28(1)
W3-O14	1.73(1)	W3-O15	1.75(1)
W3-O7#1	1.89(1)	W3-O16	1.96(1)
W3-O13	2.21(1)	W3-O1	2.22(1)
W4-O17	1.75(1)	W4-O18	1.75(1)
W4-O16	1.88(1)	W4-O19	1.91(1)
W4-O3	2.29(1)	W4-O13	2.34(1)
W5-O20	1.73(1)	W5-O21	1.75(1)
W5-O5	1.89(1)	W5-O19	1.95(1)
W5-O3	2.16(1)	W5-O11	2.27(1)
W6-O12	1.74(1)	W6-O11#1	1.75(1)
W6-O13#1	1.89(1)	W6-O10	1.98(1)
W6-O8	2.11(1)	W6-O9	2.195(9)
N5-N5#2	1.2(1)	N5-C9#2	1.26(7)
N5-C9	1.73(8)	N6-C10	1.41(6)
N6-N6#3	1.44(9)	N6-C10#3	1.45(5)
N1-C2	1.45(2)	N1-C1	1.51(2)
N2-C3	1.45(3)	N2-C4	1.47(3)
N3-C5	1.44(3)	N3-C6	1.52(3)
N4-C8	1.43(3)	N4-C7	1.44(3)

O2-W1-O1	105.0(5)	O2-W1-O3	101.6(5)
O1-W1-O3	94.3(5)	O2-W1-O10	99.2(5)
O1-W1-O10	93.0(4)	O3-W1-O10	155.4(4)
O2-W1-O4	95.1(5)	O1-W1-O4	159.9(4)
O3-W1-O4	82.6(4)	O10-W1-O4	82.6(4)
O2-W1-O9	163.6(4)	O1-W1-O9	88.0(4)
O3-W1-O9	87.0(4)	O10-W1-O9	69.8(4)
O4-W1-O9	72.1(4)	O6-W2-O8	103.1(5)
O6-W2-O4	103.1(5)	O8-W2-O4	92.6(5)
O6-W2-O7	100.8(5)	O8-W2-O7	88.0(4)
O4-W2-O7	155.3(4)	O6-W2-O5	101.1(5)
O8-W2-O5	155.2(4)	O4-W2-O5	87.4(4)
O7-W2-O5	81.9(4)	O6-W2-O9	178.8(5)
O8-W2-O9	75.8(4)	O4-W2-O9	76.5(4)
O7-W2-O9	79.7(4)	O5-W2-O9	80.1(4)
O14-W3-O15	102.9(6)	O14-W3-O7#1	97.2(5)
O15-W3-O7#1	99.3(5)	O14-W3-O16	96.3(5)
O15-W3-O16	95.9(5)	O7#1-W3-O16	156.9(5)
O14-W3-O13	162.8(5)	O15-W3-O13	92.1(5)
O7#1-W3-O13	88.5(4)	O16-W3-O13	73.6(4)
O14-W3-O1	87.9(5)	O15-W3-O1	168.5(5)
O7#1-W3-O1	82.9(4)	O16-W3-O1	78.9(4)
O13-W3-O1	76.7(4)	O17-W4-O18	103.7(6)
O17-W4-O16	101.1(6)	O18-W4-O16	96.4(5)

O17-W4-O19	97.2(5)	O18-W4-O19	100.5(5)
O16-W4-O19	151.3(4)	O17-W4-O3	163.1(5)
O18-W4-O3	91.3(5)	O16-W4-O3	84.8(4)
O19-W4-O3	71.9(4)	O17-W4-O13	91.8(5)
O18-W4-O13	162.4(5)	O16-W4-O13	72.1(4)
O19-W4-O13	85.5(4)	O3-W4-O13	74.8(4)
O20-W5-O21	102.5(5)	O20-W5-O5	100.4(5)
O21-W5-O5	99.8(5)	O20-W5-O19	96.6(5)
O21-W5-O19	91.8(5)	O5-W5-O19	156.7(4)
O20-W5-O3	90.1(5)	O21-W5-O3	162.3(5)
O5-W5-O3	89.9(4)	O19-W5-O3	74.3(4)
O20-W5-O11	167.5(5)	O21-W5-O11	88.8(5)
O5-W5-O11	82.5(4)	O19-W5-O11	77.6(4)
O3-W5-O11	77.7(4)	O12-W6-O11#1	103.4(5)
O12-W6-O13#1	103.2(5)	O11#1-W6-O13#1	96.2(5)
O12-W6-O10	95.4(5)	O11#1-W6-O10	93.2(5)
O13#1-W6-O10	156.6(4)	O12-W6-O8	89.6(5)
O11#1-W6-O8	166.3(4)	O13#1-W6-O8	84.9(4)
O10-W6-O8	81.0(4)	O12-W6-O9	159.2(5)
O11#1-W6-O9	93.7(4)	O13#1-W6-O9	86.4(4)
O10-W6-O9	71.6(4)	O8-W6-O9	72.7(4)
W1-O1-W3	137.2(5)	W1-O3-W5	139.0(6)
W1-O3-W4	125.5(5)	W5-O3-W4	95.2(4)
W2-O4-W1	117.5(5)	W5-O5-W2	143.1(6)
W3#1-O7-W2	147.0(6)	W2-O8-W6	114.9(5)
W6-O9-W2	96.6(4)	W6-O9-W1	97.5(4)
W2-O9-W1	93.9(4)	W1-O10-W6	119.8(5)
W6#1-O11-W5	141.5(6)	W6#1-O13-W3	137.7(5)
W6#1-O13-W4	127.4(5)	W3-O13-W4	93.5(4)
W4-O16-W3	119.3(6)	W4-O19-W5	116.9(5)
N5#2-N5-C9#2	88(7)	N5#2-N5-C9	47(5)
C9#2-N5-C9	134(5)	N5#2-C9-N5	46(5)
C10-N6-N6#3	61(4)	C10-N6-C10#3	120(3)
N6#3-N6-C10#3	58(3)	N6-C10-N6#3	60(3)
C2-N1-C1	114(2)	C3-N2-C4	116(2)
C5-N3-C6	113(2)	C8-N4-C7	118(2)

Symmetry codes to generate equivalent atoms:

1. [2_755] -x+2,-y,-z
2. [2_656] -x+1,-y,-z+1
3. [2_756] -x+2,-y,-z+1

W1-O2	1.72(1)	W1-O1	1.81(1)
W1-O3	1.91(1)	W1-O10	1.93(1)
W1-O4	2.06(1)	W1-O9	2.31(1)
W2-O6	1.73(1)	W2-O8	1.85(1)
W2-O4	1.86(1)	W2-O7	1.95(1)
W2-O5	1.98(1)	W2-O9	2.28(1)
W3-O14	1.73(1)	W3-O15	1.75(1)
W3-O7#1	1.89(1)	W3-O16	1.96(1)

W3-O13	2.21(1)	W3-O1	2.22(1)
W4-O17	1.75(1)	W4-O18	1.75(1)
W4-O16	1.88(1)	W4-O19	1.91(1)
W4-O3	2.29(1)	W4-O13	2.34(1)
W5-O20	1.73(1)	W5-O21	1.75(1)
W5-O5	1.89(1)	W5-O19	1.95(1)
W5-O3	2.16(1)	W5-O11	2.27(1)
W6-O12	1.74(1)	W6-O11#1	1.75(1)
W6-O13#1	1.89(1)	W6-O10	1.98(1)
W6-O8	2.11(1)	W6-O9	2.195(9)
N5-N5#2	1.2(1)	N5-C9#2	1.26(7)
N5-C9	1.73(8)	N6-C10	1.41(6)
N6-N6#3	1.44(9)	N6-C10#3	1.45(5)
N1-C2	1.45(2)	N1-C1	1.51(2)
N2-C3	1.45(3)	N2-C4	1.47(3)
N3-C5	1.44(3)	N3-C6	1.52(3)
N4-C8	1.43(3)	N4-C7	1.44(3)

O2-W1-O1	105.0(5)	O2-W1-O3	101.6(5)
O1-W1-O3	94.3(5)	O2-W1-O10	99.2(5)
O1-W1-O10	93.0(4)	O3-W1-O10	155.4(4)
O2-W1-O4	95.1(5)	O1-W1-O4	159.9(4)
O3-W1-O4	82.6(4)	O10-W1-O4	82.6(4)
O2-W1-O9	163.6(4)	O1-W1-O9	88.0(4)
O3-W1-O9	87.0(4)	O10-W1-O9	69.8(4)
O4-W1-O9	72.1(4)	O6-W2-O8	103.1(5)
O6-W2-O4	103.1(5)	O8-W2-O4	92.6(5)
O6-W2-O7	100.8(5)	O8-W2-O7	88.0(4)
O4-W2-O7	155.3(4)	O6-W2-O5	101.1(5)
O8-W2-O5	155.2(4)	O4-W2-O5	87.4(4)
O7-W2-O5	81.9(4)	O6-W2-O9	178.8(5)
O8-W2-O9	75.8(4)	O4-W2-O9	76.5(4)
O7-W2-O9	79.7(4)	O5-W2-O9	80.1(4)
O14-W3-O15	102.9(6)	O14-W3-O7#1	97.2(5)
O15-W3-O7#1	99.3(5)	O14-W3-O16	96.3(5)
O15-W3-O16	95.9(5)	O7#1-W3-O16	156.9(5)
O14-W3-O13	162.8(5)	O15-W3-O13	92.1(5)
O7#1-W3-O13	88.5(4)	O16-W3-O13	73.6(4)
O14-W3-O1	87.9(5)	O15-W3-O1	168.5(5)
O7#1-W3-O1	82.9(4)	O16-W3-O1	78.9(4)

O13-W3-O1	76.7(4)	O17-W4-O18	103.7(6)
O17-W4-O16	101.1(6)	O18-W4-O16	96.4(5)
O17-W4-O19	97.2(5)	O18-W4-O19	100.5(5)
O16-W4-O19	151.3(4)	O17-W4-O3	163.1(5)
O18-W4-O3	91.3(5)	O16-W4-O3	84.8(4)
O19-W4-O3	71.9(4)	O17-W4-O13	91.8(5)
O18-W4-O13	162.4(5)	O16-W4-O13	72.1(4)
O19-W4-O13	85.5(4)	O3-W4-O13	74.8(4)
O20-W5-O21	102.5(5)	O20-W5-O5	100.4(5)
O21-W5-O5	99.8(5)	O20-W5-O19	96.6(5)
O21-W5-O19	91.8(5)	O5-W5-O19	156.7(4)
O20-W5-O3	90.1(5)	O21-W5-O3	162.3(5)
O5-W5-O3	89.9(4)	O19-W5-O3	74.3(4)
O20-W5-O11	167.5(5)	O21-W5-O11	88.8(5)
O5-W5-O11	82.5(4)	O19-W5-O11	77.6(4)
O3-W5-O11	77.7(4)	O12-W6-O11#1	103.4(5)
O12-W6-O13#1	103.2(5)	O11#1-W6-O13#1	96.2(5)
O12-W6-O10	95.4(5)	O11#1-W6-O10	93.2(5)
O13#1-W6-O10	156.6(4)	O12-W6-O8	89.6(5)
O11#1-W6-O8	166.3(4)	O13#1-W6-O8	84.9(4)
O10-W6-O8	81.0(4)	O12-W6-O9	159.2(5)
O11#1-W6-O9	93.7(4)	O13#1-W6-O9	86.4(4)
O10-W6-O9	71.6(4)	O8-W6-O9	72.7(4)
W1-O1-W3	137.2(5)	W1-O3-W5	139.0(6)
W1-O3-W4	125.5(5)	W5-O3-W4	95.2(4)
W2-O4-W1	117.5(5)	W5-O5-W2	143.1(6)
W3#1-O7-W2	147.0(6)	W2-O8-W6	114.9(5)
W6-O9-W2	96.6(4)	W6-O9-W1	97.5(4)
W2-O9-W1	93.9(4)	W1-O10-W6	119.8(5)
W6#1-O11-W5	141.5(6)	W6#1-O13-W3	137.7(5)
W6#1-O13-W4	127.4(5)	W3-O13-W4	93.5(4)
W4-O16-W3	119.3(6)	W4-O19-W5	116.9(5)
N5#2-N5-C9#2	88(7)	N5#2-N5-C9	47(5)
C9#2-N5-C9	134(5)	N5#2-C9-N5	46(5)
C10-N6-N6#3	61(4)	C10-N6-C10#3	120(3)
N6#3-N6-C10#3	58(3)	N6-C10-N6#3	60(3)
C2-N1-C1	114(2)	C3-N2-C4	116(2)
C5-N3-C6	113(2)	C8-N4-C7	118(2)

Symmetry codes to generate equivalent atoms:
1. [2_755] -x+2,-y,-z

2. [2_656] -x+1,-y,-z+1
3. [2_756] -x+2,-y,-z+1

SI Table 7. Torsion angles (°) of **TRIC1** (**1T**) to be deposited

O6-W2-O8-W6	179.2(6)	O4-W2-O8-W6	-76.7(6)
O7-W2-O8-W6	78.6(6)	O5-W2-O8-W6	13(1)
O9-W2-O8-W6	-1.3(5)	O17-W4-O16-W3	77.2(7)
O18-W4-O16-W3	-177.6(6)	O19-W4-O16-W3	-52(1)
O3#1-W4-O16-W3	-86.8(6)	O13-W4-O16-W3	-11.1(5)
O2-W1-O1-W3#1	-58.8(9)	O3-W1-O1-W3#1	44.4(9)
O10-W1-O1-W3#1	-159.2(8)	O4-W1-O1-W3#1	124(1)
O9-W1-O1-W3#1	131.3(8)	O12-W6-O11-W5	77(1)
O13-W6-O11-W5	-28(1)	O10-W6-O11-W5	173.4(9)
O8-W6-O11-W5	-122(2)	O9-W6-O11-W5	-114.9(9)
O14-W3-O7-W2	-171(1)	O15-W3-O7-W2	85(1)
O16-W3-O7-W2	-46(2)	O13-W3-O7-W2	-7(1)
O1#1-W3-O7-W2	-84(1)	O12-W6-O13-W3	128.8(9)
O11-W6-O13-W3	-125.8(9)	O10-W6-O13-W3	-12(2)
O8-W6-O13-W3	40.4(9)	O9-W6-O13-W3	-32.4(8)
O12-W6-O13-W4	-69.1(8)	O11-W6-O13-W4	36.3(7)
O10-W6-O13-W4	149.7(9)	O8-W6-O13-W4	-157.5(7)
O9-W6-O13-W4	129.6(7)	O6-W2-O4-W1	179.6(6)
O8-W2-O4-W1	75.5(6)	O7-W2-O4-W1	-16(1)
O5-W2-O4-W1	-79.7(6)	O9-W2-O4-W1	0.8(5)
N5#2-C9-N5-C9#2	0.001	N6#3-C10-N6-C10#3	-0.003

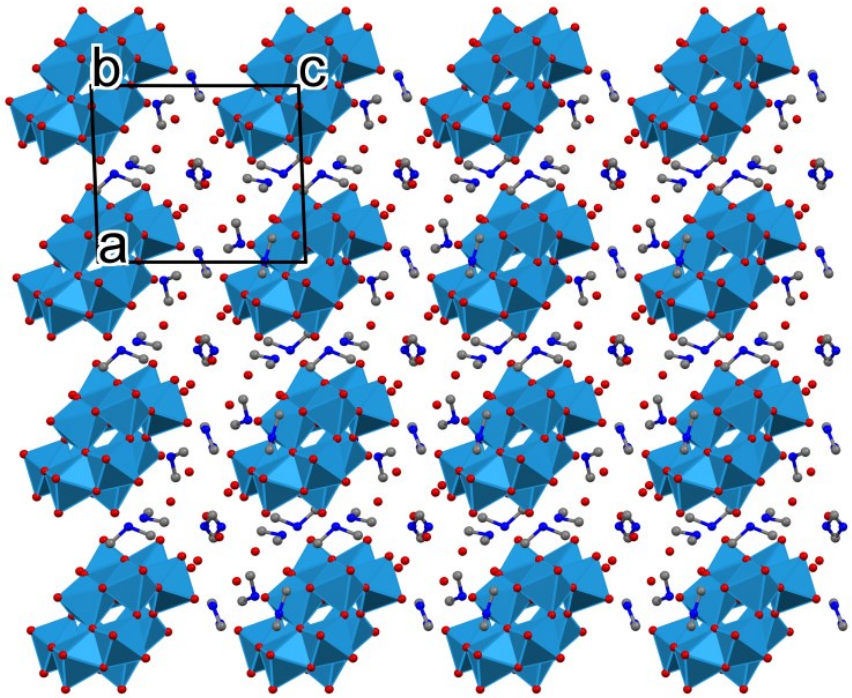
SI Table 8. Hydrogen bonds in **1T**

Hydrogen bonding and short inter contacts of the ammonium ions

SI Table 9. Summary of the shortest inter contacts with d(I-J) < R(I) + R(J) + 0.2 of the water molecules in compound **1T**

Nr	D-H...A		D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	sym op
1	O(1W)	.... O(2W)	-	-	2.87(3)	-	x,y,z
2	O(1W)	.... O(5W)	-	-	2.79(7)	-	x,y,z
3	O(1W)	.... O(17)	-	-	2.80(2)	-	x,y,z
4	O(1W)	.... O(21)	-	-	2.76(2)	-	1-x,1-y,-z
5	O(2W)	.... O(1W)	-	-	2.87(3)	-	x,y,z
6	O(2W)	.... O(3W)	-	-	2.79(3)	-	x,y,z
7	O(2W)	.... O(4W)	-	-	2.76(3)	-	x,y,z
8	O(3W)	.... O(2W)	-	-	2.79(3)	-	x,y,z
9	O(3W)	.... O(4W)	-	-	2.81(3)	-	1-x,1-y,1-z
10	O(3W)	.... O(6)	-	-	2.96(2)	-	1-x,-y,1-z
11	O(4W)	.... O(2W)	-	-	2.76(3)	-	x,y,z
12	O(4W)	.... O(18)	-	-	2.85(2)	-	x,y,z
13	O(4W)	.... O(3W)	-	-	2.81(3)	-	1-x,1-y,1-z
14	O(5W)	.... O(1W)	-	-	2.79(7)	-	x,y,z
15	O(5W)	.... W(3)	-	-	3.88(3)	-	1-x,-y,1-z
16	O(5W)	.... O(14)	-	-	2.79(4)	-	1-x,-y,1-z

1T crystallizes in the triclinic system, in the *P*-1 space group (Figure 3). The asymmetric unit contains one half of a dihydrododecatungstate(10-) anion, four entire and two half dimethylammonium cations (nitrogens disordered over two positions) and five water molecules. An inversion centre is situated at the centre of the $[H_2W_{12}O_{42}]^{10-}$ anion.



