Supplementary Information for

A Novel Nonanuclear Hafnium Oxide/Hydroxide-Sulphate Cluster Crystallised from Aqueous Solutions

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S1. Crystallographic information and X-ray structure determination of 1. Refelctions were collected at 100 K on a Bruker AKX SMART diffractometer equipped with an APEXII CCD detecytor using Mo Kα radiation. The data were integrated and corrected for absorption using the APEX2 suite of crystallographic software. The structure was solved by direct methods and refined using XShell (SHELXL-97).

All non-hydrogen atoms were located using difference Fourier maps and were ultimately refined anisotropically. Once all the Hf, S and O atoms in the cluster were located, 27 large residual electron density peaks were observed in the voids including one on a special position. These were assigned to 14 N (NH_4^+) and 13 O (H_2O) atoms. Every effort was made to correctly identify the 14 NH_4^+ ions from solvent H_2O. By increasing the number of electron density peaks (Q) to 100-200, it was possible to distinguish between the two species by inspecting the hydrogen atom Q peak arrangement around them. Four Q peaks appearing in a tetrahedral geometry indicated NH_4^+, whereas H_2O were in a bent geometry or had larger thermal disorder with no Q peaks. In a few case only three of the four protons on NH_4^+ were detected. Despite our assignments, switching the identity of these species between N/O had no effect on the refinement R factors due to the electronic similarity between NH_4^+ and H_2O. The authors acknowledge that some of the species in the voids may have the incorrect N/O assignment, but have found no evidence that this affects the structure of the cluster. Six small Q peaks were found around 0.8 Å away from each hydroxo oxygen in the cluster core (O9-O14), whereas no such peaks were detected near to the oxo oxygens (O1-O8). This helped confirm our O^{2-}/OH^- assignment in the core. These peaks were labelled as hydrogen atoms (H1-H6), but were not refined anisotropically. The O-H bond distances were fixed to 0.82 ± 0.02 Å using the DFIX command to prevent the hydrogen atoms from moving substantially during the refinement. Due to disorder, it was necessary to part one oxygen atom over two sites giving O79 and O80 with final refined occupancies 0.670(15) and 0.330(15), respectively. O84 was found on special position (0, 0.5, 0.5).

Table S1: Crystallographic Data for $(NH_4)_{14}[Hf_9O_8(OH)_6(SO_4)_{14}]\cdot nH_2O$ (**1**)

empirical formula (n = 12.5)	$H_{87}N_{14}O_{82.5}S_{14}Hf_9$
crystal size (mm)	0.18 x 0.12 x 0.10
Temperature (K)	100
λ (Mo Kα)	0.71073
crystal system	monoclinic
space group	$P2_1/c$ (no. 14)
a (Å)	23.8604(6)
b (Å)	13.9420(4)
c (Å)	25.1027(7)
α (deg)	90
β (deg)	114.68
γ (deg)	90
V (Å^3)	7587.6(4)
Z	4
formula weight (n = 12.5) (g/mol)	3659.09
calculated density (g cm^{-3})	3.203
absorption coefficient (mm^{-1})	12.792
total no. of reflections	131525
unique reflections	27168
R_1 [$I > 2\sigma(I)$]	2.61
wR_2	5.79
largest diffraction peak and hole (e$^-$ Å^{-3})	3.20, − 1.82
goodness of fit	1.117

Table S2: List of bridging μ_3-O atoms in the nonanuclear core and their assignments obtained using bond-valence summation.

Atom	Distance to Hf₃ plane (Å)	Bond-valence sums	Assignment
O1	0.423(1)	1.694	O^{2-}
O2	0.430 (1)	1.680	O^{2-}
O3	0.420(1)	2.068	O^{2-}
O4	0.424(1)	2.049	O^{2-}
O5	0.423(1)	2.062	O^{2-}
O6	0.388(1)	2.088	O^{2-}
O7	0.442(1)	2.071	O^{2-}
O8	0.422(1)	2.066	O^{2-}
O9	0.986(1)	1.128	$(OH)^{-}$
O10	1.007(1)	1.084	$(OH)^{-}$
O11	0.980(1)	1.138	$(OH)^{-}$
O12	0.987(1)	1.143	$(OH)^{-}$
O13	0.990(1)	1.102	$(OH)^{-}$
O14	0.981(1)	1.126	$(OH)^{-}$

Table S3: List of Hf-Hf distances shorter than 4 Å within the nonamer cluster (i.e. between Hf atoms bridged by oxo or hydroxo groups). The Hf atoms above and below the equatorial plane are bridged to five other Hf atoms and are highlighted in blue. Those in the equatorial plane are only bridged to four other Hf atoms and are highlighted in green. The short Hf-Hf distances along the pseudo C_3 axis are shown in red.

