Controlled assembly and solution observation of a 2.6 nm polyoxometalate 'super' tetrahedron cluster: $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$†

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A nanoscale Fe^{III}-substituted polyoxotungstate $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$ is synthesized starting from the trilacunary $\{P_2W_{15}\}$ Dawson cluster and $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]^{1+}$ to give a 2.6 nm tetrahedral cluster species and the 16 kDa cluster can be directly observed in solution as revealed by mass spectrometry studies.

Polyoxometalates (POMs) are metal-oxygen clusters[1] of W, Mo, V and represent a class of inorganic materials with an almost unmatched range of structure types and physical properties with applications in areas as diverse as biology[2] and catalysis.[3] Polyoxometalate clusters cover an enormous size range and comprise conserved building blocks; it is this feature which means they hold considerable promise for the controlled assembly of large nanostructures and framework materials.[4] The main limitation in the development of a universal polyoxometalate 'lego' kit lies with the great sensitivity between synthetic conditions and the overall cluster architecture formed.[5,6] For instance, reaction systems that yield lacunary POMs, have been shown to self-assemble under conditions where many possible species are present, with factors such as subtle changes in pH,[7] buffer capacity, ionic strength and cation size and type[5] having a significant effect on the products isolated. Therefore, the engineering of architectures using lacunary POMs requires a new approach that can manipulate building blocks in solution leading to the controlled growth of the architectures.[8]

Herein, we present an approach to observe and control the self assembly of nanoscale polyoxometalate clusters, in this case $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$ (**1a**), using the combination of solution control (adjustment of solution in terms of pH, metal ion concentrations and buffer) and direct observation of the species present with electrospray and cryospray mass spectrometry, an approach that we have recently found can be used to observe reactive building blocks[8] and high nuclearity clusters.[9] In this work, we selected a well known lacunary, relatively stable, building block, $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$, for our studies since lacunary-based building blocks have been proved to be extremely useful in the development of POM-based architectures. This has been shown in other systems, including the tetra-Dawson polyoxothiometalate $[(\alpha\text{-}H_2P_2W_{15}O_{56})_4\{Mo_2O_2S_2(H_2O)_2\}_4\{Mo_4S_4O_4(OH)_2(H_2O)\}_2]^{28-}$,[10a] a polyoxotungstate wheel $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$ from self-assembled Keggin fragments,[10b] a tetradecanuclear copper(II) polyoxotungstate $[\{(SiW_9O_{34})\text{-}\{SiW_9O_{33}(OH)\}(Cu(OH))_6Cu\}_2X]^{23-}$ (X = Cl or Br),[10c] and a wheel shaped tungstophosphate $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$,[10d] as well as a ball-shaped heteropolyoxotungstophosphate $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A\text{-}XW_9O_{34})_{12}]^{36-}$.[10e] Also some supertetrahedral polyoxometalates have been structurally characterized and include tetrameric titanium-substituted $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$, and $[(P_2W_{15}Ti_3O_{60.5})_4Cl]^{37-}$,[11a,b] polyoxotungstates based on the Wells–Dawson fragment. A Nb-containing tetra-Keggin polyoxometalate compound $[Nb_4O_6(\alpha\text{-}Nb_3SiW_9O_{40})_4]^{20-}$,[11c] and a uranium containing tetrahedral POM $[(UO_2)_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$ have also been reported.[11d]

Here, we utilized an oxo-centred iron-acrylate cluster $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]Cl\cdot 7H_2O$[12] as the metal ion source, which slowly decomposes during reaction with trilacunary Dawson cluster $\{P_2W_{15}\}$ and gives a nanosized Fe-substituted tetrahedral polyoxotungstate molecule which itself is stable in solution and forms a porous framework in the solid state. The reaction of trilacunary $\{P_2W_{15}\}$ cluster with *ca.* equimolecular amount of iron-acrylate trimer $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]Cl\cdot 7H_2O$ in aqueous medium at normal conditions gives the giant tetrahedral polyoxotungstate **1**, having the molecular formula $K_{21}Na_8[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]\cdot 70H_2O$ in good yields. The compound was well characterized by elemental analysis, IR, TGA/DSC studies, solution mass spectroscopy and single crystal XRD analysis, see Fig. 1.†‡§