SI Figure 5. Packing of the **1T** form (view *b* axis)

Crystal structure of 2T[4]

Colourless single crystals of **2T** were grown from water solvent by slow evaporation. A single crystal with the size of 0.15 x 0.3 x 0.3 mm has been mounted on a loop and measured by single crystal X-ray diffraction method. The diffraction measurement was performed at -120 °C using MoK_α radiation. Intensity data were collected on a RIGAKU RAXIS-RAPID diffractometer equipped with graphite monochromator. A numerical absorption correction was applied to the data. The structure was solved by charge flipping method. Non-hydrogen atomic positions have been refined by anisotropic full-matrix least-squares refinement except the O1, O25 and O41 atomic positions which have been refined by isotropic full-matrix least-squares refinement. Hydrogen atomic positions were calculated from assumed geometries. The water hydrogen positions could not be determined. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. Unusually large residual electron densities were calculated in the proximity of the tungsten atoms. The final R factor is 6.88 %. Crystal data and details of structure determination and refinement are listed in Table 10, atomic coordinates and equivalent isotropic displacement parameters in Table 11, hydrogen coordinates and equivalent isotropic displacement parameters in Table 12, anisotropic displacement parameters in Table 13, bond lengths and angles, respectively in Table 14 and 15, as well the intermolecular interactions are listed in Table 16 and 17.

SI Table 10. Crystal data and structure refinement of **TRIC2 (2T)**

Label	**2T**
Empirical formula	C20 H80 N10 O53 W12
Formula weight	3515.14
Temperature	153(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å
Crystal system	triclinic
Space group	*P* -1
Unit cell dimensions	*a* =13.5917(3)Å *b* =16.6057(4)Å *c* =18.6449(4)Å α =90.344(6)° β =105.743(7)° γ =112.051(8)°
Volume	3726.5(3)Å^3
Z	2
Density (calculated)	3.133 Mg/m^3
Absorption coefficient, μ	18.538 mm^{-1}
F(000)	3164
Crystal colour	colorless
Crystal description	platelet
Crystal size	0.32 x 0.28 x 0.15 mm
Absorption correction	numerical
Max. and min. transmission	0.9980.999
θ–range for data collection	3.015 ≤ θ ≤ 30.491°
Index ranges	-19 ≤ *h* ≤19;-23≤ *k* ≤23;-26 ≤ *l* ≤25
Reflections collected	199047
Completeness to 2θ	0.998
Independent reflections	22666 [*R*(int) =0.1837]
Reflections *I*>2σ(*I*)	17352
Refinement method	full-matrix least-squares on *F*2
Data / restraints / parameters	22666 /663 /876
Goodness-of-fit on *F*2	1.142
Final *R* indices [*I*>2σ(*I*)]	*R*1 =0.0687, *wR*2 =0.1387
R indices (all data)	*R*1 =0.1038, *wR*2 =0.1505
Max. and mean shift/esd	0.001;0.000
Largest diff. peak and hole	4.215;-4.202 e.Å^{-3}

SI Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) of **2T** *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
W1	-1087.5(5)	592.5(3)	1673.7(3)	16(1)
W2	1579.4(5)	1162.1(3)	2525.4(3)	17(1)
W3	3051.3(5)	799.9(3)	1500.6(3)	16(1)
W4	-1702.1(5)	1264.5(3)	-221.5(3)	15(1)
W5	1018.3(5)	1786.3(3)	590.4(3)	13(1)
W6	147.8(5)	-963.0(3)	1235.9(3)	13(1)
O1	-2202(8)	-219(6)	1874(5)	21(1)
O2	-1035(9)	1552(6)	2120(5)	21(2)
O3	129(8)	474(5)	2477(4)	17(1)
O4	1696(9)	2149(6)	2954(5)	25(2)
O5	2191(9)	709(6)	3267(5)	23(2)
O6	2776(8)	1636(6)	2095(5)	18(1)
O7	4124(8)	1617(6)	1262(5)	21(1)
O8	3757(8)	407(6)	2261(5)	23(2)
O9	2714(8)	-89(5)	747(5)	17(1)
O10	-1829(8)	693(5)	673(4)	16(1)
O11	-2637(9)	1765(6)	-317(5)	22(2)
O12	-402(8)	2105(5)	360(4)	16(1)
O13	501(8)	1326(5)	1419(4)	15(1)
O14	1927(8)	2830(6)	987(5)	18(1)
O15	1870(8)	1183(5)	620(4)	15(1)
O16	881(8)	1954(5)	-466(4)	14(1)
O17	-450(7)	637(5)	-139(4)	13(1)
O18	-1291(8)	1481(5)	-1089(4)	15(1)
O19	1452(8)	52(5)	1671(4)	15(1)
O20	-810(8)	-434(5)	1094(4)	15(1)
O21	-21(9)	-1517(6)	2002(5)	20(2)
W7	8812.4(5)	6060.9(3)	4458.3(3)	14(1)
W8	11530.8(5)	7297.5(3)	4959.3(3)	16(1)
W9	6776.2(5)	3771.6(3)	3865.6(3)	18(1)
W10	7802.0(5)	4784.7(4)	2558.3(3)	20(1)
W11	10485.4(5)	6002.2(3)	3098.9(3)	17(1)
W12	10409.3(5)	6208.6(3)	6228.8(3)	14(1)
O22	8079(8)	4917(5)	4582(4)	16(1)
O23	7751(8)	6416(6)	4153(5)	21(1)
O24	9058(8)	5786(5)	3546(4)	14(1)
O25	10076(8)	7244(5)	4510(5)	17(1)
O26	11403(8)	6708(5)	4028(5)	18(1)
O27	12320(9)	8385(6)	4876(5)	24(2)
O28	12646(8)	6855(5)	5388(5)	17(1)
O29	5854(9)	3973(6)	4266(5)	26(2)
O30	5880(9)	2864(6)	3192(5)	28(2)
O31	6832(8)	4620(6)	3153(5)	19(1)
O32	7087(9)	3820(7)	1940(5)	27(2)
O33	7465(9)	5583(7)	2044(5)	27(2)
O34	9222(8)	5024(6)	2451(5)	19(1)
O35	10184(9)	6812(6)	2593(5)	25(2)
O36	11502(9)	5881(6)	2765(5)	26(2)
O37	10490(8)	4907(5)	3766(5)	18(2)
O38	10467(8)	6754(6)	7038(5)	19(2)

O39	11335(8)	7380(5)	5892(5)	17(1)
O40	9196(8)	6429(5)	5528(4)	15(1)
O41	10422(7)	5927(5)	5062(4)	13(1)
O42	8221(8)	3922(5)	3476(4)	16(1)
N1	2880(19)	5119(17)	4228(10)	106(6)
C1	3610(20)	5970(20)	4016(13)	106(6)
C2	3180(20)	4380(20)	4158(13)	106(6)
N2	146(12)	3239(8)	1668(7)	31(3)
C3	-540(20)	3690(14)	1248(10)	69(6)
C4	1265(17)	3832(12)	2095(12)	55(5)
N3	8986(14)	6462(9)	989(7)	40(3)
C5	9930(20)	6293(13)	889(11)	60(5)
C6	7852(19)	5879(11)	498(9)	54(4)
N4	4379(12)	3320(8)	1983(6)	30(3)
C7	4154(15)	3944(12)	2455(9)	40(4)
C8	4556(16)	3692(11)	1303(9)	38(4)
N5	6525(14)	8702(10)	325(8)	47(3)
C9	6600(17)	7953(12)	719(9)	47(3)
C10	5668(17)	8976(12)	418(9)	47(3)
N6	2324(19)	8331(15)	2524(10)	87(4)
C11	2440(20)	8803(18)	3151(12)	86(4)
C12	3020(20)	7949(19)	2481(12)	87(4)
N7	4540(15)	1517(10)	3805(8)	54(4)
C13	4480(20)	1976(18)	4463(14)	95(9)
C14	5073(17)	915(15)	4066(10)	61(5)
N8	682(12)	2021(7)	6761(6)	28(3)
C15	1900(18)	2363(14)	7200(11)	59(5)
C16	260(20)	1133(11)	6397(9)	51(5)
N9	170(13)	1739(8)	3903(7)	36(3)
C17	1141(17)	1714(11)	4426(9)	42(4)
C18	-859(18)	943(12)	3851(10)	49(4)
N10	7150(13)	2086(8)	2209(8)	41(3)
C19	6670(20)	1795(15)	1351(9)	63(6)
C20	6640(20)	1425(13)	2623(9)	60(6)
O1W	2254(12)	6431(8)	429(7)	52(4)
O2W	4810(20)	5579(13)	356(10)	118(8)
O3W	2879(13)	5923(9)	1844(7)	57(4)
O4W	3794(12)	2867(9)	5894(7)	55(4)
O5W	5096(12)	7079(9)	2616(8)	59(4)
O6W	2686(13)	1096(8)	5908(7)	54(4)
O7W	3768(12)	1083(9)	7430(7)	49(3)
O8W	2614(14)	90(8)	4710(7)	60(4)
O9W	5710(20)	6065(14)	1795(11)	133(10)
O10W	6287(12)	3476(8)	375(6)	49(3)
O11W	4500(20)	9310(20)	1725(15)	187(14)

SI Table 12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) of **2T**

	x	*y*	*z*	*U*(iso)
H1A	2184	4976	3942	127
H1B	2893	5212	4702	127
H1C	3544	5899	3492	160
H1D	4368	6122	4307	160
H1E	3374	6426	4115	160
H2C	3910	4501	4489	159
H2D	3170	4265	3650	159
H2E	2654	3868	4288	159
H2A	192	2867	1346	37
H2B	-192	2928	1983	37
H3A	-205	3999	886	104
H3B	-590	4097	1590	104
H3C	-1272	3267	995	104
H4A	1225	4281	2398	83
H4B	1680	4094	1755	83
H4C	1628	3510	2412	83
H3D	9094	7013	911	48
H3E	8992	6416	1466	48
H5C	9811	5693	948	90
H5D	10600	6668	1259	90
H5E	9992	6406	396	90
H6A	7800	5970	-17	81
H6B	7300	6016	640	81
H6C	7732	5279	556	81
H4D	3804	2805	1865	36
H4E	4978	3234	2244	36
H7A	3374	3822	2303	60
H7B	4559	4536	2383	60
H7C	4389	3869	2975	60
H8A	5298	4130	1415	57
H8B	4032	3954	1109	57
H8C	4456	3239	935	57
H5A	7178	9152	488	56
H5B	6399	8563	-163	56
H9C	6705	8085	1243	71
H9D	7218	7840	659	71
H9E	5927	7446	513	71
H10C	4959	8495	247	71
H10D	5657	9452	131	71
H10E	5821	9164	939	71
H6D	1647	7907	2403	104
H6E	2325	8678	2162	104
H11A	3096	8837	3531	130
H11B	1802	8529	3325	130
H11C	2503	9383	3044	130
H12A	3727	8249	2854	131
H12B	3129	7977	1991	131
H12C	2719	7348	2567	131
H7D	4927	1902	3553	64
H7E	3858	1223	3499	64
H13A	5189	2175	4843	142
H13B	3921	1583	4658	142

H13C	4303	2469	4316	142
H14A	5613	1155	4547	91
H14B	5436	829	3713	91
H14C	4524	364	4108	91
H8D	292	2039	7070	33
H8E	584	2371	6414	33
H15A	2017	1983	7571	88
H15B	2126	2941	7444	88
H15C	2331	2380	6865	88
H16A	610	1121	6018	77
H16B	-532	934	6168	77
H16C	407	757	6762	77
H9A	71	2211	4039	44
H9B	274	1789	3451	44
H17A	1258	1210	4280	63
H17B	1046	1682	4918	63
H17C	1773	2235	4431	63
H18A	-999	902	4329	74
H18B	-757	430	3707	74
H18C	-1479	987	3481	74
H10A	7050	2568	2315	50
H10B	7878	2214	2348	50
H19A	5892	1692	1194	95
H19B	6756	1267	1236	95
H19C	7054	2248	1091	95
H20A	6674	886	2471	90
H20B	5876	1345	2530	90
H20C	7020	1596	3149	90

SI Table 13. Anisotropic displacement parameters (Å^2 x 10^3) of **2T**. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	18(1)	16(1)	16(1)	3(1)	7(1)	9(1)
W2	19(1)	16(1)	15(1)	2(1)	4(1)	7(1)
W3	14(1)	17(1)	18(1)	3(1)	3(1)	6(1)
W4	17(1)	16(1)	16(1)	4(1)	6(1)	10(1)
W5	15(1)	11(1)	14(1)	2(1)	4(1)	6(1)
W6	16(1)	12(1)	14(1)	3(1)	5(1)	6(1)
O1	18(2)	24(3)	21(3)	5(2)	9(2)	7(2)
O2	25(5)	22(3)	20(3)	-3(3)	6(3)	12(3)
O3	20(1)	17(1)	15(1)	2(1)	5(1)	7(1)
O4	32(5)	19(2)	18(3)	-5(2)	6(3)	6(2)
O5	22(3)	22(4)	15(2)	3(2)	-2(2)	3(4)
O6	17(1)	17(1)	17(1)	2(1)	3(1)	5(1)
O7	13(2)	21(3)	26(4)	1(2)	5(2)	3(2)
O8	20(3)	33(5)	19(2)	6(3)	3(3)	16(4)
O9	14(2)	18(2)	20(2)	3(1)	4(1)	7(1)
O10	18(1)	17(1)	17(1)	2(1)	7(1)	10(1)
O11	24(3)	29(5)	23(4)	4(3)	6(3)	21(3)
O12	19(1)	15(2)	16(2)	3(1)	6(1)	10(1)
O13	17(1)	13(1)	15(1)	1(1)	4(1)	6(1)
O14	18(2)	15(2)	19(3)	-4(2)	9(3)	2(2)
O15	16(2)	15(2)	16(1)	2(1)	3(1)	7(1)
O16	15(2)	12(2)	15(1)	2(1)	4(1)	5(1)
O17	14(2)	12(2)	14(2)	2(2)	4(2)	7(1)
O18	18(2)	15(2)	16(1)	4(1)	5(1)	10(2)
O19	16(1)	14(1)	16(2)	2(1)	4(1)	6(1)
O20	16(2)	13(1)	15(2)	2(1)	4(1)	7(1)
O21	32(6)	16(4)	19(4)	9(3)	13(4)	13(3)
W7	16(1)	13(1)	14(1)	3(1)	4(1)	9(1)
W8	17(1)	11(1)	20(1)	3(1)	6(1)	4(1)
W9	14(1)	17(1)	20(1)	0(1)	2(1)	5(1)
W10	21(1)	24(1)	14(1)	2(1)	2(1)	12(1)
W11	22(1)	18(1)	16(1)	6(1)	9(1)	10(1)
W12	18(1)	13(1)	13(1)	1(1)	4(1)	8(1)
O22	16(2)	15(1)	16(1)	1(1)	5(1)	3(1)
O23	21(2)	31(4)	19(3)	4(4)	5(3)	18(2)
O24	18(1)	14(2)	14(1)	5(1)	5(1)	9(1)
O25	19(1)	13(1)	19(1)	3(1)	5(1)	6(1)
O26	20(1)	15(1)	19(1)	5(1)	8(1)	6(1)
O27	23(3)	11(2)	32(4)	5(2)	7(4)	2(2)
O28	16(1)	12(2)	21(2)	4(2)	6(1)	3(1)
O29	15(3)	30(5)	32(4)	5(3)	9(3)	6(3)
O30	14(4)	21(2)	35(5)	-6(2)	-4(3)	0(3)
O31	17(1)	22(1)	19(1)	1(1)	2(1)	9(1)
O32	21(3)	35(3)	19(3)	-8(2)	-5(3)	13(3)
O33	24(5)	35(4)	21(3)	9(3)	0(2)	16(4)
O34	23(1)	21(1)	15(1)	3(1)	6(1)	11(1)
O35	32(6)	21(2)	24(3)	15(2)	11(3)	11(3)
O36	25(2)	27(5)	29(4)	3(3)	16(3)	10(3)
O37	23(5)	16(2)	20(3)	5(2)	6(3)	14(3)
O38	19(5)	20(4)	17(2)	-5(2)	6(2)	8(4)
O39	19(2)	11(2)	19(1)	0(1)	4(1)	6(1)
O40	17(1)	14(1)	16(1)	1(1)	5(1)	9(1)
O41	13(1)	11(1)	13(1)	1(1)	4(1)	5(1)
O42	15(3)	13(2)	16(3)	0(2)	2(2)	4(2)
N1	60(10)	176(15)	54(7)	-29(9)	39(7)	2(10)
C1	61(10)	177(15)	54(7)	-28(9)	38(7)	2(10)
C2	60(10)	176(15)	55(7)	-29(9)	39(7)	2(10)
N2	45(8)	27(6)	36(7)	4(5)	25(6)	21(5)
C3	121(17)	63(13)	41(11)	18(9)	12(11)	64(13)
C4	40(9)	45(11)	85(14)	-7(9)	40(8)	6(7)
N3	71(10)	32(7)	25(6)	9(5)	19(6)	26(6)
C5	90(12)	53(12)	59(12)	8(10)	34(11)	44(11)
C6	82(10)	34(9)	37(9)	6(7)	13(8)	17(9)

