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

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A nanoscale FeIII-substituted polyoxotungstate [KFe_{12}(OH)_{18}(\alpha-1,2,3-P_2W_{15}O_{56})]^{29-} is synthesized starting from the trilacunary [P_2W_{15}] Dawson cluster and [Fe_3(μ-O)-(CH_2=CHCOO)_6(H_2O)]^{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 clusters1 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 biology2 and catalysis.3 Unmatched range of structure types and physical properties with applications in areas as diverse as biology2 and catalysis.3

Herein, we present an approach to observe and control the self-assembly of nanoscale polyoxometalate clusters, in this case [KFe_{12}(OH)_{18}(\alpha-1,2,3-P_2W_{15}O_{56})]^{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 blocks4 and high nuclearity clusters.9 In this work, we selected a well known lacunary, relatively stable, building block, [α-2P_2W_{15}O_{56}]^{29-}, 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 [(α-H_2P_2W_{15}O_{56})_2(Mo_2S_2O_8(H_2O))_4(Mo_2S_2O_8(OH)_2(H_2O))]^{28-} as well as ball-shaped heteropolyoxotungstophosphates [(Sn(CH_3)_2(H_2O))_24(Sn(CH_3)_2)_2(A-XW_9O_34)_12]^{36-},4b Also some supertetrahedral polyoxometalates have been structurally characterized and include tetrameric titanium-substituted [(Ti_3P_2W_{15-O}_{57.5}(OH)_3)]^{4-} and [(P_2W_{15}(Ti_3O_{15.5})Cl)]^{2-},11a,b polyoxotungstates based on the Wells–Dawson fragment. A Nb-containing tetra-Keggin polyoxometalate compound [Nb_3O_6(μ-NbSiW_{15}O_{40})]^{20-},11b and a uranium containing tetrahedral POM [(UO_2)_2(μ-O)(μ_2-H_2O)](P_2W_{15}O_{56})^{32-} have also been reported.11d Here, we utilized an oxo-centred iron-acrylate cluster [Fe_3(μ-O)(CH_2=CHCOO)_6(H_2O)]Cl^{-}H_2O 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 α. equimolecular amount of iron-acrylate trimer [Fe_3(μ-O)(CH_2=CHCOO)_6(H_2O)]Cl^{-}H_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-1,2,3-P_2W_{15}O_{56})]^{29-}7H_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 FeIII tri-substituted Wells–Dawson units linked together through Fe–O–Fe bonds giving an overall Td symmetry. The resulting structure contains a central Fe_{12}O_{36} core, consisting of four groups of three edge-shared, corner-linked FeO_6 octahedra, about which the four FeIII-capped Dawson units are arranged in a tetrahedral fashion around the central KO_{12} templating unit. The arrangement of the central Fe_{12}O_{36} core resembles one set of the four corner-shared faces of an octahedron, see Fig. 2. The central cavity of this Fe_{12}O_{36} 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 “α-P_2W_{15}Fe_3” Dawson units substitute the three

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angle bridging the four Dawson units is found to be 141.2°, forming the tetrahedral geometry of the molecule. The Fe–O–Fe bridges are linked to three other Dawson units through Fe–O–Fe bonds, which thus leads to the composition \([\text{KFe}_{12}(\text{OH})_{18}]^{12-}\), that all the Fe–O–Fe bridges present in the molecule are氧原子 are found to be in the range of 1.15–1.29, indicating approximate 3-fold axis. Colour scheme: O = pink, W = cyan, Fe = brown, PO₄ = green polyhedra, K = orange, KO₁₂ = purple polyhedra.

Fig. 1 Structure of the tetrahedral anion 1a, \([\text{KFe}_{12}\text{(OH)}_{18}(\alpha-1,2,3-\text{P}_{2}\text{W}_{15}\text{O}_{60})\text{H}_{2}\text{O}]^{29-}\), with a K⁺ captured at the cluster centre, viewed down an approximate 3-fold axis. Colour scheme: O = pink, W = cyan, Fe = brown, PO₄ = green polyhedra, K = orange, KO₁₂ = purple polyhedra.