	Hf1	Hf2	Hf3	Hf4	Hf5	Hf6	Hf7	Hf8	Hf9
Hf1		3.609(1)	3.625(1)	3.552(1)	-	3.544(1)	3.378(1)	-	-
Hf2	3.609(1)		3.636(1)	3.553(1)	3.539(1)	-	-	3.391(1)	-
Hf3	3.625(1)	3.636(1)		-	3.561(1)	3.537(1)	-	-	3.369(1)
Hf4	3.552(1)	3.553(1)	-		-	-	3.544(1)	3.541(1)	-
Hf5	-	3.539(1)	3.561(1)	-		-	-	3.546(1)	3.556(1)
Hf6	3.544(1)	-	3.537(1)	-	-		3.552(1)	-	3.541(1)
Hf7	3.378(1)	-	-	3.544(1)	-	3.552(1)		3.604(1)	3.631(1)
Hf8	-	3.391(1)	-	3.541(1)	3.546(1)	-	3.604(1)		3.645(1)
Hf9	-	-	3.369(1)	-	3.556(1)	3.541(1)	3.631(1)	3.645(1)	

Upon inspecting the cluster and the nearby species in the voids, it becomes clear that hydrogen bonding plays an important role in stabilising the structure. Perhaps one reason that the sulphate groups are not perfectly aligned with one another is that some μ_2-sulphates appear to 'bend' back towards the cluster core, bringing one of their terminal oxygen atoms within the H-bonding range (2.8 – 3.1 Å) from a hydroxo group (O9-O14). For each hydroxo group, there are two nearby sulphate oxygens that may act as an H-bonding acceptor, but in most cases only one sulphate bends towards the OH group, forming one H-bond. These interactions are summarised in Table S4, below. For O12, however, no such bending occurs, and so the sulphate oxgyens are too far to act as H-bond acceptors. Instead, a nearby water molecule in the void, O74, is close enough to form a H-bond (2.961(6) Å). This is the only such interaction between a void species and a hydroxo group in the nonamer core. This also confirms the assignment of O74 as a water molecule rather than an ammonium ion. Interestingly, the sulphate oxygens taking part in H-bonding with the OH groups generally have smaller thermal ellipsoids than those that do not, indicating that the former are more tightly bound to the cluster and have less vibrational freedom due to the H-bond. It is worth noting that all species in the voids are within the hydrogen bonding range to the sulphate oxygens, with the exception of O76, which can only be H-bonded to other void species.

Table S4: List of possible hydrogen bonding interactions between the μ_3-OH groups in the cluster core and the μ_2-sulphate oxygen atoms. Note that O12 does not have such an interaction but is instead H-bonding with a water molecule in the void, O74. The presence of these H-bonds generally results in smaller thermal ellipsoids for the sulphate oxygens involved.