N4	35(9)	22(6)	26(6)	0(4)	3(6)	7(6)
C7	28(10)	60(11)	37(8)	-4(7)	8(7)	23(9)
C8	41(11)	42(10)	36(7)	10(7)	17(8)	18(9)
N5	46(7)	51(6)	31(5)	4(4)	11(5)	6(5)
C9	47(7)	51(6)	32(5)	3(4)	10(5)	7(5)
C10	47(7)	52(6)	32(5)	3(5)	10(5)	7(5)
N6	85(11)	134(12)	56(7)	-12(7)	-3(7)	76(9)
C11	85(11)	134(12)	56(7)	-11(8)	-3(7)	76(9)
C12	86(11)	134(12)	57(7)	-12(8)	-3(7)	76(9)
N7	47(11)	50(10)	42(8)	7(6)	12(8)	-3(7)
C13	48(17)	120(10)	96(17)	-26(14)	47(15)	-3(14)
C14	28(12)	91(15)	44(10)	20(10)	1(9)	9(10)
N8	48(8)	26(5)	26(6)	17(4)	26(5)	22(6)
C15	50(9)	73(13)	49(11)	10(9)	18(8)	16(9)
C16	90(15)	33(7)	33(9)	6(6)	30(9)	19(8)
N9	78(10)	35(6)	25(6)	16(5)	30(6)	43(6)
C17	64(9)	31(9)	35(9)	1(7)	15(7)	22(8)
C18	58(9)	59(10)	47(10)	18(9)	17(9)	39(7)
N10	28(9)	23(7)	60(7)	0(5)	2(7)	4(6)
C19	85(18)	104(17)	42(6)	44(8)	27(9)	74(15)
C20	79(18)	60(11)	23(7)	-7(7)	20(9)	5(11)
O1W	66(11)	39(7)	54(8)	11(6)	12(7)	29(7)
O2W	180(30)	114(15)	94(13)	40(12)	29(15)	108(18)
O3W	85(13)	56(8)	56(8)	21(7)	36(8)	45(9)
O4W	48(10)	55(8)	69(9)	16(7)	20(8)	27(8)
O5W	33(9)	57(9)	91(10)	5(8)	24(8)	19(7)
O6W	76(12)	47(8)	45(7)	-5(6)	24(7)	27(8)
O7W	48(9)	73(9)	47(7)	25(7)	31(7)	33(8)
O8W	85(13)	32(7)	60(8)	7(6)	31(8)	13(8)
O9W	130(10)	141(19)	124(15)	-35(14)	-46(14)	111(18)
O10W	50(10)	49(8)	43(7)	0(6)	0(6)	22(7)
O11W	120(30)	260(30)	170(10)	-70(10)	-31(19)	130(30)

SI Table 14. Bond lengths (Å) and angles (°) of **2T**

W1-O1	1.741(9)	W1-O2	1.761(8)
W1-O10	1.907(8)	W1-O3	1.979(9)
W1-O20	2.213(8)	W1-O13	2.227(9)
W2-O5	1.740(9)	W2-O4	1.753(8)
W2-O3	1.85(1)	W2-O6	1.914(9)
W2-O13	2.268(8)	W2-O19	2.353(8)
W3-O7	1.742(9)	W3-O8	1.761(9)
W3-O9	1.866(8)	W3-O6	1.973(8)
W3-O19	2.173(9)	W3-O15	2.243(8)
W4-O11	1.734(9)	W4-O12	1.827(9)
W4-O18	1.846(8)	W4-O10	1.940(8)
W4-O9#1	1.973(9)	W4-O17	2.278(8)
W5-O14	1.720(9)	W5-O15	1.783(8)
W5-O13	1.915(8)	W5-O16	1.959(8)
W5-O12	2.124(9)	W5-O17	2.260(8)
W6-O21	1.725(8)	W6-O20	1.792(8)
W6-O19	1.898(9)	W6-O16#1	1.969(8)
W6-O18#1	2.112(8)	W6-O17#1	2.225(8)
W7-O23	1.717(9)	W7-O22	1.834(8)
W7-O24	1.905(8)	W7-O40	1.951(8)
W7-O25	2.048(9)	W7-O41	2.266(9)
W8-O27	1.755(9)	W8-O39	1.840(8)
W8-O25	1.894(9)	W8-O28	1.914(9)
W8-O26	1.922(8)	W8-O41	2.252(8)
W9-O29	1.75(1)	W9-O30	1.762(9)
W9-O28#2	1.916(8)	W9-O31	1.936(9)
W9-O22	2.167(9)	W9-O42	2.204(9)
W10-O32	1.744(9)	W10-O33	1.766(9)
W10-O34	1.89(1)	W10-O31	1.889(9)
W10-O24	2.279(9)	W10-O42	2.327(8)
W11-O36	1.74(1)	W11-O35	1.757(9)
W11-O26	1.906(9)	W11-O34	1.950(9)
W11-O37	2.210(8)	W11-O24	2.223(9)
W12-O38	1.723(8)	W12-O37#2	1.798(9)
W12-O42#2	1.888(9)	W12-O40	1.962(9)
W12-O39	2.090(9)	W12-O41	2.229(8)
N1-C2	1.45(4)	N1-C1	1.52(3)
N2-C4	1.46(2)	N2-C3	1.48(2)
N3-C5	1.47(2)	N3-C6	1.50(2)
N4-C8	1.45(2)	N4-C7	1.52(2)
N5-C10	1.45(2)	N5-C9	1.47(2)
N6-C11	1.34(2)	N6-C12	1.35(3)
N7-C14	1.46(3)	N7-C13	1.47(2)
N8-C16	1.45(2)	N8-C15	1.51(2)
N9-C17	1.43(2)	N9-C18	1.50(2)
N10-C20	1.42(2)	N10-C19	1.55(2)

O1-W1-O2	102.5(4)	O1-W1-O10	98.5(4)
O2-W1-O10	98.2(4)	O1-W1-O3	98.3(4)
O2-W1-O3	95.8(4)	O10-W1-O3	155.3(4)
O1-W1-O20	89.2(4)	O2-W1-O20	168.0(4)
O10-W1-O20	82.4(3)	O3-W1-O20	79.8(3)
O1-W1-O13	163.9(4)	O2-W1-O13	91.5(4)
O10-W1-O13	87.1(3)	O3-W1-O13	72.2(3)
O20-W1-O13	76.6(3)	O5-W2-O4	103.6(4)
O5-W2-O3	96.0(4)	O4-W2-O3	99.6(4)
O5-W2-O6	99.9(4)	O4-W2-O6	97.8(4)
O3-W2-O6	152.9(4)	O5-W2-O13	162.9(4)
O4-W2-O13	91.7(4)	O3-W2-O13	73.6(3)
O6-W2-O13	85.3(3)	O5-W2-O19	90.0(4)
O4-W2-O19	164.5(4)	O3-W2-O19	86.2(3)
O6-W2-O19	72.1(3)	O13-W2-O19	76.0(3)
O7-W3-O8	103.3(5)	O7-W3-O9	98.8(4)
O8-W3-O9	98.8(4)	O7-W3-O6	93.5(4)

O8-W3-O6	97.2(4)	O9-W3-O6	157.0(4)
O7-W3-O19	162.0(4)	O8-W3-O19	92.2(4)
O9-W3-O19	87.7(4)	O6-W3-O19	75.2(3)
O7-W3-O15	87.2(4)	O8-W3-O15	168.8(4)
O9-W3-O15	83.2(3)	O6-W3-O15	78.1(3)
O19-W3-O15	76.9(3)	O11-W4-O12	102.9(4)
O11-W4-O18	101.7(4)	O12-W4-O18	92.9(4)
O11-W4-O10	102.1(4)	O12-W4-O10	87.7(4)
O18-W4-O10	155.4(3)	O11-W4-O9#1	100.1(4)
O12-W4-O9#1	156.6(4)	O18-W4-O9#1	86.2(4)
O10-W4-O9#1	83.6(3)	O11-W4-O17	177.5(4)
O12-W4-O17	76.8(3)	O18-W4-O17	75.8(3)
O10-W4-O17	80.4(3)	O9#1-W4-O17	80.3(3)
O14-W5-O15	105.2(4)	O14-W5-O13	101.0(4)
O15-W5-O13	96.1(4)	O14-W5-O16	98.4(4)
O15-W5-O16	93.0(4)	O13-W5-O16	155.5(4)
O14-W5-O12	93.7(4)	O15-W5-O12	161.0(4)
O13-W5-O12	81.6(3)	O16-W5-O12	82.5(3)
O14-W5-O17	162.8(4)	O15-W5-O17	89.2(3)
O13-W5-O17	86.4(3)	O16-W5-O17	71.1(3)
O12-W5-O17	71.8(3)	O21-W6-O20	104.7(4)
O21-W6-O19	102.1(4)	O20-W6-O19	96.5(4)
O21-W6-O16#1	96.4(4)	O20-W6-O16#1	93.1(4)
O19-W6-O16#1	156.1(4)	O21-W6-O18#1	91.7(4)
O20-W6-O18#1	163.3(3)	O19-W6-O18#1	83.3(4)
O16#1-W6-O18#1	81.2(4)	O21-W6-O17#1	161.0(3)
O20-W6-O17#1	91.0(3)	O19-W6-O17#1	86.3(3)
O16#1-W6-O17#1	71.7(3)	O18#1-W6-O17#1	72.2(3)
W2-O3-W1	118.7(4)	W2-O6-W3	116.9(4)
W3-O9-W4#1	147.9(5)	W1-O10-W4	146.6(5)
W4-O12-W5	116.0(4)	W5-O13-W1	139.7(5)
W5-O13-W2	125.2(5)	W1-O13-W2	94.2(3)
W5-O15-W3	137.2(4)	W5-O16-W6#1	118.2(4)
W6#1-O17-W5	97.5(3)	W6#1-O17-W4	96.2(3)
W5-O17-W4	95.3(3)	W4-O18-W6#1	115.7(4)
W6-O19-W3	139.9(4)	W6-O19-W2	124.7(4)
W3-O19-W2	94.0(3)	W6-O20-W1	139.4(5)
O23-W7-O22	102.7(5)	O23-W7-O24	102.6(4)
O22-W7-O24	94.8(4)	O23-W7-O40	97.9(4)
O22-W7-O40	91.4(4)	O24-W7-O40	156.7(4)
O23-W7-O25	96.2(4)	O22-W7-O25	160.7(4)
O24-W7-O25	84.6(4)	O40-W7-O25	82.2(4)
O23-W7-O41	165.0(4)	O22-W7-O41	87.8(4)
O24-W7-O41	86.9(3)	O40-W7-O41	70.9(3)
O25-W7-O41	72.9(3)	O27-W8-O39	102.9(4)
O27-W8-O25	100.5(4)	O39-W8-O25	89.6(4)
O27-W8-O28	102.7(4)	O39-W8-O28	88.6(4)
O25-W8-O28	156.6(4)	O27-W8-O26	101.2(4)
O39-W8-O26	155.9(4)	O25-W8-O26	87.2(4)
O28-W8-O26	84.9(4)	O27-W8-O41	176.2(4)
O39-W8-O41	75.8(3)	O25-W8-O41	76.0(3)
O28-W8-O41	80.9(3)	O26-W8-O41	80.3(3)
O29-W9-O30	102.0(5)	O29-W9-O28#2	99.7(4)
O30-W9-O28#2	97.4(4)	O29-W9-O31	97.4(4)
O30-W9-O31	94.6(4)	O28#2-W9-O31	156.5(4)
O29-W9-O22	87.4(4)	O30-W9-O22	170.0(4)
O28#2-W9-O22	83.9(3)	O31-W9-O22	80.9(3)
O29-W9-O42	163.4(4)	O30-W9-O42	93.1(4)
O28#2-W9-O42	84.9(3)	O31-W9-O42	74.3(4)
O22-W9-O42	77.2(3)	O32-W10-O33	104.3(4)
O32-W10-O34	97.4(4)	O33-W10-O34	99.9(4)
O32-W10-O31	99.9(5)	O33-W10-O31	97.4(4)
O34-W10-O31	151.6(4)	O32-W10-O24	161.2(4)
O33-W10-O24	93.4(4)	O34-W10-O24	73.0(3)
O31-W10-O24	83.7(4)	O32-W10-O42	86.8(4)
O33-W10-O42	166.2(4)	O34-W10-O42	86.5(3)
O31-W10-O42	72.2(3)	O24-W10-O42	76.6(3)

O36-W11-O35	103.1(5)	O36-W11-O26	99.4(4)
O35-W11-O26	98.8(4)	O36-W11-O34	97.2(4)
O35-W11-O34	95.0(4)	O26-W11-O34	155.4(4)
O36-W11-O37	88.9(4)	O35-W11-O37	167.1(4)
O26-W11-O37	83.7(3)	O34-W11-O37	78.6(3)
O36-W11-O24	165.0(4)	O35-W11-O24	89.5(4)
O26-W11-O24	86.6(4)	O34-W11-O24	73.2(3)
O37-W11-O24	78.0(3)	O38-W12-O37#2	104.4(4)
O38-W12-O42#2	101.0(4)	O37#2-W12-O42#2	98.3(4)
O38-W12-O40	98.7(4)	O37#2-W12-O40	91.6(4)
O42#2-W12-O40	154.9(3)	O38-W12-O39	91.4(4)
O37#2-W12-O39	163.3(3)	O42#2-W12-O39	83.6(4)
O40-W12-O39	80.6(4)	O38-W12-O41	161.5(4)
O37#2-W12-O41	91.8(3)	O42#2-W12-O41	85.1(3)
O40-W12-O41	71.5(3)	O39-W12-O41	71.7(3)
W7-O22-W9	135.5(4)	W7-O24-W11	138.3(5)
W7-O24-W10	126.7(5)	W11-O24-W10	94.0(3)
W8-O25-W7	115.7(4)	W11-O26-W8	149.2(6)
W8-O28-W9#2	149.0(5)	W10-O31-W9	118.8(5)
W10-O34-W11	118.3(4)	W12#2-O37-W11	138.4(5)
W8-O39-W12	116.1(4)	W7-O40-W12	119.1(4)
W12-O41-W8	96.3(3)	W12-O41-W7	97.2(3)
W8-O41-W7	95.3(3)	W12#2-O42-W9	141.6(4)
W12#2-O42-W10	123.4(4)	W9-O42-W10	93.2(3)
C2-N1-C1	116(2)	C4-N2-C3	114(2)
C5-N3-C6	117(1)	C8-N4-C7	109(1)
C10-N5-C9	115(2)	C11-N6-C12	123(2)
C14-N7-C13	109(2)	C16-N8-C15	113(2)
C17-N9-C18	113(1)	C20-N10-C19	112(1)

