

B- α -[AsW₉O₃₃]⁹⁻ polyoxometalates incorporating hexanuclear uranium {U₆O₈}-like clusters bearing the U^{IV} form or unprecedented mixed valence U^{IV} - U^{VI} involving cation-cation interaction.

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Experimental section

Single-crystal X-ray diffraction

Crystal of **1-3** were selected under polarizing optical microscope and glued on a mitegen loop for single-crystal X-ray diffraction experiments. Because of the instability of the crystalline network due to the loss of crystallization water from the lattice, all measurements were performed at 100K under a nitrogen flow. X-ray intensity data were collected on a Bruker X8-APEX2 CCD area-detector diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) with an optical fiber as collimator. Several sets of narrow data frames (10 s per frame) were collected at different values of θ for two initial values of ϕ and ω , respectively, using 0.3° increments of ϕ or ω . Data reduction was accomplished using SAINT V7.53a.¹ The absorption was performed using a numerical absorption correction based on the faces indexation of the crystal (SADABS V2.10).² The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELX program suite.³ The final refinements include anisotropic thermal parameters of all non-hydrogen atoms, except the nearly NPD oxygen atoms of the molecules or solvent water molecules. The crystal data are given in Table S1. Supporting information is available in CIF format.

Infrared spectroscopy

Infrared spectra of the compounds (see Supplementary information) were measured on Perkin Elmer Spectrum TwoTM spectrometer between 4000 and 400 cm^{-1} , equipped with a diamond Attenuated Total Reflectance (ATR) accessory. Spectra are shown in Figure S5.

Micro-Raman spectroscopy

Micro-Raman spectroscopy was performed on a LabRam HR visible spectrometer equipped with a HeNe laser at 633 nm. Spectra were measured between 1200 and 400 cm^{-1} . The spectrum is equipped with a CCD 1024x256 pixels chip MPP Back illuminated Deep

Depleted detector cooled with liquid nitrogen. The samples are placed on a motorized XY sample holder with 0.1 μm resolution. Spectra are shown in Figure S6.

SEM photography's

Images of the crystals of the three compounds are shown in Figure S7. Photography's of the crystals were performed on a HITACHI S3400N SEM equipped with a tungsten filament.

Thermogravimetric analysis

The thermogravimetric experiments have been carried out on a thermoanalyzer TGA 92 SETARAM under air atmosphere with a heating rate of $1^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature up to 800°C . Curves are shown in Figure S8.

Inductively Coupled Plasma Spectroscopy

Crystals of compound **1-3** were dissolved in 2% HNO_3 solutions and were analyzed using a Vista-Pro Varian ICP-OES. Each compound was analyzed separately to determine the Na/As/W/U ratios. Based on the number of W atoms in each compounds, the percentages of each element can be determined.

EPR measurements

The spectra of the compounds were recorded at a temperature of 5K using an ELEXYS E580E X band spectrometer. The amplitude modulation and microwave power was set to respectively 5G and 2mW

Synthesis

Caution! Uranium tetrachloride (UCl_4) is a radioactive and chemically toxic reactant, so precautions with suitable care and protection for handling such substances have been followed.

The compound has been synthesized by using the following chemical reactants: uranium tetrachloride (UCl_4 , obtained from the protocol using the reaction of hexachloropropene with uranium oxide), acetate buffer (solution made by using glacial acetic acid (Carlo Erba reagent, 99.9%) and sodium acetate (Merck, 99%)). The starting chemical reactants (except UCl_4) are commercially available and have been used without any further purification. $\text{B-Na}_9[\alpha\text{-AsW}_9\text{O}_{33}]\cdot 13\text{H}_2\text{O}$ was synthesized according to a literature procedure.⁴

Compound 1 and 2

$\text{Na}_9[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]\cdot 13\text{H}_2\text{O}$ (250 mg, 0.093 mmol) is dissolved in 5 ml of 1M acetate buffer (pH = 4.7). The solution is then added to green solid UCl_4 (106 mg, 0.28 mmol). The solution turns to brown quickly and is stirred and heated to 70°C for 30 minutes. The solution is left to crystallize at room temperature by slow evaporation of the solvent. After 1 day, brown block like crystals started to appear (compound **1**) and were collected. The following day, small clear brown parallelepiped crystals (compound **2**) suitable for X-ray diffraction analyses started to appear and were gathered after 1 day before accumulation of a great quantity of $\text{Na}[\text{U}^{\text{VI}}\text{O}_2(\text{OAc})_3]$ (OAc = acetate) as yellow octahedral crystals obtained by partial oxidation

of the tetravalent uranium in solution.⁵ ($m_{cp1} = 31$ mg, yield = 11% and, $m_{cp2} = 78$ mg, yield = 26% based on AsW_9O_{33}).

