Electronic Supplementary Material (ESI) for CrystEngComm.

Influence of the pH for the Ce^{IV} - $[As^{III}W_9O_{33}]^{9-}$ association to the formation of hexanuclear cerium(IV) oxo-hydroxo-clusters stabilized by trivacant polyanions.

Maxime Dufaye[†], Sylvain Duval[†,*], Gregory Stoclet[‡] and Thierry Loiseau[†]

Contribution from [†]Université de Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du solide, F-59000 Lille, France. [‡] Unité Matériaux et Transformation (UMET) – UMR CNRS 8207, Université de Lille Nord de France, USTL-ENSCL, Bat C6, BP 90108, 59652 Villeneuve d'Ascq, France.

[*] To whom correspondence should be addressed. E-mail: sylvain. duval@univ-lille1.fr. Phone: (33) 3 20 434 973, Fax: (33) 3 20 43 48 95.

Supplementary Informations

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Comments on structure alerts.

Comments on the structure alerts can be found embedded in the CheckCif files.

Tables

Table S1: Crystal data and structure refinement for compounds **1-4**.

	Compound **1**	Compound **2**	Compound **3**	Compound **4**
Formula	$C_{3.42}H_{3.42}AsCe_6Na_{0.5}O_{73.5}W_9$	$C_9H_9AsCe_6Na_6O_{85.75}W_9$	$C_3H_3As_3Ce_6Na_{15}O_{156}W_{27}$	$As_6Ce_{12}Na_{18}O_{341}W_{58}$
Formula weight	3802.32	4197.39	8909.33	18664.08
Temperature/K	100	100.01	100	99.99
Crystal color	Orange	Orange	Clear Yellow	Clear Yellow
Crystal size/mm	0.04 x 0.04 x 0.02	0.06 x 0.02 x 0.01	0.08 x 0.06 x 0.06	0.09 x 0.05 x 0.05
Crystal system	Tetragonal	Triclinic	Triclinic	Triclinic
Space group	$I\bar{4}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	24.7106(15)	11.9097(7)	18.4264(12)	18.6179(13)
b/Å	24.7106(15)	15.2185(8)	19.3634(12)	19.6067(15)
c/Å	23.2547(14)	21.8082(13)	26.7239(15)	27.947(2)
α/°	90	90.152(3)	105.118(3)	99.610(4)
β/°	90	101.470(3)	98.139(3)	105.262(4)
γ°	90	101.060(3)	112.226(2)	108.594(4)
Volume/Å^3	14199.6(19)	3798.4(4)	8207.4(9)	8970.0(12)
Z, $\rho_{calculated}$/g.cm^{-3}	8, 3.557	2, 3.670	2, 3.605	1, 3.455
μ/mm^{-1}	18.857	17.682	21.208	20.674
Θ range/°	1.165 – 26.36	0.954 – 26.408	1.289 – 26.415	1.481 – 26.412
Limiting indices	$-30 \le h \le 29$ $-25 \le k \le 30$ $-29 \le l \le 28$	$-14 \le h \le 14$ $-19 \le k \le 18$ $-23 \le l \le 27$	$-23 \le h \le 22$ $-24 \le k \le 24$ $-33 \le l \le 32$	$-23 \le h \le 23$ $-24 \le k \le 24$ $-34 \le l \le 34$
Collected reflections	53274	50492	110252	124246
Unique reflections	14485 [R(int) = 0.0505]	15358 [R(int) = 0.0744]	32729 [R(int) = 0.0626]	36338 [R(int) = 0.0971]
Parameters	891	591	1102	1138
Goodness-of-fit on F^2	1.019	1.056	1.054	1.015
Final R indices [I>2σ(I)]	R1 = 0.0326 wR2 = 0.0670	R1 = 0.0709 wR2 = 0.1719	R1 = 0.0649 wR2 = 0.1513	R1 = 0.0590 wR2 = 0.1233
R indices (all data)	R1 = 0.0420 wR2 = 0.0712	R1 = 0.1101 wR2 = 0.1991	R1 = 0.1086 wR2 = 0.1838	R1 = 0.1258 wR2 = 0.1454
Largest diff. peak and hole/e.Å^{-3}	1.47 and –1.32	15.62 and –3.33	5.75 and –3.50	3.85 and –2.25

Table S2: BVS calculations for cerium and arsenic atoms in compounds **1-4**.