The molecular structure of **1a** is shown in Fig. 1 which consists of four Fe^{III} tri-substituted Wells–Dawson units linked together through Fe–O–Fe bonds giving an overall T_d symmetry. The resulting structure contains a central $Fe_{12}O_{46}$ core, consisting of four groups of three edge-shared, corner-linked FeO_6 octahedra, about which the four Fe_3-capped Dawson units are arranged in a tetrahedral fashion around the central KO_{12} templating unit. The arrangement of the central $Fe_{12}O_{46}$ core resembles one set of the four corner-shared faces of an octahedron, see Fig. 2. The central cavity of this $Fe_{12}O_{46}$ moiety is occupied by a potassium ion which links up the four α-Dawson units present in the molecular structure. The tetrahedral anion **1a** has a crystallographically imposed mirror symmetry and the distance between two opposite lobes of this giant molecule is ~2.6 nm.

The three edge-sharing octahedral sites of the Fe atoms (Fe_3 cap) in each of these "$\alpha\text{-}P_2W_{15}Fe_3$" Dawson units substitute the three

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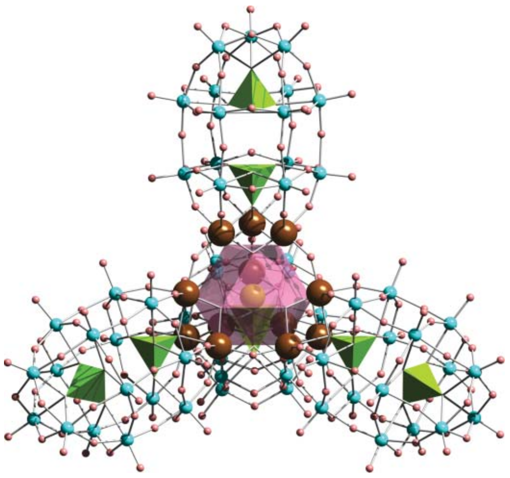

Fig. 1 Structure of the tetrahedral anion **1a**, $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$, with a K^+ captured at the cluster centre, viewed down an approximate 3-fold axis. Colour scheme: O = pink, W = cyan, Fe = brown, PO_4 = green polyhedra, K = orange, KO_{12} = purple polyhedra.

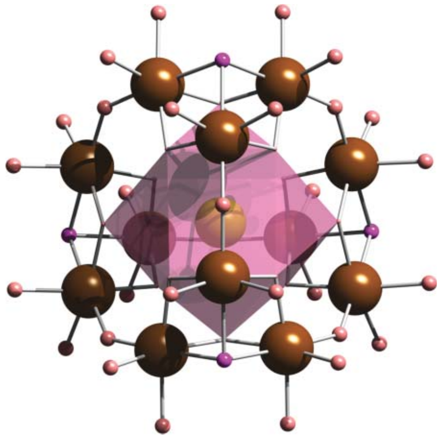

Fig. 2 The polyhedral representation of the central $Fe_{12}O_{46}$ core of the anion **1a** showing the encapsulated potassium ion such that the KO_{12} unit effectively acts as a template for the whole molecule. Colour scheme as in Fig. 1 except the μ_3 oxo atoms from the PO_4 templates are shown in purple.

edge-sharing octahedral sites of the tungsten(VI) atoms (W_3 cap site) of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. The 12 Fe(III) centres in **1a** are coordinated by six oxygen atoms in a distorted octahedral fashion. The distortion from the ideal octahedral geometry is of an axial type. Each of the four $\{P_2W_{15}Fe_3\}$ subunits is connected by three Fe–O–Fe bridges. The three terminal oxygen atoms of the Fe_3 cap are linked to three other Dawson units through Fe–O–Fe bonds, forming the tetrahedral geometry of the molecule. The Fe–O–Fe angle bridging the four Dawson units is found to be 141.2°.

The calculated bond valence sums[13] (BVS) for the bridging oxygen atoms are found to be in the range of 1.15–1.29, indicating that all the Fe–O–Fe bridges present in the molecule are protonated, which thus leads to the composition $[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]^{29-}$. The bond valence sums calculated based on observed bond lengths for Dawson units were in the range of 3.07–3.19 for three Fe atoms, 6.10–6.49 for the fifteen W atoms and 4.86–5.13 for the two P atoms, which correspond to formal valences of Fe^{3+}, W^{6+} and P^{5+}, respectively.