(1) IR (cm^{-1}): 939 (w), 857(m), 808(shoulder), 776(w), 715(shoulder), 669(m), 635(m), 455(m).

ICP-OES for $Na_{19}[(AsW_9O_{33})_3(OAc)_2(U^{IV})_{5.5}(\mu^3-OH)_4(\mu^3-O)_4(U^{VI}O)_{0.5}] \cdot 47H_2O$: Na (3.77%), As (2.10%), W (47.34%), U(14.26%). Calculated: Na (4.22%), As (2.17%), W (47.93%), U(13.79%)/

(2) IR (cm^{-1}): 980 (shoulder) 946 (w), 852(m), 818(shoulder), 785(w), 717 (shoulder), 672(m), 640(m), 499(m), 460(m).

ICP-OES for $Na_{15}[(AsW_9O_{33})_3(U^{IV})_3(U^{VI}O)_3](\mu^3-OH)_4(\mu^3-O)_4 \cdot 32H_2O$: Na (3.36%), As (2.38%), W (50.73%), U(15.08%). Calculated: Na (3.54%), As (2.31%), W (50.93%), U(14.65%).

Compound 3:

$Na_9[B-\alpha-AsW_9O_{33}] \cdot 13H_2O$ (250 mg, 0.093 mmol) is dissolved in 3 ml of 0.2M acetate buffer (pH = 4.7). The solution is then added to green solid UCl_4 (74 mg, 0.19 mmol). The solution turns to brown quickly and is stirred and heated to 70 °C for 30 minutes. The solution is left to crystallize at room temperature by slow evaporation of the solvent. After 3 days, small brown octahedral crystals suitable for X-ray diffraction analyses started to appear. After 1 week, the crystals were collected quickly ($m = 17$ mg, yield = 6% based on AsW_9O_{33}).

IR (cm^{-1}): 944(w), 864(m), 784(w), 676(s), 646(s), 457(s).

ICP-OES for $Na_{24}[(AsW_9O_{33})_4(U^{IV})_6(\mu^3-OH)_4(\mu^3-O)_4] \cdot 42H_2O$ Na (4.15%), As (2.30%), W (53.34%), U(11.32%). Calculated: Na (4.42%), As (2.40%), W (53.02%), U(11.44%).

Characterisations

X-Ray diffraction

Table S1: Crystal data and structure refinement for compound 1, 2 and 3.

	Compound 1	Compound 2	Compound 3
Formula	$Na_{15.50}As_3W_{27}U_6C_{3.89}O_{164.47}$	$Na_{7.5}As_{1.5}W_{13.5}U_3O_{84.5}$	$Na_{12}As_4W_{36}U_6O_{198}$
Formula weight	9651.54	4832.87	11790.34
Temperature/K	100	100	100
Crystal color	brown	clear brown	brown
Crystal size/mm	0.15 x 0.15 x 0.1	0.08 x 0.05 x 0.05	0.1 x 0.1 x 0.1
Crystal system	monoclinic	monoclinic	cubic
Space group	$P2_1/n$	$P2_1/m$	$Fd-3$
$a/\text{Å}$	17.9019(5)	13.7846(8)	38.6891(8)
$b/\text{Å}$	35.9438(11)	31.0033(14)	38.6891(8)
$c/\text{Å}$	26.0511(9)	17.7568(8)	38.6891(8)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	103.4544(19)	91.543(3)	90
$\gamma/^\circ$	90	90	90
Volume/ Å^3	16302.9(9)	7585.9(7)	57912(2)