		Ce^{III}/As^{III}	Ce^{IV}/As^{V}	Attribution
Compound **1**	Ce1	4 ,40	3,88	Ce^{4+}
	Ce2	4,25	3,74	Ce^{4+}
	Ce3	4,17	3,68	Ce^{4+}
	Ce4	4,33	3,82	Ce^{4+}
	Ce5	4,17	3,68	Ce^{4+}
	Ce6	4,11	3,62	Ce^{4+}
	As	3,48	3,49	As^{3+}

		Ce^{III}/As^{III}	Ce^{IV}/As^{V}	Attribution
Compound **2**	Ce1	4,25	3,74	Ce^{4+}
	Ce2	4,33	3,82	Ce^{4+}
	Ce3	4,05	3,57	Ce^{4+}
	Ce4	4,25	3,74	Ce^{4+}
	Ce5	4,22	3,72	Ce^{4+}
	Ce6	4,21	3,71	Ce^{4+}
	As	3,58	3,59	As^{3+}

		Ce^{III}/As^{III}	Ce^{IV}/As^{V}	Attribution
Compound **3**	Ce1	4,17	3,68	Ce^{4+}
	Ce2	4,33	3,82	Ce^{4+}
	Ce3	4,28	3,75	Ce^{4+}
	Ce4	4,23	3,79	Ce^{4+}
	Ce5	4,33	3,82	Ce^{4+}
	Ce6	4,28	3,76	Ce^{4+}
	As	4,92	4,93	As^{5+}

		Ce^{III}/As^{III}	Ce^{IV}/As^{V}	Attribution
Compound **4**	Ce1	4,34	3,82	Ce^{4+}
	Ce2	4,32	3,80	Ce^{4+}
	Ce3	4,26	3,75	Ce^{4+}
	Ce4	4,24	3,72	Ce^{4+}
	Ce5	4,12	3,63	Ce^{4+}
	Ce6	4,15	3,65	Ce^{4+}
	As	4,93	4,94	As^{V}

Table S3: BVS calculations for tungsten atoms in the POM moieties of compounds **3** and **4**.

		BVS
Compound **3**	W1	6.01
	W2	5.99
	W3	5.96
	W4	6.22
	W5	6.09
	W6	6.37
	W7	6.28
	W8	6.09
	W9	6.26
	W10	6.33
	W11	6.07
	W12	6.18
	W13	6.04
	W14	6.34
	W15	6.26
	W16	6.32
	W17	6.39
	W18	6.14
	W19	6.16
	W20	6.18
	W21	6.27
	W22	6.06
	W23	6.26
	W24	6.45
	W25	6.27
	W26	6.23
	W27	6.14

		BVS
Compound **4**	W1	6.19
	W2	6.24
	W3	5.96
	W4	6.14
	W5	6.06
	W6	6.25
	W7	6.02
	W8	6.11
	W9	6.25
	W10	5.93
	W11	6.17
	W12	5.85
	W13	6.08
	W14	6.18
	W15	6.33
	W16	6.10
	W17	6.14
	W18	6.43
	W19	6.04
	W20	6.20
	W21	6.06

	W22	6.22
	W23	5.99
	W24	6.05
	W25	6.12
	W26	6.31
	W27	5.97

Table S4: Values of the main visible vibrations (in cm^{-1}) of the $[AsW_9O_{33}]^{9-}$ precursor and compounds **1-4**.