In electrospray mass spectroscopic measurements of compound **1** dissolved in water, the tetrahedral anion **1a** is observed in solution as the cluster anion $\{\mathbf{1a}M_{23}\}^{6-}$, in which **1a** is intact with M equal to 23 K^+, Na^+ or a combination of K^+ and Na^+ together with a number of water molecules, a typical species being $\{[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4][K_{14}Na_9](H_2O)_{10}\}^{6-}$, which gives an *m*/*z* of 16812/6 = 2802, see Fig. 3. This observation is extremely important since this gives unambiguous proof that the tetrahedral cluster anion is present in solution, and also confirms the overall protonation of the cluster which is extremely difficult to do directly. Furthermore, **1a** with a mass of 16 kDa is the largest polyoxometalate cluster, and polynuclear cluster, to be observed in solution by electrospray mass spectrometry. Also, to the best of our knowledge, compound **1** represents the first example of a tetrahedral Fe-substituted polyoxoanion reported.

The use of iron acrylate trimer as the iron source here appears to have played a crucial role in the formation of the $Fe_{12}O_{46}$ cluster core, since reaction of $\{P_2W_{15}\}$ cluster with common iron salts resulted in the formation of trisubstituted Wells–Dawson structure (1 : 3 ratio) and sandwich compounds (1 : 2 ratio).[14] Probably the slow decomposition of the Fe-acrylate cluster into its component acrylate and metal ions might have an optimum buffering effect on pH as well as metal ion concentration, facilitating the formation of the giant tetrahedral structure of **1**.

The magnetic properties of **1** indicate dominating strong antiferromagnetic intramolecular superexchange between the twelve spin-5/2 Fe(III) centres (Fig. 1) which is within the range of expectations for oxo-linked Fe(III) complexes. At room temperature the value of χT is still significantly below the expected high-temperature limit of 52.5 emu K mol^{-1} for twelve Fe(III) centres (assuming g = 2.0) and decreases steadily with decreasing temperatures to yield a singlet ground state. Below ~125 K, the susceptibility strongly deviates from a Curie–Weiss form; above 125 K, $1/\chi$ increases approximately linearly with temperature to

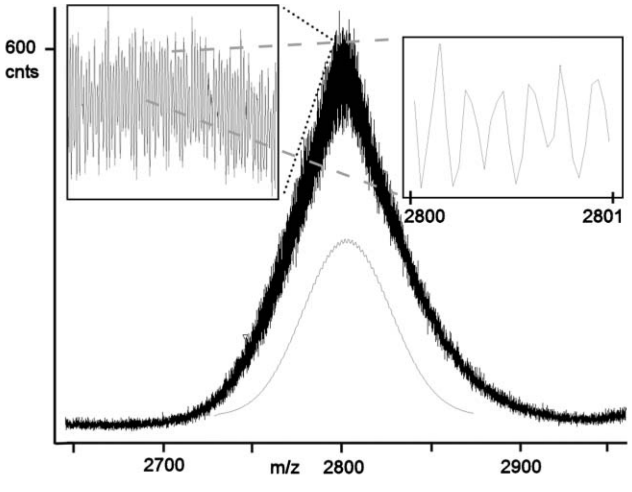

Fig. 3 Mass spectrum (black line) showing the $\{[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4][K_{14}Na_9](H_2O)_{10}\}^{6-}$ in aqueous solution at *m*/*z ca.* 2800. The simulated spectrum is shown below. The charge state can be deduced from a zoom in (TOP LEFT then TOP RIGHT) demonstrating the six minus charge state of **1a** (see ESI† for the full spectrum which also shows the presence of the −7, and −4 charge states for **1a** as well as an indication of the building blocks present).