Donor (μ_3-OH)$^-$	Possible acceptor μ_2-sulphate	Donor-acceptor distance	H-bond possible?	Thermal ellipsoid
O9	O21	2.959(4)	Yes	small
O9	O25	3.931(5)	No	small
O10	O33	3.116(6)	Yes	small
O10	O29	3.417(6)	No	large
O11	O41	2.872(4)	Yes	small
O11	O37	3.815(5)	No	large
O12	O50	3.683(5)	No	large
O12	O46	3.952(3)	No	large
O13	O54	2.897(4)	Yes	small
O13	O58	3.771(5)	No	large
O14	O66	2.877(5)	Yes	small
O14	O62	3.844(4)	No	small
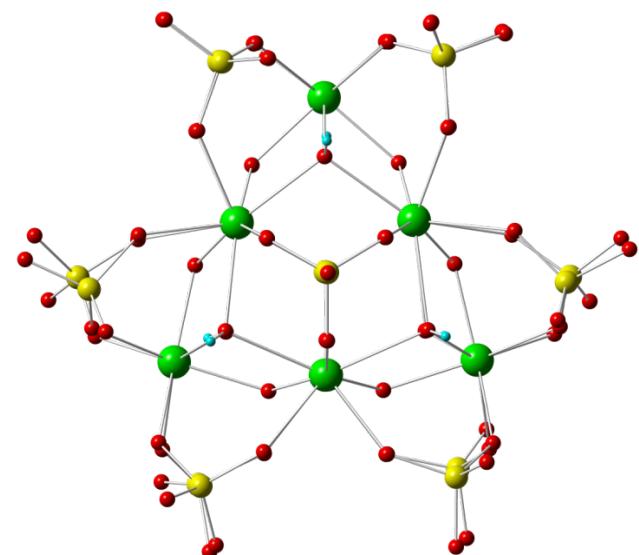
Figure S1: Molecular structure of the nonameric cluster in $(NH_4)_{14}[Hf_9O_8(OH)_6(SO_4)_{14}] \cdot nH_2O$ (**1**) viewed down the pseudo C_3 axis. The water oxygen and ammonium nitrogen atoms in the voids were omitted for clarity. Hafnium: green, sulphur: yellow, oxygen: red, hydrogen; cyan.
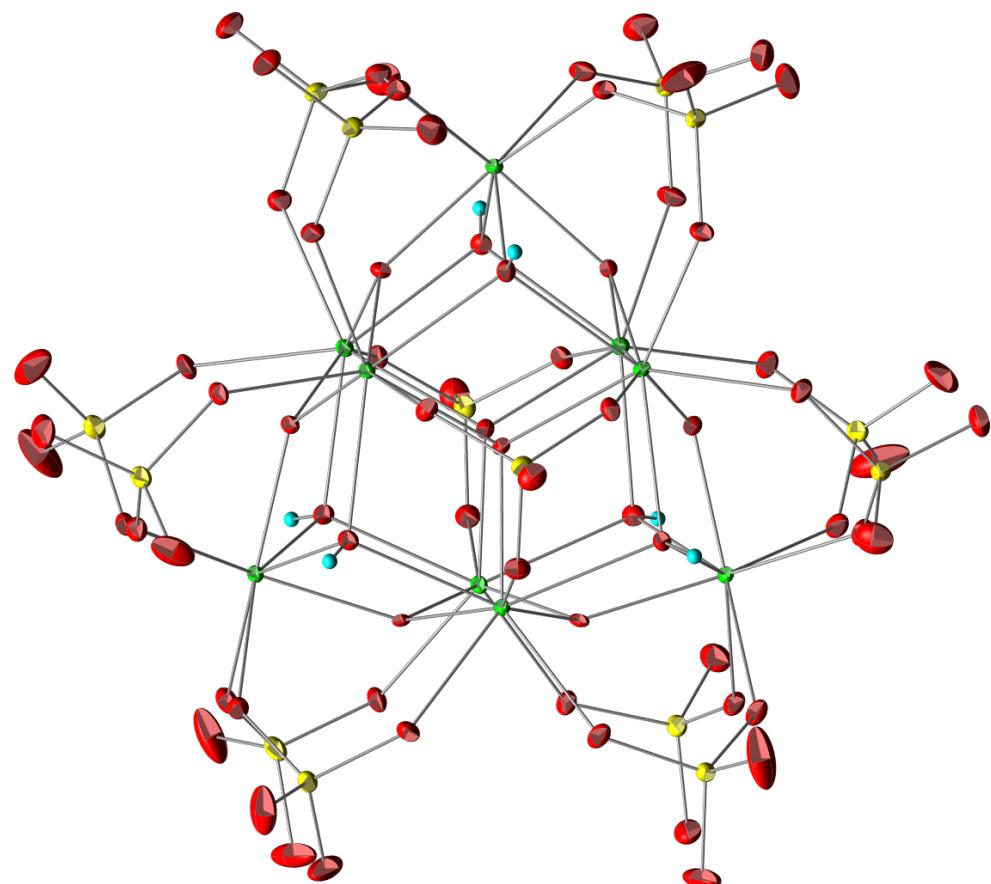

Figure S2: ORTEP diagram of the nonameric cluster in $(NH_4)_{14}[Hf_9O_8(OH)_6(SO_4)_{14}] \cdot nH_2O$ (**1**). The thermal ellipsoids are displayed at a probability of 50%. Hafnium: green, sulphur: yellow, oxygen: red, hydrogen; cyan.

S2. Further characterisation of 1.

Elemental analysis was performed at Galbraith Laboratories, Inc., 2323 Sycamore Drive, Knoxville, TN 37921-1750, USA.

Raman data were collected on randomly oriented single crystals using a Renishaw inVia Raman microscope with a circularly polarised excitation line of 532 nm. The region examined (100 – 1300 cm^{-1}) is dominated by Raman active sulphate vibrations. Multiple crystals were examined from the same sample, exhibiting identical spectra.