Z, $\rho_{\text{calculated}}/\text{g}\cdot\text{cm}^{-3}$	4, 3.932	4, 4.209	8, 2.705
μ/mm^{-1}	25.661	27.575	18.126
θ range/ $^{\circ}$	1.38-26.41	1.31-29.18	1.05-26.38
Limiting indices	-22 $\leq h \leq$ 22 -42 $\leq k \leq$ 44 -32 $\leq l \leq$ 32	-18 $\leq h \leq$ 18 -42 $\leq k \leq$ 42 -24 $\leq l \leq$ 24	-33 $\leq h \leq$ 48 -48 $\leq k \leq$ 35 -47 $\leq l \leq$ 46
Collected reflections	237316	254548	60048
Unique reflections	33291 [R(int) = 0.0684]	20819 [R(int) = 0.0681]	4979 [R(int) = 0.0800]
Parameters	1137	996	184
Goodness-of-fit on F^2	1.097	1.065	1.052
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0651 wR2 = 0.1309	R1 = 0.0380 wR2 = 0.0798	R1 = 0.0385 wR2 = 0.0894
R indices (all data)	R1 = 0.0996 wR2 = 0.1455	R1 = 0.0696 wR2 = 0.0933	R1 = 0.0558 wR2 = 0.1001
Largest diff. peak and hole/ $\text{e}\cdot\text{\AA}^{-3}$	4.20 and -4.00	2.49 and -2.47	3.10 and -0.88

Table S2: BVS calculations of bridging oxygen atoms in the uranium clusters of compound **1**.

Compound 1		
Atom	BVS	Attribution
O8	2.17	O
O9	1.13	OH
O10	1.22	OH
O11	1.17	OH
O12	2.05	O
O13	2.08	O
O14	2.08	O
O15	1.10	OH

Table S3: Oxygen coordination sphere distances and bond valence calculations of the substitutionally disordered uranium (U1) atom of compound **1** under its tetravalent and hexavalent form.

Tetravalent		Hexavalent	
U-O bond distance (\AA)	Bond valence	U-O bond distance (\AA)	Bond valence
U – O12 = 2.115	0.992	U – O1 = 1.717	2.629
U – O8 = 2.227	0.733	U – O12 = 2.115	0.897
U – O17 = 2.303	0.597	U – O8 = 2.227	0.663
U – O16 = 2.327	0.560	U – O17 = 2.303	0.540
U – O11 = 2.424	0.432	U – O16 = 2.327	0.507
U – O9 = 2.441	0.416	U – O11 = 2.424	0.391
U – O2 = 2.473	0.377	U – O9 = 2.441	0.372
U – O4 = 2.512	0.340		
BVS (U^{IV})	4.447	BVS (U^{VI})	5.999

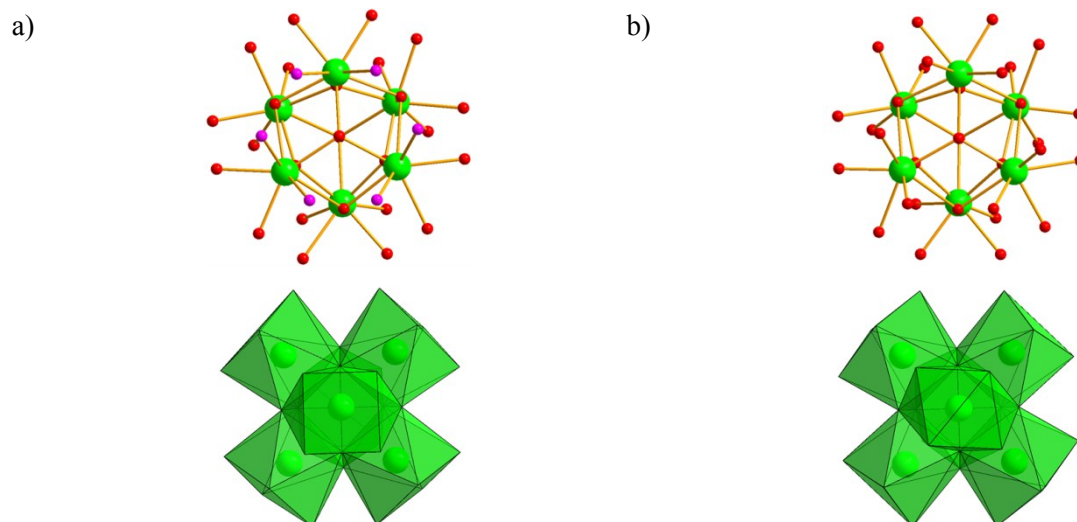


Figure S1: Comparison of the two hexameric $\{U^{IV}_6O_8\}$ clusters in compound **1** (left) and **3** (right). View through the oxygen atoms of the three acetate ligands in **1** and through one POM unit in **3**.