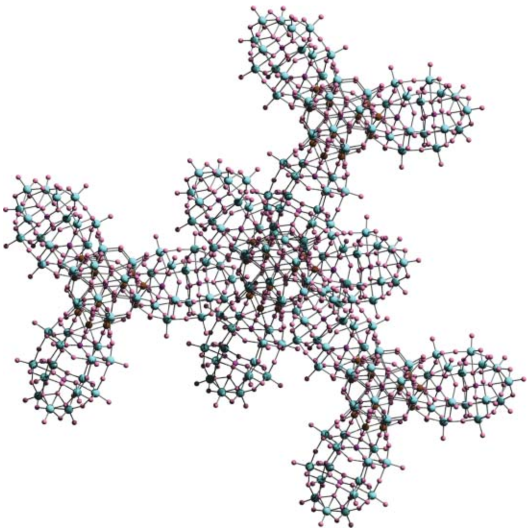

Fig. 4 Packing arrangement of **1** in the solid state. The apexes of the tetrahedral anion are connected *via* a vast set of potassium oxo/potassium water interactions (not shown) connecting the tetrahedral units to a porous framework. W = cyan, O = purple, Fe = brown.

yield a Weiss temperature of *ca.* 1100 K (see ESI† for a plot of $\chi T/T$).

The extended structure of **1a** in the solid state, see Fig. 4, is also extremely interesting since the tetrahedral anionic units are connected *via* external potassium ions to form an extended 3D network, with an accessible solvent volume of 6000 Å^3 per unit cell (see ESI† for details) capable of hosting 70 solvent water molecules per tetrahedron. Compound **1** was investigated using TGA and DSC which demonstrated that the structure is stable to *ca.* 480 °C whereby the majority of the solvent (*ca.* 7%) is lost around 100–150 °C with only the loss of 1% at 480 °C most likely assignable to decomposition of the cage framework *via* loss of the OH residues (see ESI†).

In conclusion, synthesis of the first example of a nanometre-sized tetrahedron-shaped molecule from iron substituted Wells–Dawson polyoxotungstate has been achieved by using a transition metal complex $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]Cl\cdot 7H_2O$ as the starting material instead of traditional metal salts. The compound was obtained in good yields and was found to be stable in solution. The strategy to use an oxo-centred Fe-acrylate trimer as the iron source to generate a giant molecule has proved to be successful in the case of **1**, and the formation and stability of the tetrahedral anion can be seen by electrospray mass spectrometry and represents the largest inorganic cluster to be characterised by electrospray mass spectroscopy. In future work, we will exploit the approach outlined here in more detail—using both stable POM building blocks, novel heterometal ion sources, and following the self-assembly *via* mass spectrometry, as well as in the solid state, to help design clusters with known architectures *a priori* to go from building blocks to large clusters and then on towards designed solid state materials and devices. We thank the Royal Society, the EPSRC and the University of Glasgow for support and we thank Bruker Daltonics for collaboration using the microTOFQ and the cryospray source.

Notes and references

‡ Synthesis of $K_{21}Na_8[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]\cdot 70H_2O$ (**1**): a sample of $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]Cl\cdot 7H_2O$ (0.165 g, ~0.20 mmol) was dissolved in H_2O (20 mL). Solid $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (0.8 g, ~0.18 mmol) was then added and stirred till a clear brown solution is obtained. Addition of solid KCl (0.16 g, 2.14 mmol) to this reaction mixture results in a yellow precipitate. The reaction mixture was kept at 60 °C for 2 h. The clear yellowish brown solution thus obtained was filtered while hot and kept open for slow evaporation in a conical flask. Greenish yellow crystals of **1** were collected down the conical flask within one week along with a yellow solid mass. The yellow solid mass is found to be amorphous which might be a mixture of inorganic salts as well as minor side products. Yield = 0.425 g, 0.0234 mmol (52% calculated from $\{P_2W_{15}\}$). Elemental analysis calcd (%) for $H_{158}Fe_{12}K_{22}Na_8O_{312}P_8W_{60}$: H 0.88, Fe 3.69, K 4.74, Na 1.01, W 60.80; found: H 0.72, Fe 3.88, K 4.78, Na 0.99, W 60.70. (Na, K, W and Fe were analyzed using atomic absorption spectroscopy). Characteristic IR bands (KBr): 3432, 1619, 1085, 940, 914, 883, 823, 724, 532, 459, 448, 433, 420, 409 cm^{-1}.