Fig. 2 The polyhedral representation of the central Fe₁₂O₄₆ core of the anion 1a showing the encapsulated potassium ion such that the KO₁₂ unit effectively acts as a template for the whole molecule. Colour scheme as in Fig. 1 except the μ₃-oxo atoms from the PO₄ templates are shown in purple.

In electrospray mass spectroscopic measurements of compound 1 dissolved in water, the tetrahedral anion 1a is observed in solution as the cluster anion \([\text{KFe}_{12}\text{(OH)}_{18}(\alpha-1,2,3-\text{P}_{2}\text{W}_{15}\text{O}_{60})\text{H}_{2}\text{O}]^{29-}\), 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 \([\text{[KFe}_{12}\text{(OH)}_{18}(\alpha-1,2,3-\text{P}_{2}\text{W}_{15}\text{O}_{60})\text{H}_{2}\text{O}]^{16-} \text{K}_{14}\text{Na}_{6}(\text{H}_{2}\text{O})_{10}]^{6-}\), 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 Fe₁₂O₄₆ cluster core, since reaction of \{P₃W₁₅\} cluster with common iron salts resulted in the formation of trisubstituted Wells–Dawson structure (1 : 3 ratio) and sandwich compounds (1 : 2 ratio). 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 \(\chi T\) 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 \([\text{[KFe}_{12}\text{(OH)}_{18}(\alpha-1,2,3-\text{P}_{2}\text{W}_{15}\text{O}_{60})\text{H}_{2}\text{O}]^{16-} \text{K}_{14}\text{Na}_{6}(\text{H}_{2}\text{O})_{10}]^{6-}\) 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 ESIF 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).
yield a Weiss temperature of ca. 1100 K (see ESI† for a plot of $\gamma$TT).

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($\mu_3$-O)](CH$_2$=CHCOO)$_3$(H$_2$O)$_3$Cl$^-$(H$_2$O) 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$_2$Na$_2$[KFe$_3$(OH)$_4$]($\mu$-1,2,3-P,W$_3$O$_{9}$)$_3$-7H$_2$O (1): a sample of [Fe($\mu_3$-O)](CH$_2$=CHCOO)$_3$(H$_2$O)$_3$Cl$^-$(H$_2$O) (0.165 g, ~0.20 mmol) was dissolved in H$_2$O (20 mL). Solid Na$_2$[P,W$_3$O$_9$]·2H$_2$O (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 vaporization 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,W$_3$O$_9$)). Elemental analysis calcd (%) for K$_2$Na$_2$[KFe$_3$(OH)$_4$]($\mu$-1,2,3-P,W$_3$O$_9$)$_3$·7H$_2$O: H 3.69, Fe 3.91, K 4.74, Na 1.01, W 60.70. (Na, K, W and Fe were analyzed using atomic absorption spectroscopy). Characteristic IR bands (KBr): 3432, 1619, 1085, 940, 914, 914, 823, 724, 532, 459, 448, 433, 420, 409 cm$^{-1}$.

§ Crystallographic data: I$_3$Na$_2$Fe$_3$K$_2$Na$_2$O$_{18}$P$_8$W$_{60}$H$_2$O$_{16}$M$_{f}$ = 18443.44, monoclinic, space group C2/m, a = 47.8099(15), b = 30.6240(15), c = 29.8033(11) Å, $\beta$ = 127.9292 ($^\circ$), $V$ = 6262.3(3) Å$^3$, Z = 4, $T$ = 100(2) K, $\mu$(Mo-K$_{x}$) = 19.608 mm$^{-1}$ RO$_{1/2}$ = 0.1131, final R1 = 0.0477 and wR2 = 0.1245 (all data). CCDC 647356. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b707202c