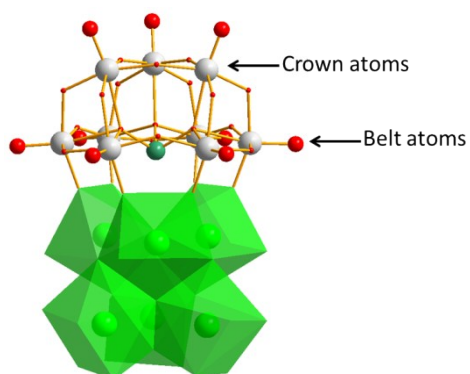


Figure S2: Position of the belt and crown atoms of the polyanionic moieties.

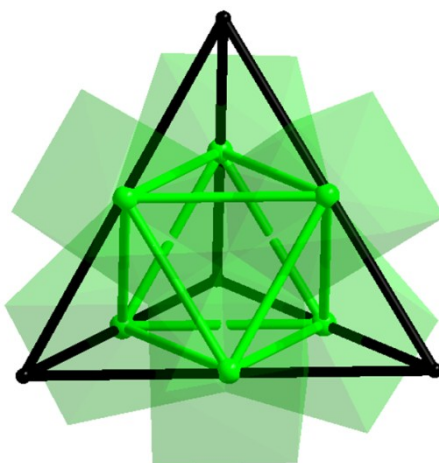


Figure S3: Octahedral inclusion of the tetraivalent uranium cluster in the tetrahedron delimited by the four As atoms of the polyanionic moieties.

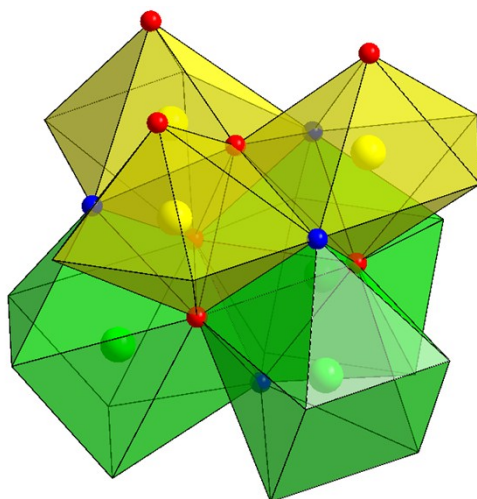


Figure S4: Polyhedral representation of the cluster involved in the CCI. Terminal O”yl” atoms and μ^3 -O bridges are represented in red and μ^3 -OH bridges are in blue. Green and yellow polyhedra respectively represent the tetravalent and hexavalent uranium atoms.