§ Crystallographic data: **1**: $H_{158}Fe_{12}K_{22}Na_8O_{312}P_8W_{60}$, M = 18 144.34, monoclinic, space group $C2/m$, a = 47.8099(15), b = 30.6240(15), c = 29.8033(11) Å, β = 122.929(2)°, V = 36 626(3) Å^3, Z = 4, T = 100(2) K, μ(Mo-Kα) = 19.608 mm^{-1}. R_{int} = 0.1131, final $R1$ = 0.0477 and w$R2$ = 0.1245 (all data). CCDC 647356. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b707202c

1 D.-L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105; L. Cronin, Polyoxometalate Clusters, *Comprehensive Coordination Chemistry Reviews 2*, Elsevier, Amsterdam, 2004, vol. 7, pp. 1–57, ISBN 0-08-043748-6.

2 B. Hasenknopf, *Front. Biosci.*, 2005, **10**, 275.

3 M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884; I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, K. I. Hardcastle, C. L. Hill and T. M. Anderson, *Inorg. Chem.*, 2003, **42**, 1163; N. Mizuno, K. Yamaguchi and K. Kamata, *Coord. Chem. Rev.*, 2005, **249**, 1944.

4 D.-L. Long and L. Cronin, *Chem.–Eur. J.*, 2006, **12**, 3698.

5 D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180; C. Ritchie, E. Burkholder, P. Kögerler and L. Cronin, *Dalton Trans.*, 2006, 1712.

6 L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong and A. Müller, *Angew. Chem., Int. Ed.*, 2002, **41**, 2805; B. Botar, P. Kögerler and C. L. Hill, *J. Am. Chem. Soc.*, 2006, **128**, 5336; K. Wassermann, M. H. Dickman and M. T. Pope, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1445.

7 J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, J. R. Galán-Mascarós, C. Giménez-Saiz and C. J. Gómez-García, *Inorg. Chem.*, 2004, **43**, 2689.

8 C. Ritchie, E. M. Burkholder, D.-L. Long, D. Adam, P. Kögerler and L. Cronin, *Chem. Commun.*, 2007, 478.

9 G. J. T. Cooper, G. N. Newton, P. Kögerler, D.-L. Long, L. Engelhardt, M. Luban and L. Cronin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1340.

10 (*a*) E. Cadot, M.-A. Pilette, J. Marrot and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2003, **42**, 2173; (*b*) F. Hussain, B. S. Bassil, L.-H. Bi, M. Reicke and U. Kortz, *Angew. Chem., Int. Ed.*, 2004, **43**, 3485; (*c*) P. Mialane, A. Dolbecq, J. Marrot, E. Rivière and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2003, **42**, 3523; (*d*) S. S. Mal and U. Kortz, *Angew. Chem., Int. Ed.*, 2005, **44**, 3777; (*e*) U. Kortz, F. Hussain and M. Reicke, *Angew. Chem., Int. Ed.*, 2005, **44**, 3773.

11 (*a*) U. Körtz, S. S. Hamzeh and N. A. Nasser, *Chem.–Eur. J.*, 2003, **9**, 2945; (*b*) Y. Sakai, K. Yoza, C. N. Kato and K. Nomiya, *Dalton Trans.*, 2003, 3581; (*c*) G.-S. Kim, H. Zeng, D. VanDerveer and C. L. Hill, *Angew. Chem., Int. Ed.*, 1999, **38**, 3205; (*d*) A. J. Gaunt, I. May, D. Collison, K. Travis Holman and M. T. Pope, *J. Mol. Struct.*, 2003, **656**, 101.

12 D.-L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Chem.–Asian J.*, 2006, **1**, 352.

13 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244; I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1973, **29**, 266.

14 X. Zhang, T. M. Anderson, Q. Chen and C. L. Hill, *Inorg. Chem.*, 2001, **40**, 418; X. Zhang, Q. Chen, D. C. Duncan, C. F. Campana and C. L. Hill, *Inorg. Chem.*, 1997, **36**, 4208; T. M. Anderson, X. Zhang, K. I. Hardcastle and C. L. Hill, *Inorg. Chem.*, 2002, **41**, 2477.