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC 1 instrument. 6.31 mg of **1** were placed in a 70 µL alumina crucible and held at 30 °C for three hours, during which time some water evaporation was observed (~ 4% mass loss). The sample was then heated to 1000 °C at 1 °/min. The experiment was performed under the flow of N_2 at 75 mL/min. Multiple mass loss steps between 30 – 500 °C indicated the loss of H_2O and NH_4^+. A large step in the 550 – 700 °C range was due to SO_3 loss (~30% loss).
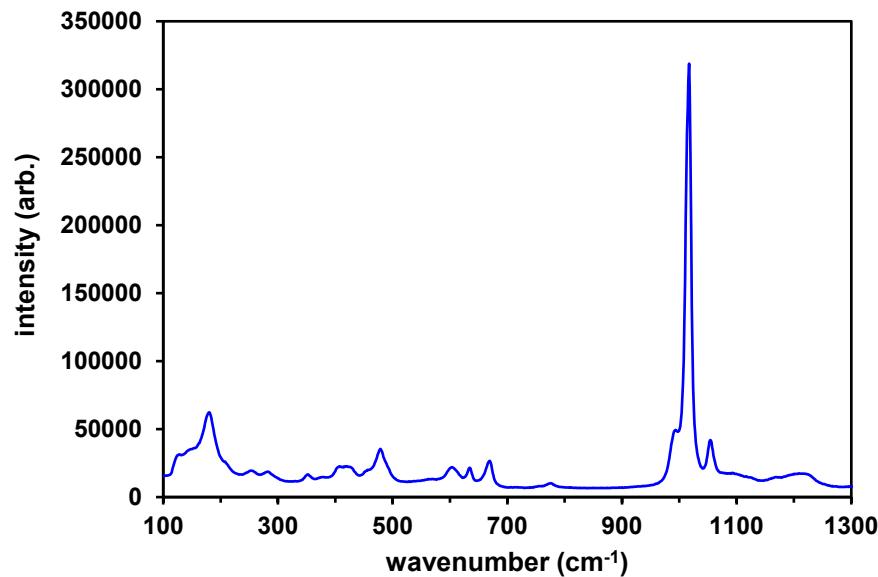

**Figure S3:** Raman spectrum of a crystal of **1**.
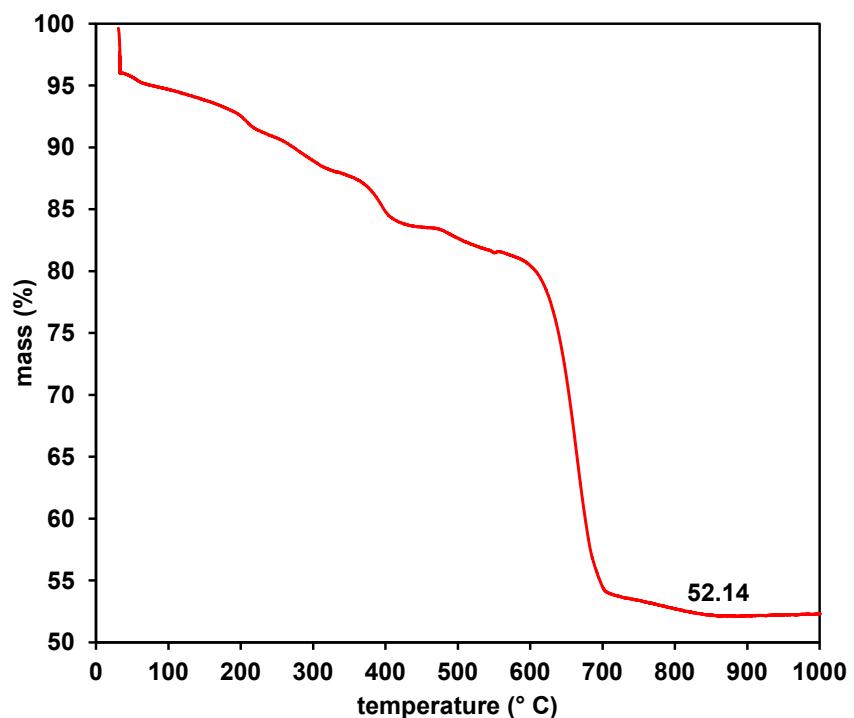
Figure S4: TGA of **1**. Note that the sample was held at 30 °C for three hours, during which some water evaporation was observed.