IR and Raman spectroscopies

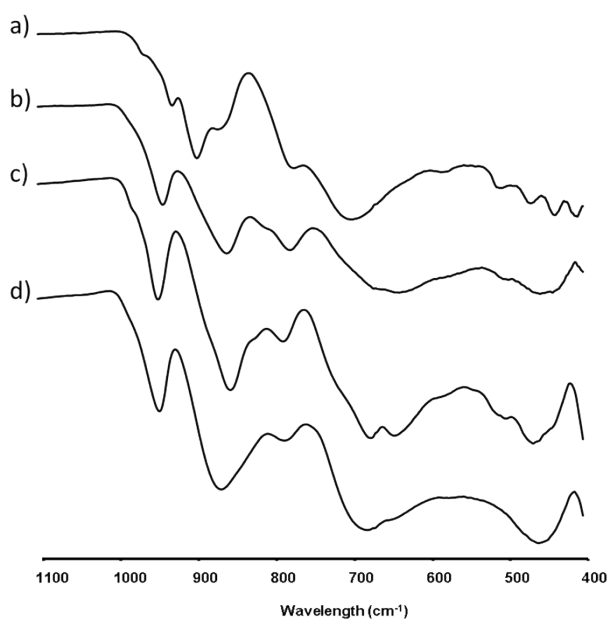


Figure S5: Comparison of the IR Spectra of $[\text{AsW}_9\text{O}_{33}]^{9-}$ (a), $\text{Na}_{19}[(\text{AsW}_9\text{O}_{33})_3(\text{OAc})_2(\text{U}^{\text{IV}})_{5.5}(\mu^3\text{-OH})_4(\mu^3\text{-O})_4\text{O}(\text{U}^{\text{VI}}\text{O})_{0.5}]$ (b), $[\text{U}^{\text{IV}}_3\text{U}^{\text{VI}}_3\text{O}_3(\text{m}^3\text{-O})_4(\text{m}^3\text{-OH})_4(\text{AsW}_9\text{O}_{33})_3]^{15-}$ (c) and $[\text{U}_6(\text{m}^3\text{-O})_4(\text{m}^3\text{-OH})_4(\text{AsW}_9\text{O}_{33})_4]^{24-}$ (d)

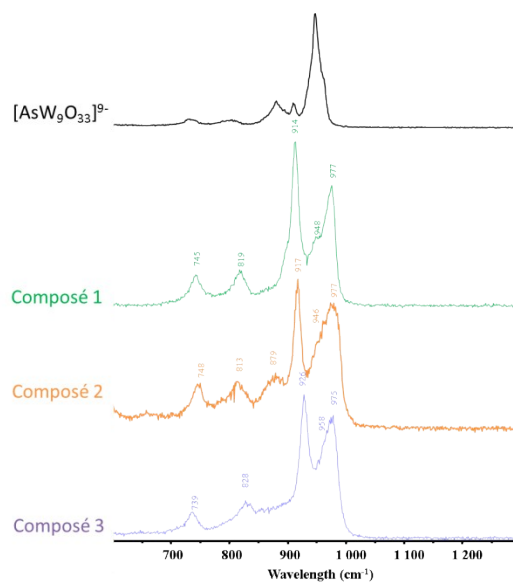


Figure S6: Comparison of the Raman Spectra of $[\text{AsW}_9\text{O}_{33}]^{9-}$, $\text{Na}_{19}[(\text{AsW}_9\text{O}_{33})_3(\text{OAc})_2(\text{U}^{\text{IV}})_{5.5}(\mu^3\text{-OH})_4(\mu^3\text{-O})_4\text{O}(\text{U}^{\text{VI}}\text{O})_{0.5}]$ (compound 1), $[\text{U}^{\text{IV}}_3\text{U}^{\text{VI}}_3\text{O}_3(\text{m}^3\text{-O})_4(\text{m}^3\text{-OH})_4(\text{AsW}_9\text{O}_{33})_3]^{15-}$ (compound 2) and $[\text{U}_6(\text{m}^3\text{-O})_4(\text{m}^3\text{-OH})_4(\text{AsW}_9\text{O}_{33})_4]^{24-}$ (compound 3)