SI Table 15. Torsion angles (°) of **TRIC2** (**2T**) to be deposited

O32-W10-O31-W9	-73.2(6)	O33-W10-O31-W9	-179.1(5)
O34-W10-O31-W9	54(1)	O24#1-W10-O31-W9	88.2(5)
O42-W10-O31-W9	10.3(4)	O23-W7-O22-W9#1	58.3(7)
O24-W7-O22-W9#1	-46.0(7)	O40-W7-O22-W9#1	156.5(7)
O25-W7-O22-W9#1	-132.9(9)	O41-W7-O22-W9#1	-132.7(7)
O38-W12-O37-W11	-66.5(7)	O42-W12-O37-W11	37.2(7)
O40-W12-O37-W11	-165.9(6)	O39-W12-O37-W11	132(1)
O41-W12-O37-W11	122.4(6)	O32-W10-O34-W11	173.9(5)
O33-W10-O34-W11	-80.2(5)	O31-W10-O34-W11	47(1)
O24#1-W10-O34-W11	10.4(4)	O42-W10-O34-W11	87.4(5)
O38-W12-O42-W9	-134.0(7)	O37-W12-O42-W9	119.4(7)
O40-W12-O42-W9	7(1)	O39-W12-O42-W9	-43.9(7)
O41-W12-O42-W9	28.3(7)	O38-W12-O42-W10	66.0(5)
O37-W12-O42-W10	-40.6(5)	O40-W12-O42-W10	-152.6(6)
O39-W12-O42-W10	156.2(5)	O41-W12-O42-W10	-131.7(4)
O27-W8-O39-W12	179.8(5)	O25-W8-O39-W12	78.9(5)
O28-W8-O39-W12	-77.7(5)	O26-W8-O39-W12	-3(1)
O41-W8-O39-W12	3.3(4)	O27-W8-O25-W7	179.4(5)
O39-W8-O25-W7	-77.6(4)	O28-W8-O25-W7	8(1)
O26-W8-O25-W7	78.6(4)	O41-W8-O25-W7	-2.2(4)
O21-W6-O20-W1	-64.7(8)	O19-W6-O20-W1	39.7(8)
O16-W6-O20-W1	-162.3(7)	O18-W6-O20-W1	128(1)
O17-W6-O20-W1	126.0(7)	O21-W6-O19-W3	-129.8(7)
O20-W6-O19-W3	123.6(7)	O16-W6-O19-W3	10(1)
O18-W6-O19-W3	-39.5(6)	O17-W6-O19-W3	33.0(7)
O21-W6-O19-W2	67.1(5)	O20-W6-O19-W2	-39.5(5)
O16-W6-O19-W2	-152.9(6)	O18-W6-O19-W2	157.4(5)
O17-W6-O19-W2	-130.1(5)	O5-W2-O3-W1	176.3(5)
O4-W2-O3-W1	-78.7(5)	O6-W2-O3-W1	51(1)
O13#2-W2-O3-W1	10.2(4)	O19-W2-O3-W1	86.8(4)
O11-W4-O12-W5	-178.0(4)	O18-W4-O12-W5	-75.2(4)
O10-W4-O12-W5	80.2(4)	O9-W4-O12-W5	12(1)
O17-W4-O12-W5	-0.4(4)	O7-W3-O9-W4	170.2(9)
O8-W3-O9-W4	-85(1)	O6-W3-O9-W4	49(2)
O19-W3-O9-W4	7.2(9)	O15#2-W3-O9-W4	84(1)
O11-W4-O18-W6	-178.9(5)	O12-W4-O18-W6	77.1(5)
O10-W4-O18-W6	-14(1)	O9-W4-O18-W6	-79.5(5)
O17-W4-O18-W6	1.5(4)	W3#2-O15-W5-O14	61.5(9)
W3#2-O15-W5-O13	-41.6(8)	W3#2-O15-W5-O16	161.1(8)
W3#2-O15-W5-O12	-124(1)	W3#2-O15-W5-O17	-127.9(8)

SI Table 16. Hydrogen bonds in **2T**

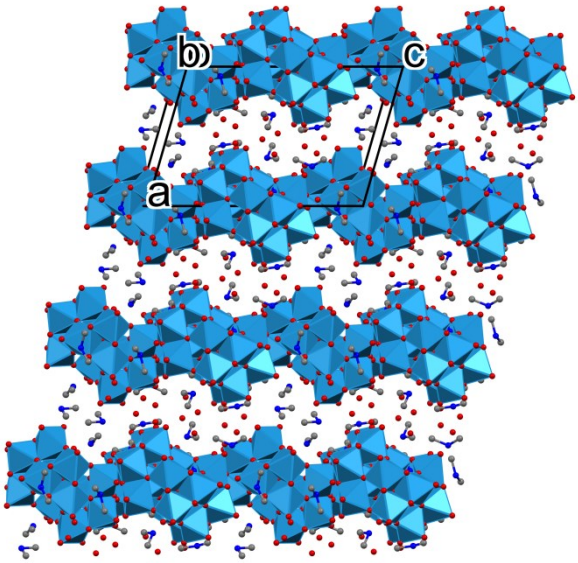
Hydrogen bonding of the ammonium ions

Nr	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	sym op
1	N(1) --H(1A) ..O(37)	0.89	2.20	3.03(3)	155	x,y,z
2	N(1) --H(1B) ..O(22)	0.89	2.12	2.87(2)	141	x,y,z
3	N(1) --H(1B) ..O(29)	0.89	2.17	2.90(2)	139	1-x,-y,-z
4	N(2) --H(2A) ..O(12)	0.89	2.00	2.817(15)	152	1-x,1-y,1-z
5	N(2) --H(2B) ..O(2)	0.89	2.19	2.919(16)	139	x,y,z
6	N(2) --H(2B) ..O(38)	0.89	2.07	2.762(17)	134	x,y,z
7	N(3) --H(3D) ..O(16)	0.89	1.91	2.772(16)	164	1-x,1-y,1-z
8	N(3) --H(3E) ..O(33)	0.89	2.54	3.20(2)	131	1-x,-y,1-z
9	N(3) --H(3E) ..O(35)	0.89	2.19	2.925(16)	139	1-x,-y,1-z
10	N(4) --H(4D) ..O(6)	0.89	2.05	2.880(17)	154	x,y,z
11	N(4) --H(4D) ..O(7)	0.89	2.49	2.982(16)	115	x,y,z
12	N(4) --H(4E) ..O(30)	0.89	2.10	2.917(17)	152	-1+x,y,z
13	N(5) --H(5A) ..O(10)	0.89	2.37	3.159(17)	148	x,y,z
14	N(5) --H(5A) ..O(1)	0.89	2.56	3.074(16)	117	1-x,1-y,1-z
15	N(5) --H(5A) ..O(20)	0.89	2.48	3.24(2)	144	1-x,1-y,1-z
16	N(5) --H(5B) ..O(7)	0.89	1.96	2.828(15)	167	x,y,z
17	N(5) --H(5B) ..O(15)	0.89	2.60	3.10(2)	117	1-x,1-y,1-z
18	N(6) --H(6D) ..O(18)	0.89	2.08	2.734(19)	130	x,y,z
19	N(6) --H(6E) ..O(35)	0.89	2.28	3.10(3)	155	x,1+y,z
20	N(7) --H(7D) ..O(30)	0.89	1.92	2.792(19)	168	-1+x,y,z
21	N(7) --H(7E) ..O(5)	0.89	2.00	2.82(2)	153	x,y,z
22	N(8) --H(8D) ..O(21)	0.89	1.99	2.717(16)	138	x,y,z
23	N(8) --H(8D) ..O(35)	0.89	2.36	3.004(19)	129	x,1+y,z
24	N(8) --H(8E) ..O(25)	0.89	1.94	2.797(14)	160	1-x,1-y,-z
25	N(9) --H(9A) ..O(39)	0.89	2.29	3.02(2)	140	x,y,z
26	N(9) --H(9A) ..O(40)	0.89	2.15	2.938(16)	148	x,y,z
27	N(9) --H(9B) ..O(2)	0.89	2.56	3.236(14)	133	x,y,z
28	N(9) --H(9B) ..O(4)	0.89	2.25	2.98(2)	138	x,y,z
29	N(10) --H(10A) ..O(32)	0.89	2.19	2.956(17)	144	x,y,z
30	N(10) --H(10B) ..O(2)	0.89	2.26	2.96(2)	135	x,y,z
31	N(10) --H(10B) ..O(38)	0.89	2.23	2.990(19)	143	x,y,z
32	C(1) --H(1E) ..O(4W)	0.96	2.58	3.31(3)	133	-1+x,-1+y,z
33	C(2) --H(2D) ..O(40)	0.96	2.45	3.20(4)	134	x,y,z
34	C(3) --H(3C) ..O(34)	0.96	2.35	3.31(2)	174	x,y,z
35	C(4) --H(4A) ..O(36)	0.96	2.59	3.49(2)	155	x,y,z
36	C(4) --H(4B) ..O(4)	0.96	2.51	3.40(2)	153	x,y,z
37	C(10) --H(10E) ..O(1)	0.96	2.59	3.22(2)	123	1-x,1-y,1-z
38	C(11) --H(11B) ..O(5)	0.96	2.46	3.34(2)	152	x,y,z
39	C(12) --H(12B) ..O(36)	0.96	2.52	3.42(3)	155	x,1+y,z
40	C(13) --H(13C) ..O(8W)	0.96	2.48	3.35(3)	150	x,y,z
41	C(14) --H(14A) ..O(27)	0.96	2.53	3.29(3)	137	-1+x,y,z
42	C(15) --H(15B) ..O(33)	0.96	2.43	3.39(2)	174	x,1+y,z
43	C(16) --H(16C) ..O(3)	0.96	2.47	3.375(18)	156	x,y,z
44	C(19) --H(19A) ..O(7)	0.96	2.40	3.31(3)	160	1+x,y,z
45	C(20) --H(20B) ..O(39)	0.96	2.46	3.303(19)	146	x,y,z

SI Table 17. Summary of the shortest inter contacts with d(I-J) < R(I) + R(J) + 0.2 of the water molecules in compound **2T**

Nr	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	sym op
1	O(1W) .... O(3W)	-	-	2.771(18)	-	x,y,z
2	O(1W) .... O(10W)	-	-	2.76(2)	-	x,y,z
3	O(1W) .... O(11)	-	-	2.869(16)	-	1-x,1-y,1-z
4	O(2W) .... O(10W)	-	-	2.69(3)	-	x,y,z
5	O(2W) .... O(2W)	-	-	2.62(3)	-	2-x,-y,1-z
6	O(2W) .... O(9W)	-	-	2.60(3)	-	2-x,-y,1-z
7	O(3W) .... O(1W)	-	-	2.771(18)	-	x,y,z
8	O(3W) .... O(5W)	-	-	2.84(2)	-	2-x,1-y,1-z
9	O(3W) .... O(36)	-	-	2.84(2)	-	1-x,-y,1-z
10	O(4W) .... O(5W)	-	-	2.759(19)	-	x,y,z
11	O(4W) .... O(6W)	-	-	2.762(18)	-	x,y,z
12	O(4W) .... O(23)	-	-	2.76(2)	-	1-x,1-y,-z
13	O(5W) .... O(4W)	-	-	2.759(19)	-	x,y,z
14	O(5W) .... O(7W)	-	-	2.872(19)	-	x,y,z
15	O(5W) .... O(9W)	-	-	2.76(3)	-	x,1+y,z
16	O(5W) .... O(3W)	-	-	2.84(2)	-	2-x,1-y,1-z
17	O(6W) .... O(4W)	-	-	2.762(18)	-	x,y,z
18	O(6W) .... O(7W)	-	-	2.830(17)	-	x,y,z
19	O(6W) .... O(8W)	-	-	2.741(19)	-	1-x,1-y,-z
20	O(7W) .... O(1)	-	-	2.731(18)	-	x,y,z
21	O(7W) .... O(5W)	-	-	2.872(19)	-	x,y,z
22	O(7W) .... O(6W)	-	-	2.830(17)	-	x,y,z
23	O(7W) .... O(11W)	-	-	2.76(3)	-	x,y,z
24	O(8W) .... O(5)	-	-	2.872(15)	-	x,y,z
25	O(8W) .... O(6W)	-	-	2.741(19)	-	1-x,1-y,-z
26	O(8W) .... O(27)	-	-	2.740(16)	-	1-x,1-y,-z
27	O(9W) .... O(5W)	-	-	2.76(3)	-	x,-1+y,z
28	O(9W) .... O(33)	-	-	2.72(3)	-	x,y,z
29	O(9W) .... O(2W)	-	-	2.60(3)	-	2-x,-y,1-z
30	O(10W) .... O(1W)	-	-	2.76(2)	-	x,y,z
31	O(10W) .... O(2W)	-	-	2.69(3)	-	x,y,z
32	O(10W) .... O(32)	-	-	2.796(14)	-	x,y,z

2T crystallizes in the triclinic system, in the same *P*-1 space group as **1T** (Figure 6). The asymmetric unit contains two half dihydrododecatungstate(10-) anions, ten dimethylammonium cations and eleven water molecules. **2T** is a solvatomorphic modification of **1T** since it contains one more water molecule per one dihydrododecatungstate(10-). At the centre of both $[H_2W_{12}O_{42}]^{10-}$ polyanions in the asymmetric unit, an inversion centre can be found.



SI Figure 6. Packing of **2T** form (view *b* axis)

Crystal structure of 1M[4]

Colourless single crystals of **1M** were grown from 96 % ethanol by slow evaporation. A single crystal with the size of 0.45 x 0.55 x 0.7 mm has been mounted on a loop and measured by single crystal X-ray diffraction method. The diffraction measurement was performed at -130 °C using MoK_α radiation. Intensity data were collected on a RIGAKU RAXIS-RAPID diffractometer equipped with graphite monochromator. A numerical absorption correction was applied to the data. The structure was solved by charge flipping method. Non-hydrogen atomic positions have been refined by anisotropic full-matrix least-squares refinement. Hydrogen atomic positions were calculated from assumed geometries. The water hydrogen positions could not be determined. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. Unusually large residual electron densities were calculated in the proximity of the tungsten atoms. The final R factor is 7.96 %. Crystal data and details of structure determination and refinement are listed in Table 18, atomic coordinates and equivalent isotropic displacement parameters in Table 19, hydrogen coordinates and equivalent isotropic displacement parameters in Table 20, anisotropic displacement parameters in Table 21, bond lengths and angles, respectively in Table 22 and 23, as well the intermolecular interactions are listed in Table 24.

SI Table 18. Crystal data and structure refinement of **1M**

Label	**1M**
Empirical formula	C20 H80 N10 O52 W12
Formula weight	3499.14
Temperature	143(2)
Radiation and wavelength	Mo-Kα, λ =0.71073Å
Crystal system	monoclinic
Space group	*C* 2/c
Unit cell dimensions	*a* =14.7682(3)Å *b* =24.7368(4)Å *c* =21.1511(4)Å α =90° β =108.924(8)° γ =90°
Volume	7309.2(4)Å^3
Z	4
Density (calculated)	3.180 Mg/m^3
Absorption coefficient, μ	18.900 mm^{-1}
F(000)	6296
Crystal colour	colorless
Crystal description	prism
Crystal size	0.70 x 0.55 x 0.46 mm
Absorption correction	numerical
Max. and min. transmission	0.1580.340
θ–range for data collection	3.041 ≤ θ ≤ 30.508°
Index ranges	-21 ≤ *h* ≤21;-35≤ *k* ≤35;-30 ≤ *l* ≤30
Reflections collected	307689
Completeness to 2θ	0.998
Independent reflections	11149 [*R*(int) =0.1595]
Reflections *I*>2σ(*I*)	10769
Refinement method	full-matrix least-squares on *F*2
Data / restraints / parameters	11149 /345 /435
Goodness-of-fit on *F*2	1.498
Final *R* indices [*I*>2σ(*I*)]	*R*1 =0.0796, *wR*2 =0.1446
R indices (all data)	*R*1 =0.0825, *wR*2 =0.1455
Max. and mean shift/esd	0.001;0.000
Largest diff. peak and hole	4.292;-5.371 e.Å^{-3}

SI Table 19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) in **1M**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
W1	5000	1366.6(3)	2500	11(1)
W2	3903.2(4)	2092.0(2)	3339.3(3)	10(1)
W3	3638.2(4)	2582.6(2)	1615.2(3)	9(1)
W4	5241.5(4)	3277.9(2)	4250.9(2)	10(1)
W5	3598.9(4)	3947.7(2)	1624.9(3)	10(1)
W6	3905.7(4)	4434.6(2)	3360.5(3)	12(1)
W7	5000	5125.7(3)	2500	14(1)
O1	4548(8)	923(4)	1831(5)	15(2)
O2	3836(7)	1559(4)	2631(5)	11(1)
O3	4193(7)	1610(4)	3977(5)	11(1)
O4	2650(7)	2138(4)	3136(5)	14(1)
O5	4256(7)	2712(4)	3840(5)	11(1)
O6	3685(7)	2633(4)	2465(5)	10(1)
O7	2683(7)	2159(4)	1262(5)	14(1)
O8	4690(7)	2097(4)	1783(5)	9(1)
O9	3867(7)	2730(4)	723(5)	11(1)
O10	4674(6)	3260(4)	1802(4)	9(1)
O11	2926(7)	3268(4)	1386(5)	10(1)
O12	2676(8)	4389(4)	1253(5)	17(2)
O13	4668(7)	4403(4)	1804(5)	12(1)
O14	6118(7)	3810(4)	4270(5)	11(1)
O15	5192(7)	3270(4)	5052(5)	14(2)
O16	4200(7)	3765(4)	3809(5)	11(1)
O17	3604(7)	3907(4)	2478(5)	11(1)
O18	2701(8)	4456(4)	3278(5)	15(1)
O19	4412(8)	4852(4)	4058(5)	16(2)
O20	3847(8)	4959(4)	2668(5)	14(1)
O21	5526(8)	5566(4)	3170(5)	14(2)
N1	2248(12)	3235(7)	2943(8)	31(3)
C1	2069(16)	3302(9)	3595(10)	36(4)
C2	1474(17)	3420(10)	2364(11)	44(5)
N2	1578(10)	3141(5)	136(7)	20(2)
C3	822(14)	3093(8)	428(9)	31(4)
C4	1523(14)	3647(7)	-262(9)	29(4)
N3	1805(13)	1429(7)	1865(9)	32(3)
C5	887(15)	1660(9)	1792(11)	35(3)
C6	1802(15)	982(8)	1404(10)	33(3)
N4	3894(9)	493(5)	3554(6)	17(2)
C7	3620(14)	90(7)	3014(9)	27(3)
C8	4241(15)	254(8)	4231(9)	32(4)
N5	1267(13)	206(7)	4545(9)	34(3)
C9	1989(15)	-83(8)	5048(10)	32(3)
C10	1211(19)	786(9)	4688(12)	41(5)
O1W	3218(9)	1769(6)	4920(6)	29(3)
O2W	4509(16)	954(8)	5781(12)	70(6)
O3W	2166(10)	1058(6)	3282(8)	37(3)
O4W	3880(11)	131(6)	6434(9)	41(4)
O5W	1308(12)	2195(7)	4559(9)	48(4)