	W–Od	W–Ob–W	W–Oc–W
$Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot 13H_2O$	928	866	775, 700, 580
Compound **1**	946	866, 849	780, 660, 560
Compound **2**	938	865(sh), 834	780, 685, 640, 540
Compound **3**	950	861, 840	775, 710, 650
Compound **4**	950	870, 840	775, 660

Figures

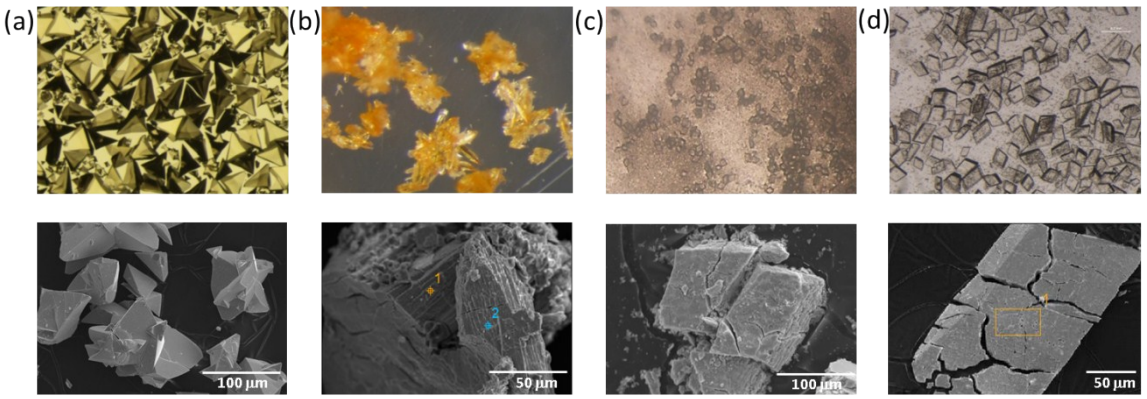

Figure S1: EDS and binocular images of crystals of (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**.

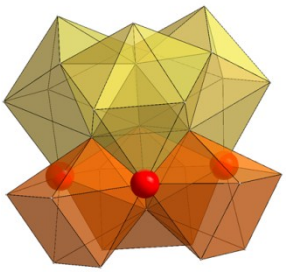

Figure S2: highlight on the coordination of the As(V)-O oxygen (red sphere) atoms to the cerium hexamers in compounds **3** and **4**.

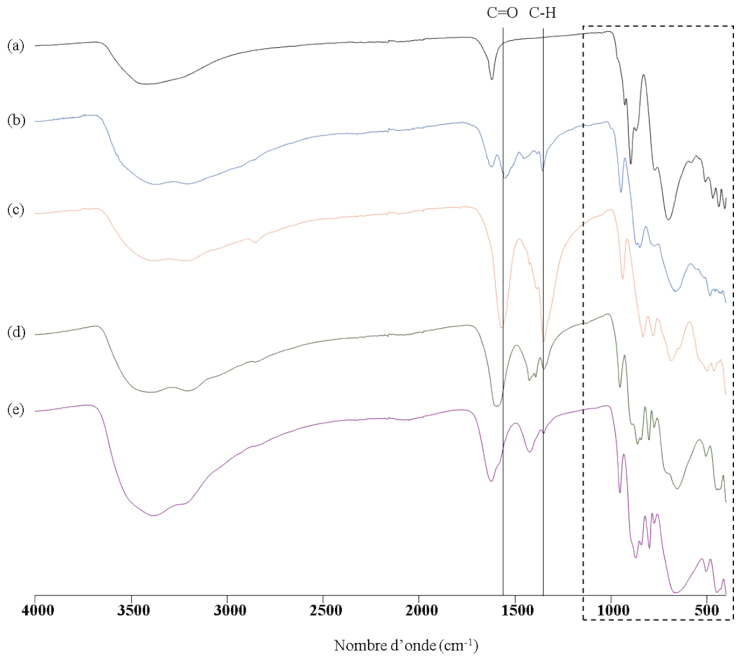

Figure S3: Infrared spectra (400-4000 cm^{-1} region) of (a) $[AsW_9O_{33}]^{9-}$, (b) compound **1**, (c) compound **2**, (d) compound **3** and (e) compound **4**.