SEM and microscopic images

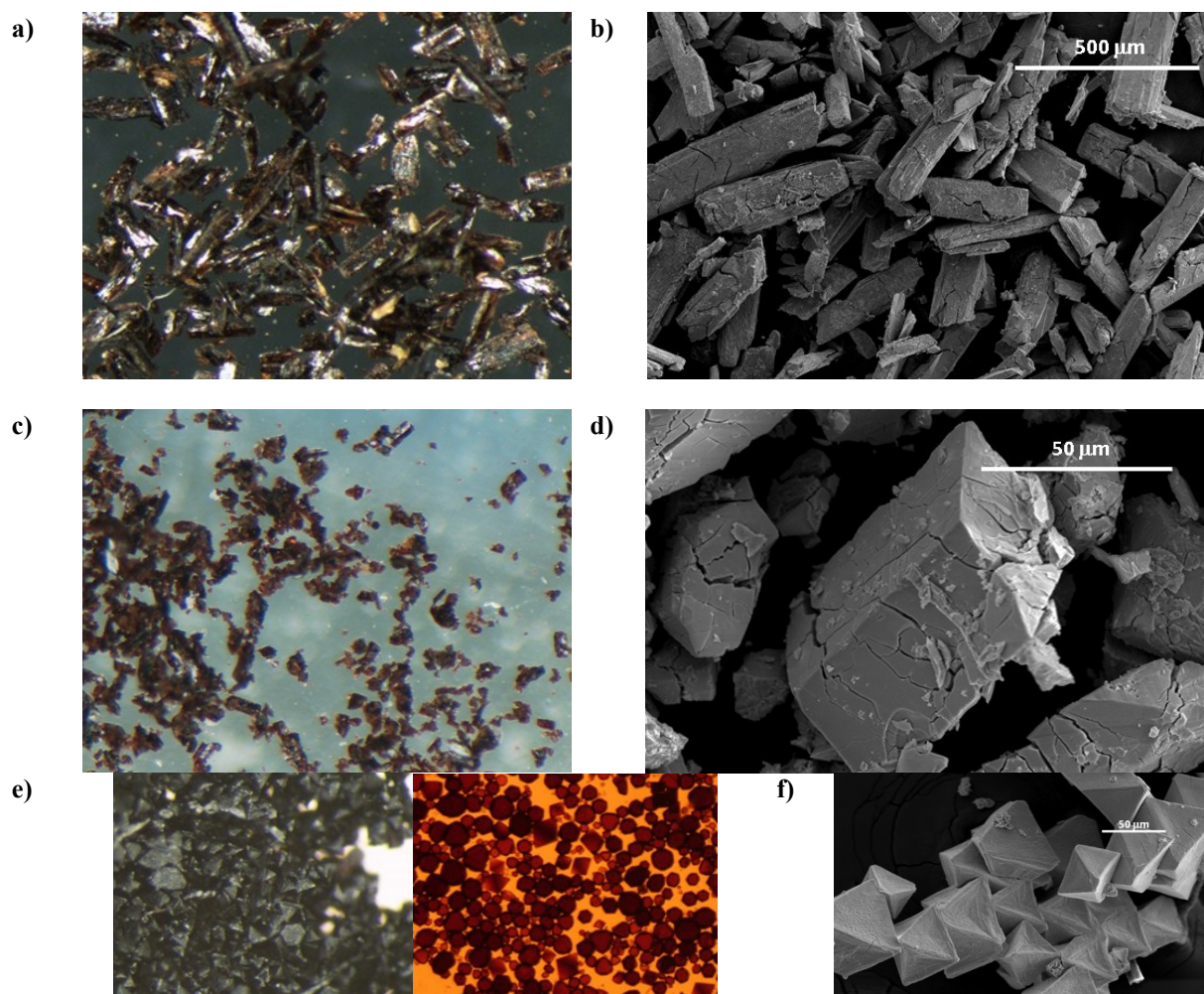


Figure S7: Binocular (left) and SEM (right) images of compound 1 (a-b), compound 2 (c-d) and compound 3 (e-f).

TGA analyses

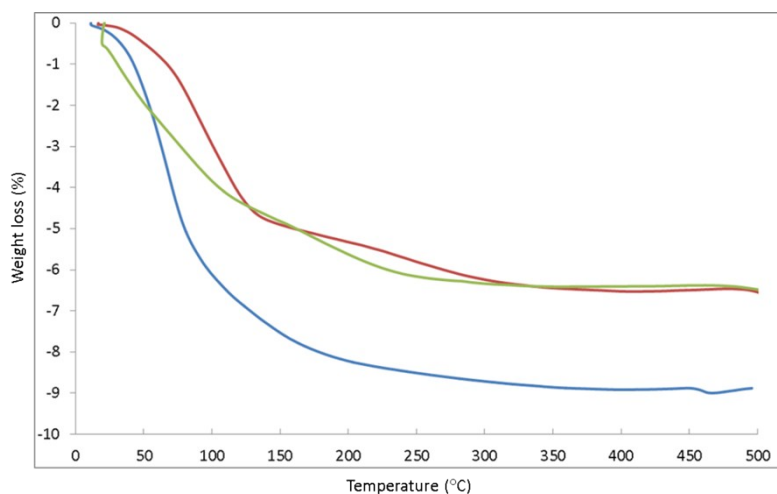


Figure S8: TGA curves of compounds 1 (blue curve), 2 (red curve) and 3 (green curve).