SI Table 20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) in **1M**.

	x	*y*	*z*	*U*(iso)
H1A	2776	3417	2961	37
H1B	2356	2887	2887	37
H1C	1958	3676	3662	54
H1D	2617	3178	3952	54
H1E	1518	3094	3591	54
H2C	974	3153	2244	66
H2D	1711	3473	1996	66
H2E	1225	3754	2468	66
H2A	1553	2858	-129	24
H2B	2140	3132	461	24
H3C	876	3380	743	47
H3D	875	2751	652	47
H3E	212	3115	82	47
H4C	906	3670	-599	43
H4D	2011	3640	-471	43
H4E	1617	3955	29	43
H3A	2058	1309	2282	39
H3B	2186	1689	1805	39
H5C	623	1811	1353	53
H5D	957	1939	2120	53
H5E	467	1384	1855	53
H6A	1477	676	1509	50
H6B	2449	884	1450	50
H6C	1478	1095	953	50
H4A	3389	701	3523	20
H4B	4350	704	3499	20
H7A	4176	-109	3011	40
H7B	3349	271	2593	40
H7C	3157	-153	3086	40
H8A	3736	48	4309	48
H8B	4439	537	4558	48
H8C	4775	20	4266	48
H5A	702	56	4499	40
H5B	1376	171	4157	40
H9A	2594	97	5135	48
H9B	2036	-444	4895	48
H9C	1824	-96	5450	48
H10A	1003	829	5070	62
H10B	763	960	4308	62
H10C	1831	948	4777	62

SI Table 21. Anisotropic displacement parameters (Å^2 x 10^3) in **1M**. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	11(1)	10(1)	12(1)	0	4(1)	0
W2	8(1)	12(1)	10(1)	0(1)	3(1)	-2(1)
W3	6(1)	12(1)	9(1)	0(1)	1(1)	0(1)
W4	10(1)	12(1)	9(1)	-1(1)	3(1)	-1(1)
W5	8(1)	11(1)	10(1)	0(1)	2(1)	1(1)
W6	11(1)	13(1)	12(1)	0(1)	4(1)	3(1)
W7	17(1)	11(1)	16(1)	0	6(1)	0
O1	16(5)	11(2)	17(4)	-5(3)	4(3)	-4(3)
O2	10(1)	12(1)	11(1)	0(1)	2(1)	-1(1)
O3	14(4)	11(2)	11(2)	-1(2)	6(3)	-5(3)
O4	9(2)	19(5)	15(4)	-3(2)	5(2)	-4(2)
O5	10(2)	12(1)	11(1)	0(1)	2(2)	-1(1)
O6	7(2)	12(2)	10(1)	0(1)	2(1)	2(2)
O7	8(2)	15(2)	18(3)	-4(3)	3(3)	-4(2)
O8	7(2)	11(1)	9(2)	-1(1)	2(1)	0(1)
O9	11(4)	12(4)	8(2)	-1(2)	1(2)	0(2)
O10	6(2)	11(2)	9(3)	-1(2)	-1(2)	0(1)
O11	7(1)	13(1)	10(1)	0(1)	1(1)	1(1)
O12	11(2)	16(2)	21(4)	6(3)	3(3)	6(2)
O13	10(2)	12(1)	12(2)	1(1)	2(1)	0(1)
O14	11(1)	12(2)	9(2)	-1(2)	2(2)	-2(1)
O15	15(4)	18(4)	9(2)	-1(2)	3(2)	-4(3)
O16	10(1)	13(1)	11(1)	-1(1)	4(1)	1(1)
O17	8(2)	13(2)	11(1)	-1(1)	3(1)	1(2)
O18	12(2)	20(5)	15(4)	0(3)	6(3)	4(2)
O19	19(4)	14(2)	15(2)	-3(2)	5(3)	1(4)
O20	14(1)	12(1)	15(1)	1(1)	4(1)	2(1)
O21	15(4)	19(5)	10(4)	-1(3)	7(3)	-2(3)
N1	30(3)	31(4)	32(3)	0(2)	10(2)	0(2)
C1	38(10)	38(10)	37(6)	11(8)	19(7)	11(9)
C2	35(10)	54(14)	38(7)	15(9)	6(6)	-8(9)
N2	19(6)	11(5)	20(6)	-7(4)	-7(4)	4(5)
C3	26(8)	40(10)	20(8)	4(7)	-3(6)	-3(7)
C4	30(9)	25(7)	23(8)	1(5)	-3(6)	-4(7)
N3	33(3)	33(3)	32(3)	0(2)	10(2)	-2(2)
C5	34(4)	35(5)	35(5)	-1(3)	11(4)	0(3)
C6	34(5)	32(4)	34(5)	0(3)	10(4)	-1(3)
N4	14(6)	20(6)	16(5)	1(4)	4(4)	-9(5)
C7	28(9)	29(8)	22(6)	-7(5)	7(6)	-11(7)
C8	38(10)	37(10)	18(5)	6(6)	4(7)	4(8)
N5	33(3)	33(3)	34(3)	1(2)	10(2)	-1(2)
C9	32(4)	33(4)	32(4)	-1(3)	10(3)	0(3)
C10	53(14)	37(5)	41(11)	0(6)	25(10)	11(7)
O1W	20(6)	48(8)	17(5)	-2(5)	5(4)	-5(6)
O2W	74(14)	58(12)	100(17)	38(12)	57(13)	21(11)
O3W	21(7)	32(7)	52(9)	8(6)	4(6)	-5(6)
O4W	46(9)	31(7)	68(10)	24(7)	48(8)	15(6)
O5W	39(9)	55(10)	60(11)	-12(8)	27(8)	-15(8)

SI Table 22. Bond lengths (Å) and angles (°) in **1M**

W1-O1	1.74(1)	W1-O1#1	1.74(1)
W1-O2	1.89(1)	W1-O2#1	1.89(1)
W1-O8#1	2.31(1)	W1-O8	2.31(1)
W2-O3	1.75(1)	W2-O4	1.76(1)
W2-O5	1.84(1)	W2-O2	1.97(1)
W2-O8#1	2.17(1)	W2-O6	2.22(1)
W3-O7	1.72(1)	W3-O6	1.782(9)
W3-O8	1.90(1)	W3-O11	1.97(1)
W3-O9	2.05(1)	W3-O10	2.21(1)
W4-O15	1.719(9)	W4-O14	1.84(1)
W4-O9#1	1.88(1)	W4-O16	1.94(1)
W4-O5	2.00(1)	W4-O10#1	2.271(9)
W5-O12	1.72(1)	W5-O17	1.81(1)
W5-O13	1.88(1)	W5-O11	1.93(1)
W5-O14#1	2.10(1)	W5-O10	2.27(1)
W6-O18	1.73(1)	W6-O19	1.76(1)
W6-O16	1.89(1)	W6-O20	1.94(1)
W6-O17	2.20(1)	W6-O13#1	2.24(1)
W7-O21#1	1.76(1)	W7-O21	1.76(1)
W7-O20	1.89(1)	W7-O20#1	1.89(1)
W7-O13	2.27(1)	W7-O13#1	2.27(1)
N1-C2	1.45(3)	N1-C1	1.50(2)
N2-C3	1.45(2)	N2-C4	1.49(2)
N3-C5	1.43(3)	N3-C6	1.47(3)
N4-C7	1.47(2)	N4-C8	1.48(2)
N5-C9	1.43(3)	N5-C10	1.47(3)

O1-W1-O1#1	102.0(7)	O1-W1-O2	98.7(5)
O1#1-W1-O2	99.6(5)	O1-W1-O2#1	99.6(5)
O1#1-W1-O2#1	98.7(5)	O2-W1-O2#1	150.8(6)
O1-W1-O8#1	165.5(4)	O1#1-W1-O8#1	91.0(4)
O2-W1-O8#1	72.6(4)	O2#1-W1-O8#1	84.4(4)
O1-W1-O8	91.0(4)	O1#1-W1-O8	165.5(4)
O2-W1-O8	84.4(4)	O2#1-W1-O8	72.6(4)
O8#1-W1-O8	76.9(5)	O3-W2-O4	102.0(5)
O3-W2-O5	99.9(4)	O4-W2-O5	99.5(5)
O3-W2-O2	94.0(4)	O4-W2-O2	93.9(4)
O5-W2-O2	158.2(4)	O3-W2-O8#1	95.3(4)
O4-W2-O8#1	159.7(4)	O5-W2-O8#1	87.7(4)
O2-W2-O8#1	74.2(4)	O3-W2-O6	171.2(4)
O4-W2-O6	84.3(4)	O5-W2-O6	85.1(4)
O2-W2-O6	79.2(4)	O8#1-W2-O6	77.5(3)
O7-W3-O6	103.8(5)	O7-W3-O8	101.6(5)
O6-W3-O8	95.4(4)	O7-W3-O11	96.9(4)
O6-W3-O11	91.8(4)	O8-W3-O11	157.9(4)
O7-W3-O9	93.7(4)	O6-W3-O9	161.9(4)
O8-W3-O9	85.2(4)	O11-W3-O9	81.6(4)
O7-W3-O10	163.5(4)	O6-W3-O10	88.2(4)
O8-W3-O10	88.2(4)	O11-W3-O10	71.1(4)
O9-W3-O10	73.7(4)	O15-W4-O14	104.0(5)
O15-W4-O9#1	102.5(5)	O14-W4-O9#1	91.9(4)
O15-W4-O16	101.6(5)	O14-W4-O16	90.5(4)
O9#1-W4-O16	154.4(4)	O15-W4-O5	99.3(4)
O14-W4-O5	156.6(4)	O9#1-W4-O5	85.0(4)
O16-W4-O5	82.8(4)	O15-W4-O10#1	178.1(4)
O14-W4-O10#1	76.9(4)	O9#1-W4-O10#1	75.7(4)
O16-W4-O10#1	80.1(4)	O5-W4-O10#1	79.9(4)
O12-W5-O17	103.7(5)	O12-W5-O13	101.6(5)
O17-W5-O13	95.8(4)	O12-W5-O11	99.7(5)
O17-W5-O11	92.7(4)	O13-W5-O11	154.4(4)
O12-W5-O14#1	92.9(5)	O17-W5-O14#1	163.2(4)
O13-W5-O14#1	83.1(4)	O11-W5-O14#1	81.9(4)
O12-W5-O10	162.8(4)	O17-W5-O10	91.0(4)
O13-W5-O10	85.4(4)	O11-W5-O10	70.4(4)
O14#1-W5-O10	72.1(3)	O18-W6-O19	102.2(5)

O18-W6-O16	98.0(5)	O19-W6-O16	97.3(5)
O18-W6-O20	96.3(5)	O19-W6-O20	98.2(5)
O16-W6-O20	156.1(4)	O18-W6-O17	90.8(4)
O19-W6-O17	167.0(4)	O16-W6-O17	81.7(4)
O20-W6-O17	79.0(4)	O18-W6-O13#1	166.1(4)
O19-W6-O13#1	89.1(4)	O16-W6-O13#1	88.5(4)
O20-W6-O13#1	73.7(4)	O17-W6-O13#1	77.9(4)
O21#1-W7-O21	103.4(7)	O21#1-W7-O20	95.6(5)
O21-W7-O20	99.9(5)	O21#1-W7-O20#1	99.9(5)
O21-W7-O20#1	95.6(5)	O20-W7-O20#1	154.9(6)
O21#1-W7-O13	91.1(4)	O21-W7-O13	163.6(4)
O20-W7-O13	86.1(4)	O20#1-W7-O13	74.0(4)
O21#1-W7-O13#1	163.6(4)	O21-W7-O13#1	91.1(4)
O20-W7-O13#1	74.0(4)	O20#1-W7-O13#1	86.1(4)
O13-W7-O13#1	75.8(5)	W1-O2-W2	117.1(5)
W2-O5-W4	149.6(6)	W3-O6-W2	138.3(5)
W3-O8-W2#1	137.3(5)	W3-O8-W1	126.4(5)
W2#1-O8-W1	94.6(4)	W4#1-O9-W3	115.1(5)
W3-O10-W4#1	95.4(3)	W3-O10-W5	97.6(3)
W4#1-O10-W5	94.7(3)	W5-O11-W3	119.7(5)
W5-O13-W6#1	139.5(5)	W5-O13-W7	126.6(5)
W6#1-O13-W7	93.3(4)	W4-O14-W5#1	116.3(5)
W6-O16-W4	143.6(6)	W5-O17-W6	138.4(5)
W7-O20-W6	117.7(5)	C2-N1-C1	115(2)
C3-N2-C4	114(1)	C5-N3-C6	115(2)
C7-N4-C8	114(1)	C9-N5-C10	114(2)

SI Table 23. Torsion angles (°) in **1M**

O7-W3-O6-W2	61.8(9)	O8-W3-O6-W2	-41.6(8)
O11-W3-O6-W2	159.3(8)	O9-W3-O6-W2	-133(1)
O10-W3-O6-W2	-129.7(8)	O18-W6-O16-W4	-173.9(9)
O19-W6-O16-W4	-70.5(9)	O20-W6-O16-W4	60(2)
O17-W6-O16-W4	96.4(9)	O13-W6-O16-W4	18.4(9)
O21-W7-O20-W6	176.9(6)	O21#1-W7-O20-W6	-78.5(6)
O20#1-W7-O20-W6	48.8(5)	O13-W7-O20-W6	9.8(5)
O13#1-W7-O20-W6	86.2(6)	O12-W5-O13-W6	-128.7(9)
O17#1-W5-O13-W6	126.0(8)	O11-W5-O13-W6	17(2)
O14-W5-O13-W6	-37.1(8)	O10-W5-O13-W6	35.4(8)
O12-W5-O13-W7	63.6(7)	O17#1-W5-O13-W7	-41.7(7)
O11-W5-O13-W7	-150.8(7)	O14-W5-O13-W7	155.2(7)
O10-W5-O13-W7	-132.3(6)	O15-W4-O14-W5	179.6(5)
O9-W4-O14-W5	76.2(6)	O16-W4-O14-W5	-78.4(5)
O5#1-W4-O14-W5	-6(1)	O10-W4-O14-W5	1.4(5)
O15-W4-O9-W3	177.5(5)	O14-W4-O9-W3	-77.7(5)
O16-W4-O9-W3	18(1)	O5#1-W4-O9-W3	79.1(5)
O10-W4-O9-W3	-1.8(5)	O1-W1-O2-W2	-178.2(5)
O1#1-W1-O2-W2	77.9(6)	O2#1-W1-O2-W2	-50.0(4)
O8#1-W1-O2-W2	-10.1(4)	O8-W1-O2-W2	-88.0(5)
O3-W2-O5-W4#1	94(1)	O4-W2-O5-W4#1	-162(1)
O2-W2-O5-W4#1	-35(2)	O8#1-W2-O5-W4#1	-1(1)
O6-W2-O5-W4#1	-79(1)		

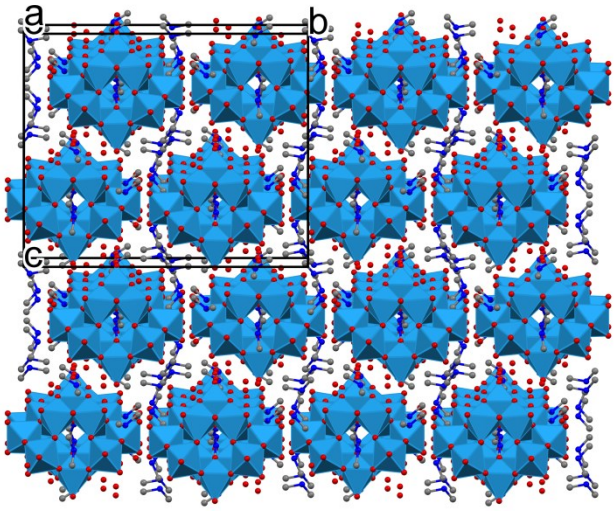
SI Table 24. Hydrogen bonds in **1M**.
Hydrogen bonding of the ammonium ions

Nr	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	sym op
1	N(1) --H(1A) ..O(16)	0.89	2.44	3.15(2)	138	x,y,z
2	N(1) --H(1A) ..O(17)	0.89	2.19	3.00(2)	150	x,y,z
3	N(1) --H(1B) ..O(4)	0.89	1.93	2.78(2)	157	1-x,y,1/2-z
4	N(1) --H(1B) ..O(6)	0.89	2.48	3.02(2)	119	1-x,y,1/2-z
5	N(2) --H(2A) ..O(9)	0.89	1.89	2.758(16)	164	1/2-x,1/2-y,-z
6	N(2) --H(2B) ..O(11)	0.89	1.95	2.763(17)	151	x,y,z
7	N(3) --H(3A) ..O(2)	0.89	2.56	2.93(2)	106	x,y,z
	N(3) --H(3A)					
8	..O(3W)	0.89	2.16	3.02(2)	160	-1/2+x,-1/2+y,z
9	N(3) --H(3B) ..O(2)	0.89	2.52	2.93(2)	109	x,y,z
10	N(3) --H(3B) ..O(7)	0.89	1.93	2.76(2)	154	x,y,z
	N(4) --H(4A)					
11	..O(3W)	0.89	1.92	2.80(2)	167	1-x,y,1/2-z
12	N(4) --H(4A) ..O(3)	0.89	2.58	2.895(16)	102	1/2-x,1/2+y,1/2-z
13	N(4) --H(4B) ..O(1)	0.89	2.04	2.883(18)	157	-1/2+x,1/2+y,z
14	N(4) --H(4B) ..O(3)	0.89	2.50	2.895(16)	107	1/2-x,1/2+y,1/2-z
15	N(5) --H(5A) ..O(19)	0.89	1.90	2.74(2)	157	x,y,z
16	N(5) --H(5B) ..O(21)	0.89	2.28	2.90(2)	126	1-x,y,1/2-z
17	C(1) --H(1C) ..O(18)	0.96	2.49	3.15(3)	125	x,y,z
18	C(2) --H(2D) ..O(11)	0.96	2.59	3.46(3)	150	1-x,y,1/2-z
19	C(3) --H(3E) ..O(3)	0.96	2.43	3.31(2)	152	-1/2+x,1/2-y,-1/2+z
20	C(4) --H(4C) ..O(3)	0.96	2.49	3.35(2)	149	-1/2+x,1/2-y,-1/2+z
21	C(5) --H(5E) ..O(21)	0.96	2.49	3.43(3)	169	1/2-x,-1/2+y,1/2-z
22	C(6) --H(6A) ..O(19)	0.96	2.52	3.30(2)	139	-1/2+x,-1/2+y,z
23	C(7) --H(7C) ..O(12)	0.96	2.42	3.32(2)	155	x,y,z
24	C(9) --H(9B) ..O(14)	0.96	2.42	3.24(2)	144	x,y,z
25	C(9) --H(9C) ..O(19)	0.96	2.45	3.28(2)	144	1-x,1-y,-z
	C(10) --H(10B)					
26	..O(21)	0.96	2.51	3.08(3)	118	1-x,y,1/2-z

SI Table 25. Summary of the shortest inter contacts with d(I-J) < R(I) + R(J) + 0.2 of the water molecules in **1M**

Nr	D-H...A			D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	sym op
1	O(1W)	....	W(2)	-	-	3.878(13)	-	1-x,y,1/2-z
2	O(1W)	....	O(3)	-	-	2.843(17)	-	1-x,y,1/2-z
3	O(1W)	....	O(2W)	-	-	2.96(3)	-	3/2-x,1/2-y,-z
4	O(1W)	....	O(5W)	-	-	2.87(2)	-	3/2-x,1/2-y,-z
5	O(2W)	....	O(4W)	-	-	2.79(3)	-	x,y,z
6	O(2W)	....	O(1W)	-	-	2.96(3)	-	3/2-x,1/2-y,-z
7	O(3W)	....	W(7)	-	-	3.853(16)	-	x,y,z
8	O(3W)	....	O(21)	-	-	2.65(2)	-	x,y,z
9	O(3W)	....	W(2)	-	-	3.599(15)	-	1/2+x,1/2+y,z
10	O(3W)	....	O(3)	-	-	3.185(19)	-	1/2+x,1/2+y,z
11	O(3W)	....	O(4)	-	-	2.813(18)	-	1/2+x,1/2+y,z
12	O(4W)	....	O(2W)	-	-	2.79(3)	-	x,y,z
13	O(4W)	....	O(18)	-	-	2.79(2)	-	x,y,z
14	O(4W)	....	O(1)	-	-	2.820(18)	-	1/2+x,1/2+y,z
15	O(5W)	....	O(1W)	-	-	2.78(2)	-	x,y,z
16	O(5W)	....	O(15)	-	-	2.85(2)	-	x,y,z
17	O(5W)	....	O(1W)	-	-	2.87(2)	-	3/2-x,1/2-y,-z

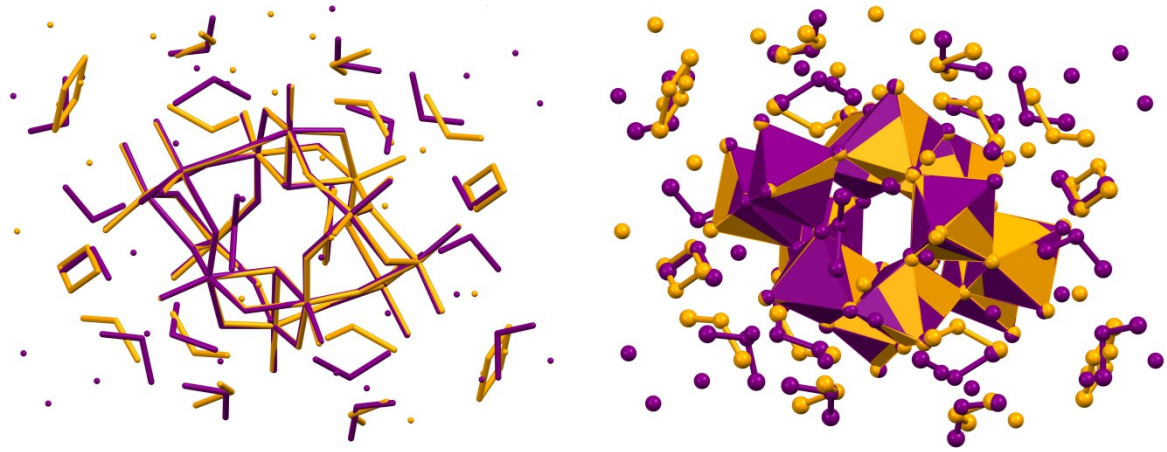
1M crystallizes in the monoclinic system, in the *C*2/*c* space group (Figure 7). The asymmetric unit contains one half dihydrododecatungstate(10-) anion, five dimethylammonium cations and five water molecules. **1M** is a polymorphic modification of **1T**. The $[H_2W_{12}O_{42}]^{10-}$ polyanion contains a twofold symmetry axis but it is not centrosymmetric.



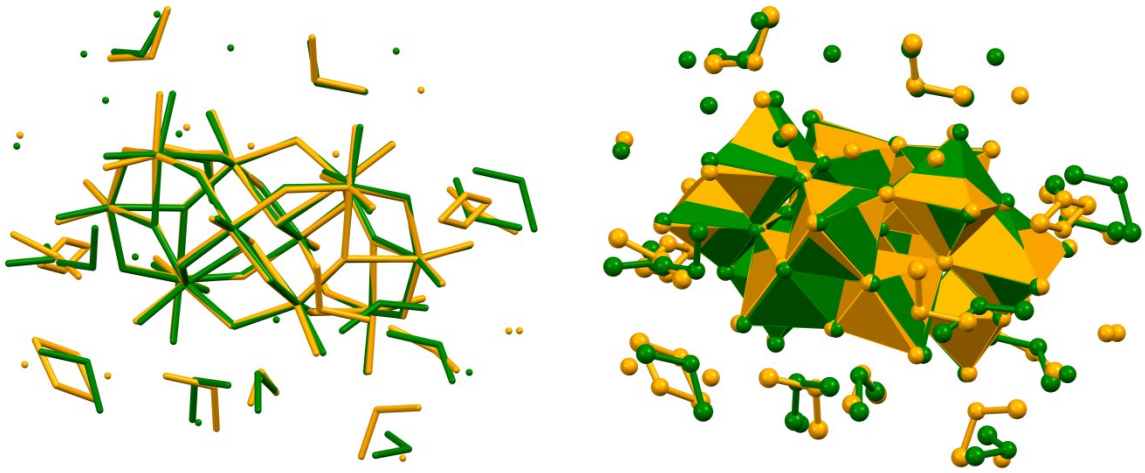
ESI STR Figure 7. Packing of the **1M** form (view *a* axis)

V. Hydrogen bonding in the three crystal forms

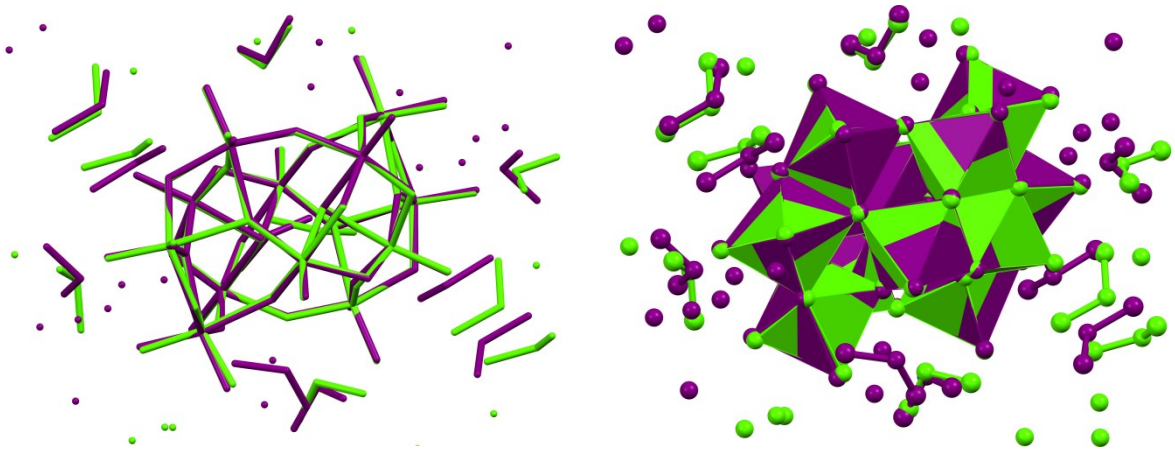
Numerous N-H...O and C-H...O hydrogen bonds are formed in the studied crystal structures between the ammonium cations and the heteropolytungstate anions. The water molecules take part in the hydrogen bond system as well. The 10 ammonium cations form a large number of hydrogen bonds in each structure mainly with the polytungstate anion. Ammonium cation...water hydrogen bonds are few and only present in the **1M** structure. The largest number of N-H...O(cage) hydrogen bonds (31) is formed in the **2T** modification. The hydrogen bonds of the three structures are listed in Tables 9-10, 17-18 and 24-25. The cage molecules of the $[H_2W_{12}O_{42}]^{-10}$ anions are nicely superimposable in all of the three structures. Thus, the positions of the dimethylammonium cations are mostly similar in the different crystal forms. On the other hand, the water molecules are placed rather randomly in the three different unit cells.



SI Figure 8. Overlay of **1T** (orange) and **2T** (purple) structures (stick and polyhedral representations)



SI Figure 9. Overlay of **1T** (orange) and **1M** (green) structures (stick and polyhedral representations)

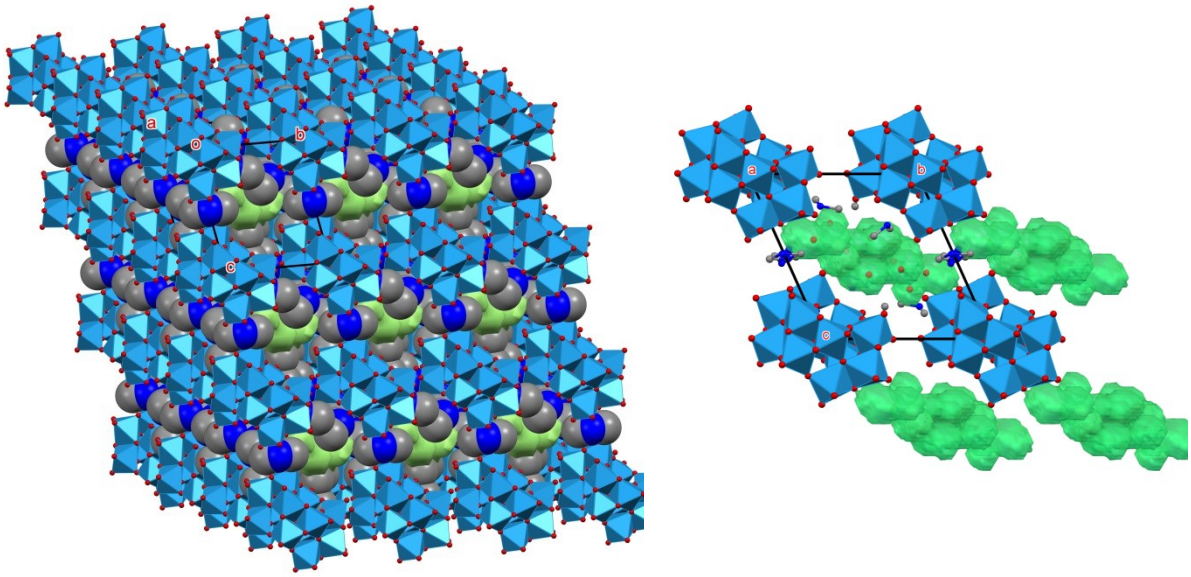


SI Figure 10. Overlay of **2T** (purple) and **1M** (green) structures (stick and polyhedral representations)

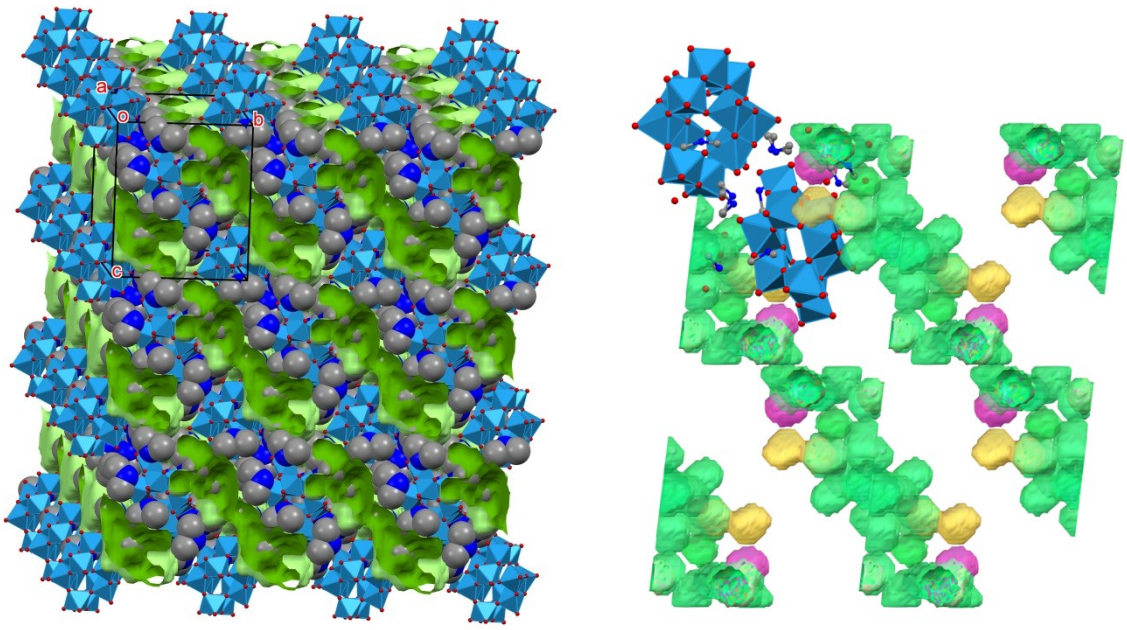
The two disordered ammonium nitrogens of **1T** are linked by an inversion centre and are disordered between two possible hydrogen bonding sites. On the basis of the inter-atomic distances, the disordered ammonium cations are relatively less strongly bonded than the other amines.

VI. Water channels or islands in the three structures

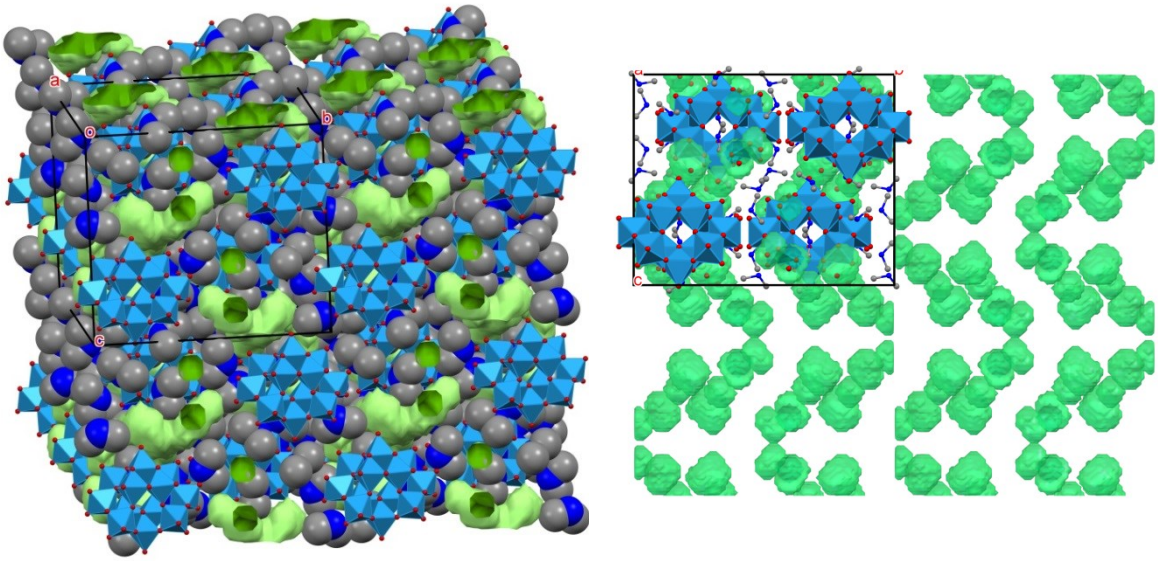
The percentage of the occupied space by the 10 crystal water in **1T** is 11.8 % (SI Fig. 11) and in **1M** 9.3 %. The water molecules are located in drops between the polytungstate cages. The **2T** structure has 11 water molecules per unit cell. The 11 water molecules occupy 14.6 % of the unit cell volume and the water drops are merged two by two and quasi contiguous water channels are formed in the structure.