TGA analyses were performed on compound **1-3** to determine the water content of the compound out of their mother liquor. Calculations were performed on the observation of the first loss weight for water molecules until a plateau at 300°C for **1**, **2** and **3** which give respectively 47, 32 and 42 water molecules. These measurements were compared to the calculated values obtained from the water molecules in the RX studies (obs.: 8.7%; calc.: 9.5% for compound **1**, obs.: 6.2%; calc.: 10.4% for compound **2** and obs.: 6.3%; calc.: 8.5% for compound **3**). These differences are due to the loss of disordered water molecules from the lattice when the crystals are removed from the solution which is a classical behavior in polyoxometalate based compounds and result in the collapse of the lattice as can be observed in the SEM images of the compounds.

EPR measurements

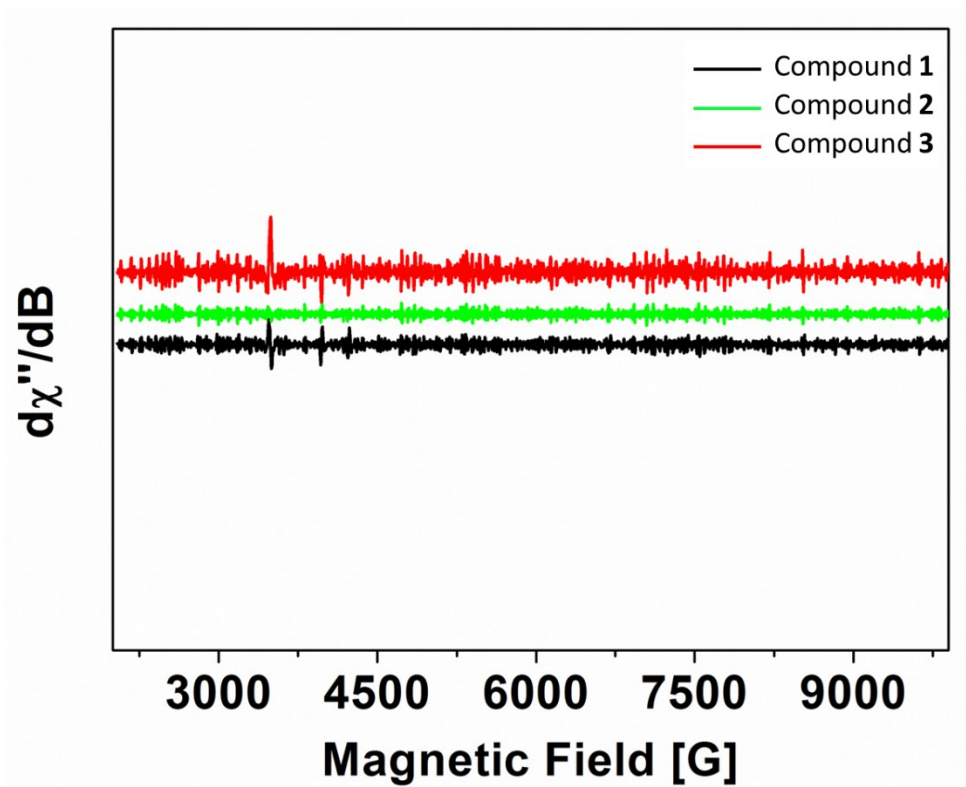


Figure S9: EPR spectra of compound 1, 2 and 3.

¹ SAINT Plus Version 7.53a; *Brucker Analytical X-ray Systems: Madison, WI*, 2008.

² G. M. Sheldrick, SADABS, *Brucker-Siemens Area detector Absorption and Other Correction, Version 2008/1; Brucker: Madison, WI*, 2008.

³ G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.

⁴ F. Robert, M. Leyrie and G. Hervé, *Acta Cryst.*, 1982, **B38**, 358.

⁵ A. Navaza, P. Charpin, D. Vigner and G. Heger, *Acta Crystallogr. C*, 1991, **47**, 1842-1845.