SI Figure 11. Water drops (green) in the structure of **1T** (polytungstate anions are illustrated by polyhedral representation and the ammonium cations by spacefill or ball and stick representation)



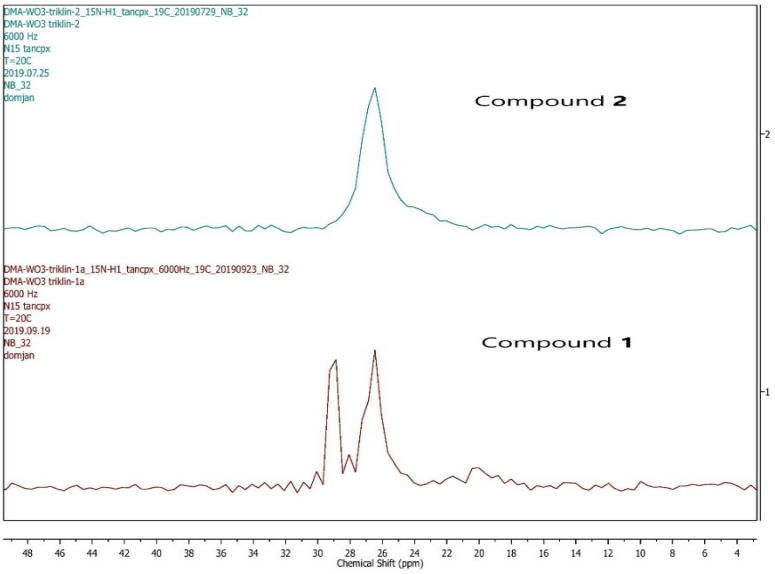
SI Figure 12. Water drops (green) in the structure of **2T** (polytungstate anions are illustrated by polyhedral representation and the ammonium cations by spacefill or ball and stick representation)



SI Figure 13. Water drops (green) in the structure of **1M** (polytungstate anions are illustrated by polyhedral representation and the ammonium cations by spacefill or ball and stick representation)

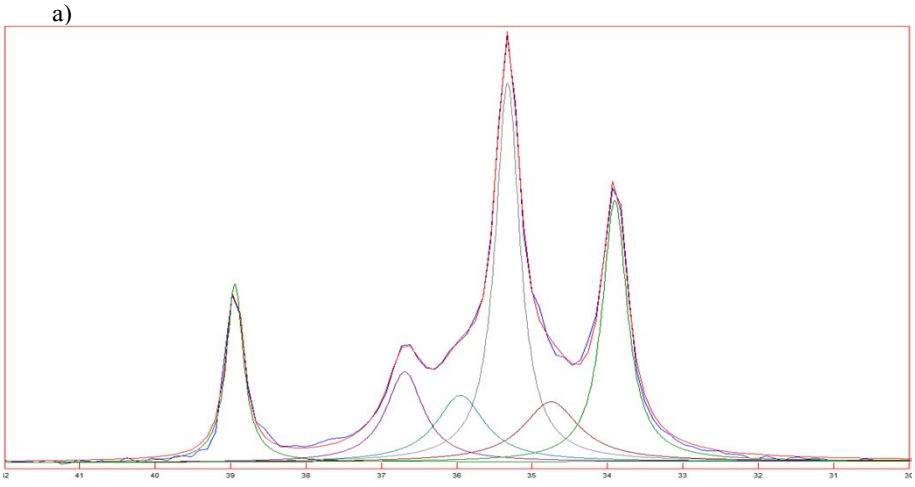
VII. Solid state NMR studies

Solid-state NMR magic angle spinning (MAS) spectra of samples were recorded on a Varian System spectrometer with a Chemagnetics 3.2 mm narrow-bore triple resonance T3 probe in double resonance mode. The spinning rate of the rotor was 10 kHz for the ^{1}H, ^{13}C and 6 kHz for the ^{15}N measurements. For the CP MAS (cross polarization magic angle spinning) spectra 12000 transients were recorded with SPINAL-64 decoupling, 2 ms of contact time for the ^{13}C and 50000 transient with 4 ms contact time for the ^{15}N experiments. For the cross polarization experiments 10 seconds of recycle delay was used. The measuring temperature was 20 °C. Adamantane was used as external chemical shift reference (38.55 and 29.50 ppm) for the ^{13}C and labeled glycine (32.5 ppm) for the ^{15}N channel. The 90° pulse lengths were 2.9 µs for carbon, 6.5 µs for the ^{15}N and 2.9 µs for the proton channel. Windowed DUMBO [REF-DUMBO] experiment was used for the ^{1}H CRAMPS (Combined Rotation and Multiple-Pulse Sequence) measurements with 10 kHz of spinning rate.[5]



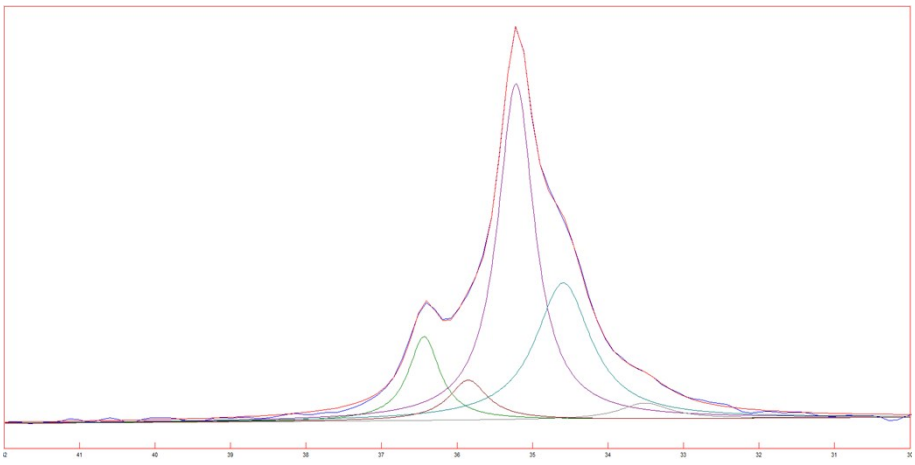
SI Figure 14. $^{15}N\{^{1}H\}$ Solid phase CP MAS NMR of compounds **1 (1T)** and **2 (2T)**

a)



No	Chem. Shift (ppm)	Integral (%)	Ratio
1	38.9	10.6	1.00
2	36.7	11.6	1.09
3	36.0	11.0	1.04
4	35.3	31.9	3.01
5	34.8	12.5	1.18
6	33.9	22.5	2.12

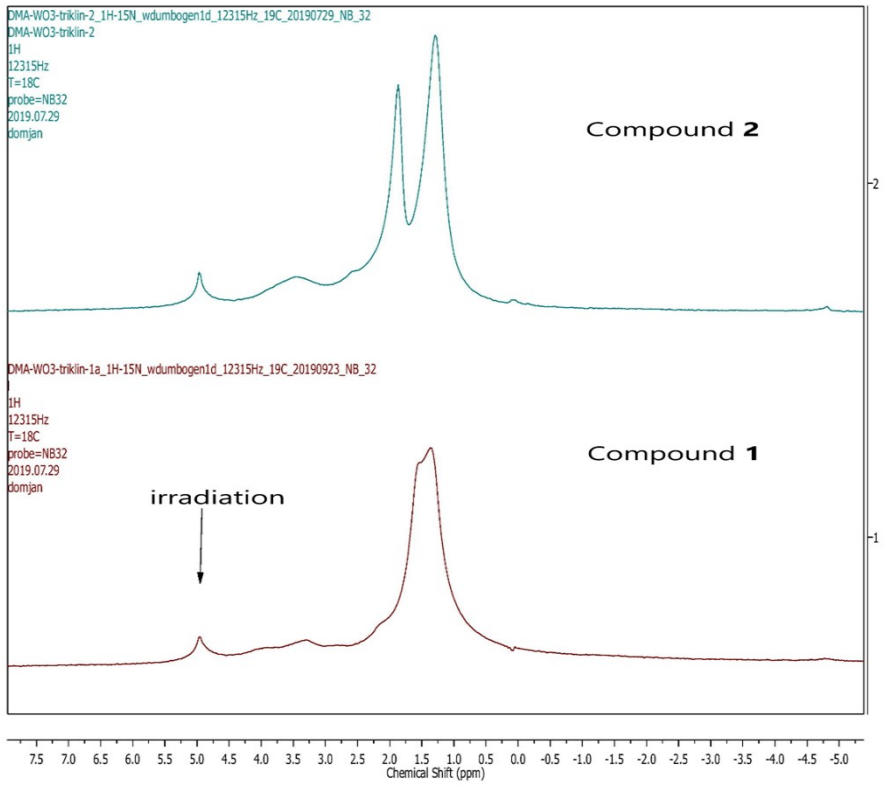
b)



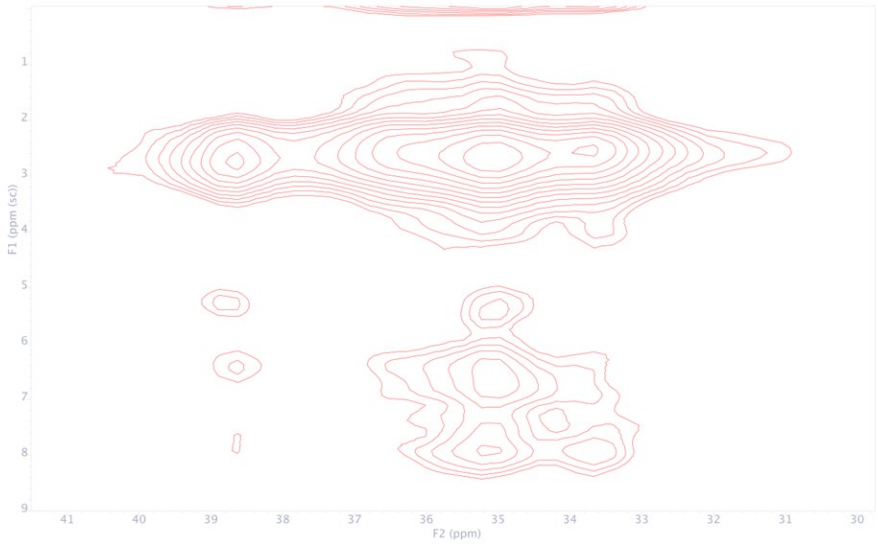
(b)

No	Chem. Shift (ppm)	Integral (%)	Ratio
1	36.435.9	10.7	3.34
2	35.9	6.2	1.93
3	35.2	49.9	15.6
4	34.6	30.1	9.40
5	33.5	3.2	3.34

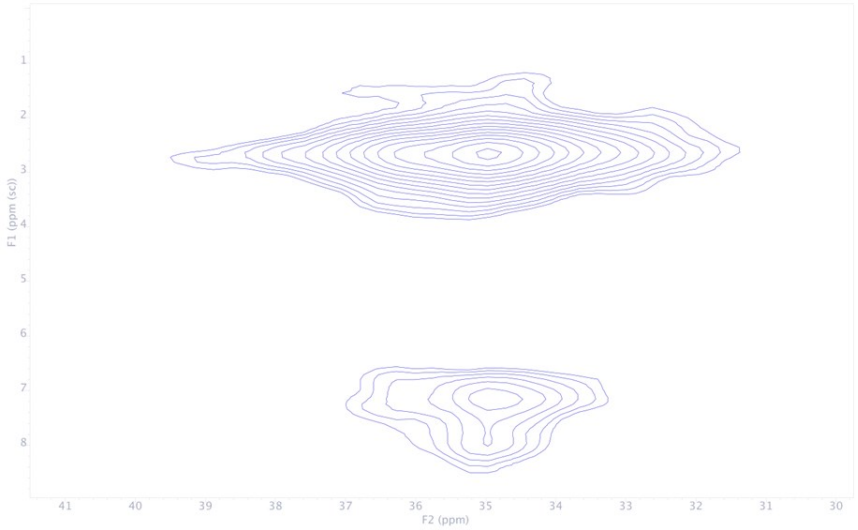
SI Figure 15a and 15b.. ^{13}C CP MAS NMR spectra of compounds **1 (1T)** (a) and **2 (2T)** (b).



SI-Figure 16. $^{1}H\{^{15}N\}$ Solid phase CRAMPS NMR of compounds **1 (1T)** and **2 (2T)**



a)



b)

SI Figure 17. ^{13}C-^{1}H heterocorrelation CP MAS NMR of compounds **1 (1T)** (a) and **2 (2T)** (b)

VIII. Conductivity studies

The conductivity of a solution is the sum of the conductivities of the ions present in it. If some of the tungstate anions carrying 10 negative charge are associated to *m* cations, then these associated cations will not contribute to the conductivity, and the participation of the anion, carrying now only 10-*m* charge is also reduced. Measurement of the conductivity then can help one to estimate the average amount of ion associates. To assess the degree of association, we measured the electric conductivities of aqueous solutions of $Na_{10}H_2W_{12}O_{42}$ and of $(Me_2NH_2)_{10}H_2W_{12}O_{42}$ at various concentrations at room temperature. The sodium ion cannot form hydrogen bonds, and in the solution only electrostatic attraction can induce ion association, the amount of which increases with increasing concentration (resulting in a relative reduction of conductivity). The electrostatic interaction operates roughly the same way in the salt of dimethylammonium cations, but, based on the reduced deuterium exchange, we expect additional conductivity decrease due to the propensity of $Me_2NH_2^+$ to form hydrogen-bonded associates with the anion. The comparison of the *relative* association degree obtained for the two solutions will be a measure of the contribution caused by the ability of the ammonium ions to form hydrogen bonds.

If one assumes that neither the dimethylammonium nor the Na^+ cation forms associates with the dodecatungstate anion in dilute aqueous solutions of compound **1T** (or **2T**), one can formulate two pairs of solutions in which the overall number and type of ions is identical, so that the overall electric conductivities of the two pairs of solutions should be equal. One pair consists of the solution of one equivalent of $[Me_2NH_2]_{10}H_2W_{12}O_{42}$ and another containing 10 equivalents of fully dissociated NaCl. In the other pair the cations are interchanged, the solutions being that of one equivalent of $Na_{10}H_2W_{12}O_{42}$ and that of 10 equivalents of fully dissociated $[Me_2NH_2]Cl$. Knowledge of the limiting conductivities of the ions can help one to obtain quantitative information from measurable conductivity data. Literature data are available on the limiting molar conductivities of the cations: $Me_2NH_2^+$ (51.8 S/(cm^{2}mol) and Na^+ ions (50.08 S/(cm^{2}mol), and that of one of the anions, Cl^- (76.31 S/(cm^{2}mol).[6] The limiting molar conductivity of the $H_2W_{12}O_{42}^{10-}$ ion is not available in the literature, and so we determined it. It was found to be λ^0(1/10[$H_2W_{12}O_{42}$](10-))=69.90 S/(cm^{2}mol). The numbers show that the conductivities of the two cations are essentially the same, and those of the two anions also differ by less than 10 %, which is in the order of accuracy of the measurements.

ESI CDT Table 26. Limiting molar conductivities of the aqueous solutions of decakis(dimethylammonium) dihydrogendodecatungstate(10-), decasodium dihydrogendodecatungstate(10-), $[Me_2NH_2]Cl$ and NaCl at 25 °C

Ion	λ_+^0 (S cm^2- mol)	λ_-^0 (S cm^2- mol)	Λ^0, (S cm^2- mol)
NaCl	50.08	76.31	126.39
Me_2NH_2Cl	51.80	76.31	128.11
$Na_{10}H_2W_{12}O_{42}$	50.08	69.90	120.00
$(Me_2NH_2)_{10}W_{12}O_{42}$	51.80	69.90	121.70

It is known that the dihydrogendodecatungstate(10-) ion slowly hydrolyzes in aqueous solution, thus the electric conductivity increases with time and temperature.[7] This complicates the measurement of the molar conductivity of $H_2W_{12}O_{42}^{10-}$ ion. To ensure that the measurement yields the value corresponding to the undissociated ion, we performed it at room temperature, where the hydrolysis reaction is slow, within five minutes after dissolution. We believe that the value we obtained, characterizes the undissociated dihydrogendodecatungstate(10-) ion.

From this one can deduce that the conductivity of the solution of compound **1T** (**2T**) and that of $Na_{10}H_2W_{12}O_{42}$ at the same concentrations should also be relatively close to each other, if none of them forms associates, or when the degree of association in the two solutions is identical. So, if any difference can be found experimentally between the two conductivities, it must be proportional to the difference in the association degree of the two salts.

The measured conductivity values of the solutions of the two dodecatungstate solutions of identical concentrations (*c*=0.1-0.0001 M) are shown in SI Table 27.

SI Table 27. Conductivity of $Na_{10}[H_2W_{12}O_{42}]$ (a) and $(Me_2NH_2)_{10}[H_2W_{12}O_{42}]$ (b) solutions at room temperature

Concentration	conductivity, μS/cm
0.01 M	3849.9
0.005 M	2211.3
0.001 M	584.8
0.0005 M	185.7
0.0001 M	78.61
0.00005 M	47.97
0.00001 M	15.89
0.000005 M	7.90

Concentration	Conductivity, μS/cm
0.1 M	3428.6
0.05 M	2068.5
0.01	582.0
0.005	344.2
0.001	80.06
0.0005	46.30
0.0001	12.20
0.00005	6.59

IX. Limited solution-phase H/D exchange in heavy water

We attempted to determine the number of crystallization water molecules with the help of NMR spectroscopy, and found an unexpected curiosity. If one exchanges the water protons with deuterium by dissolving the compound in heavy water, the amount of the formed HDO can be measured by proton NMR spectroscopy. The method, described in more detail in ref.[8] relies on the presence of some non-exchangeable protons whose signal can be used as a reference, by comparing the HDO signal area determined by ^{1}H NMR with that obtained for the known amount of "permanent" protons. The method can be reliably applied if the H/D exchange is quick, which happens when the protons are capable of ionic dissociation, what is common for crystallization water molecules. In compounds **1T**, and **2T** the six covalently bound methyl H atoms contained by each $Me_2NH_2^+$ group are permanent, cannot be exchanged at all and so they can be used as a reference. The N-H protons of dimethylammonium cations and the O-H protons of the crystallization water molecules, on the other hand, are expected to be able to dissociate and as such, to be easily exchanged by deuterium. (The two internal hydrogen atoms in the polytungstate anion have been shown not to be easy to exchange by D so they would not contribute to HDO formation in **1T** or **2T**.) Accordingly, dissolution of compound **1** in excess of heavy water should turn each molecule of compound **1** into 10 perdeuterated $(CH_3)_2ND_2^+$ cations and one undeuterated polytungstate anion, with a concomitant formation of 20 mol of HDO from the cation, resulting in a methyl:HDO signal area of 60:20 corresponding to the 10:20 $(CH_3)_2ND_2$:HDO ratio. The HDO molecules formed from the *n* crystallization water molecules (*n* is 10 in **1** and 11 in **2** according to the indirect TG method, see the previous section**)** would contribute 2*n* HDO molecules). Thus, one expects a 10:(20+2*n*) $(CH_3)_2ND_2$:HDO ratio. The ratio we obtained with the deuterium isotope exchange-^{1}H NMR method (SI Fig. 18), however, is 1:2.5. If one supposes that all N–H protons of the cations are exchanged by D, then this ratio corresponds to only 2.5 water molecules per each dodecatungstate unit, which is much less than what we expected based on the TG data. Reduced $(CH_3)_2ND_2$:HDO ratio can also result from partial instead of complete deuteration of the amine groups. As the other extreme, if one supposes that *n*=10 as the TG method suggests, and all the 20 water protons are exchanged by D, then from the measured ratio one gets that only 25% of the N–H protons are exchanged. In either case, the conclusion is that a large fraction of the crystallization water molecules and/or the $Me_2NH_2^+$ ions do not release protons, from which one can surmise that these molecules/ions remain associated with one or more polytungstate anion in the solution through bonds that are able to prevent their ionic dissociation.

Another observation that deuteration of the dodecatungstates we synthesized is not easy and quick was made when we attempted to deuterate compound **2**. (Note that **1** cannot be deuterated in aqueous solution, because it is converted into **2** when placed in (heavy) water). While recrystallization of **1** from pure water resulted in the triclinic solvatomorph **2** with 11 crystallization water molecules, recrystallization from D_2O produced only partially deuterated **2**. For the preparation of the perdeuterated isotopolog of **2** four recrystallization steps were needed in a vacuum desiccator filled with fresh anhydrous CaO in each step. In all four deuteration steps we made certain that the D/H ratio exceeded 50. This aggressive procedure was necessary to ensure that both the dimethylammonium groups and the crystallization water molecules be completely deuterated. This observation supports the assumption that the ionic dissociation of the water and ammonium protons is far from being fast.

We note that the internal H atoms of the dihydrogen-dodecatungstate anions remain protium atoms even after such a vigorous treatment, supporting the observations in the literature.[8]

One expects that the crystallization water molecules and organic cation are connected to the decakis(dimethylammonium) dodecatungstate by NH…O, OH…N, OH…O and possibly CH…O hydrogen bonds. The H atoms making these bonds can generally dissociate as ions, allowing facile complete deuteration. The observation that some of such H atoms cannot be exchanged by D suggests that they are in an environment that prevents their ionic dissociation. A possible scenario is that some of such H atoms are involved in multiple hydrogen bonds by being bound to not one but two or more H-bond acceptors in addition to the one to which they are covalently bound. Such branching of hydrogen bonds is often termed bi- or trifurcation, and this bonding pattern has the propensity to form 3-dimensional networks. In principle, the number of such bonds could be determined by the NMR method described above, by using the signal corresponding to hydrogen atoms involved in multiple bonds. However, such protons give extremely broad and weak NMR signals, which are indistinguishable from the baseline.

A possible explanation for these observations is that the H atoms that are not exchangeable by deuterium are immobilized in multiple hydrogen bonds.

X. Powder X-ray diffraction and indexing

dimethyl amin WO3 (KL_1601a.rd, Kótai, 2016 okt.)

Zero error contribution removed from observed and calculated values

SG=P-1 3 0 vol=**1915.79** GOF=12.72 zero=0.0323

11.2081 11.3835 16.8441

96.629 103.057 110.504

h	k	l	dc	do	do-dc	2Thc	2Tho	2Tho-2Thc
0	0	1	16.0312	15.9638	-0.0674	5.5082	5.5315	0.0233
0	1	0	10.4171	10.3712	-0.0459	8.4813	8.5189	0.0376
1	0	0	10.0586			8.7841		
1	0	-1	9.8898	9.8512	-0.0386	8.9343	8.9694	0.0351
0	-1	1	9.7347	9.6974	-0.0374	9.0770	9.1120	0.0350
1	-1	0	9.2548	9.2275	-0.0273	9.5487	9.5770	0.0283
1	-1	-1	8.2848	8.2515	-0.0333	10.6699	10.7130	0.0432
0	0	2	8.0156			11.0293		
0	1	1	7.9910	7.9885	-0.0025	11.0633	11.0668	0.0035
1	-1	1	7.7701	7.7335	-0.0366	11.3798	11.4329	0.0541
1	0	1	7.5872	7.5716	-0.0257	11.6386	11.6782	0.0396
1	0	-2	7.3828			11.9778		
0	-1	2	7.1298	7.1172	-0.0126	12.4046	12.4267	0.0221
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1	-1	-2	6.2937			14.0603		
1	1	0	6.1403			14.4134		
1	-1	2	5.8487	5.8344	-0.0143	15.1361	15.1734	0.0373
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0	1	2	5.7844	5.7715	-0.0129	15.3055	15.3399	0.0344
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1	1	1	5.2329			16.9297		
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2	0	1	4.4487			19.9421		
1	-2	-2	4.4466			19.9516		
0	1	3	4.3897			20.2132		
2	-2	1	4.3608			20.3483		
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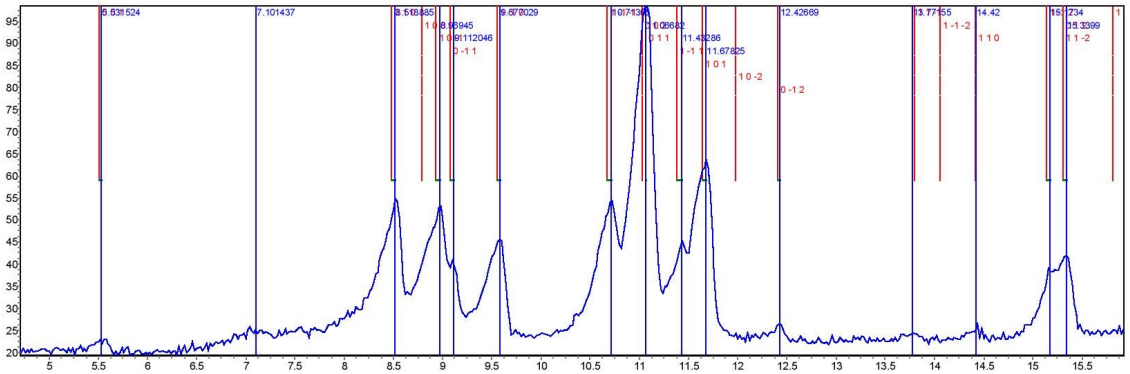

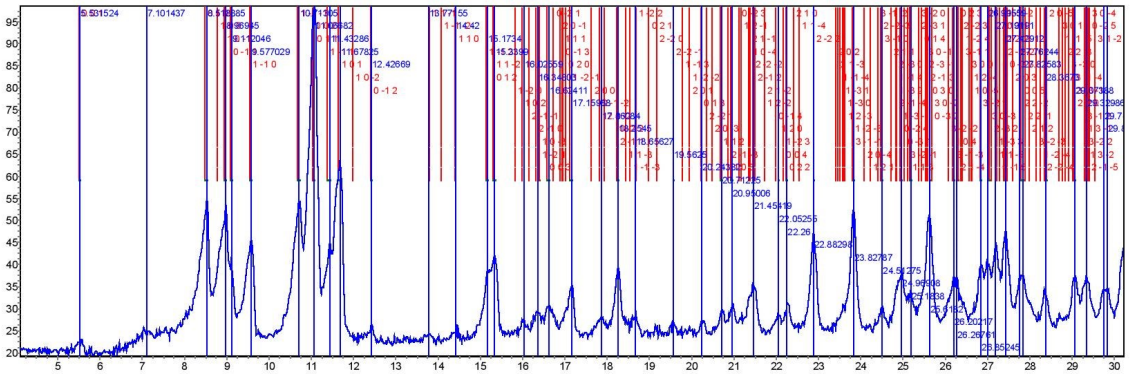

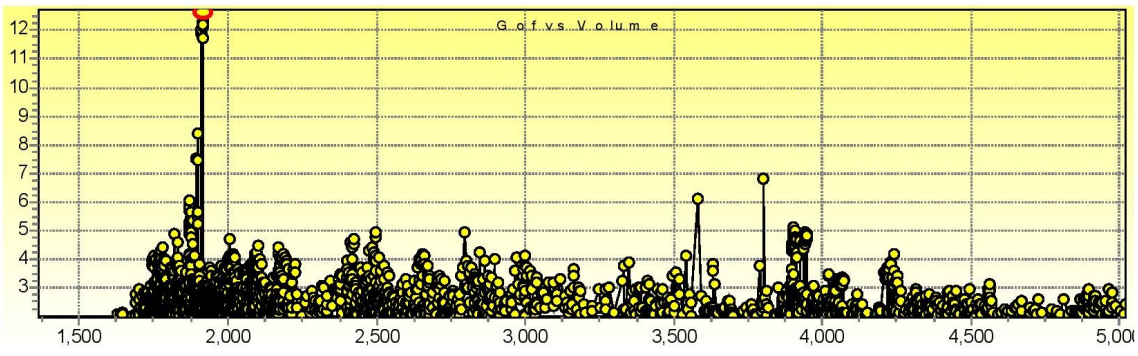

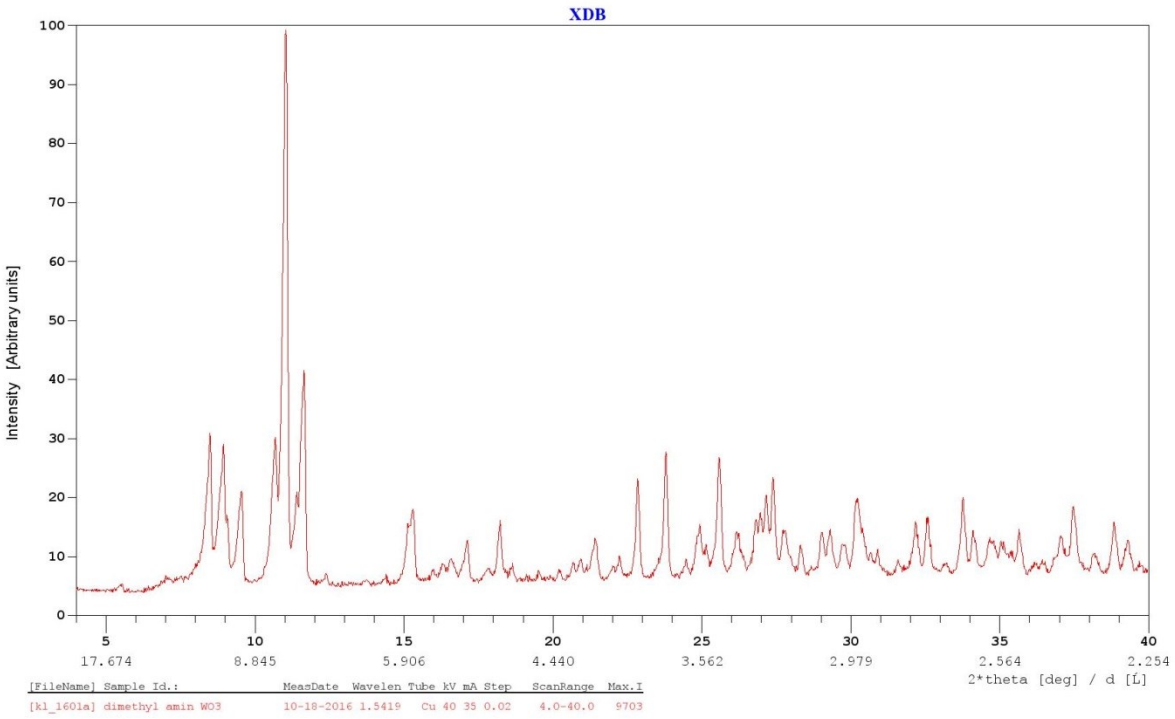
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4.440
3.562
2.979
2.564
2.254
2*theta [deg] / d [Å]
[FileName] Sample Id.: MeasDate Wavelen Tube kV mA Step ScanRange Max.I
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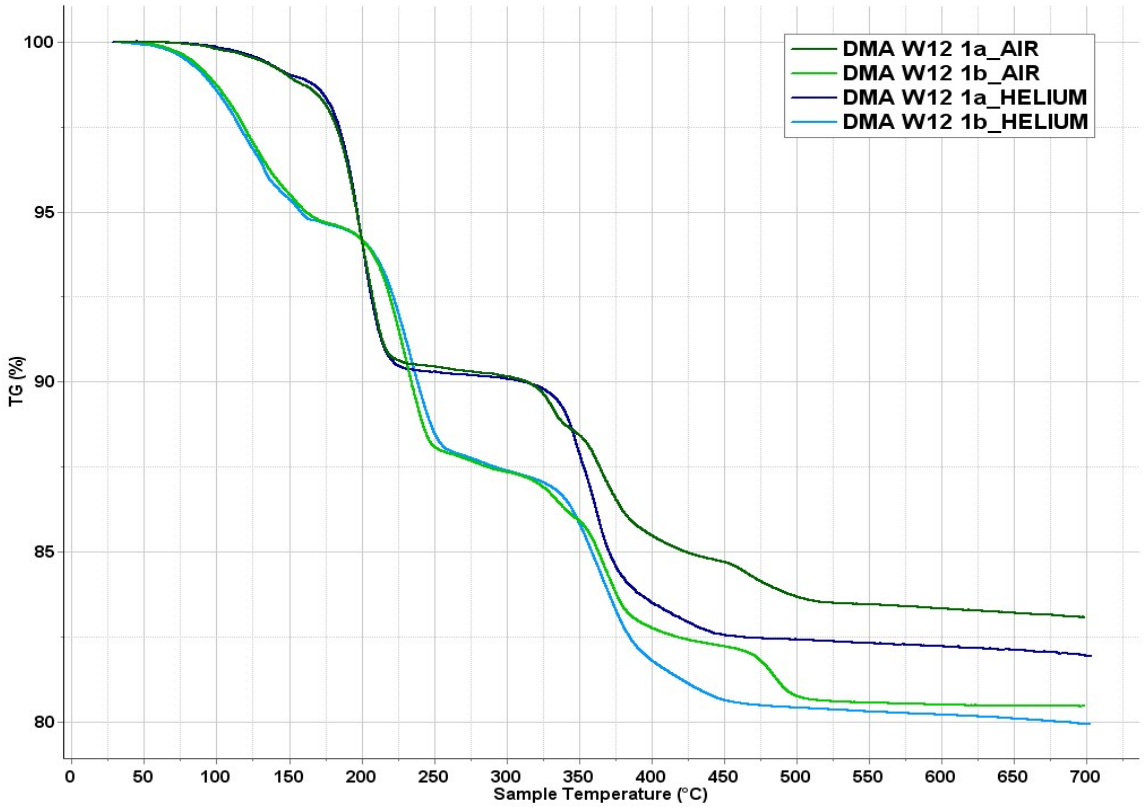
XI. TGA study


DMA W12 1a_AIR
DMA W12 1b_AIR
DMA W12 1a_HELIUM
DMA W12 1b_HELIUM
TG (%)
100
95
90
85
80
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
Sample Temperature (°C)

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