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Trapping the elusive polyanionic δ isomer of the Keggin Cluster with a tripodal ligand**

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Abstract: We report the synthesis, structural, and electronic characterization of the theoretically predicted, but experimentally elusive δ -isomer of the Keggin polyanion. A family of δ -Keggin polyoxoanions of the general formula, $(TEA)H_pNa_q[H_2M_{12}(XO_4)O_{33}(TEA)]rH_2O$ where $p, q, r = [2,3,8]$ for **1** and $[4,1,4]$ for **2** were isolated by the reaction of tungstate(VI) and vanadium(V) with triethanolammonium ions (TEAH), acting as a tripodal ligand grafted to the surface of the cluster leading to the entrapment and stabilization of the elusive polyanionic δ Keggin archetype. The δ -Keggin species were characterized by single-crystal X-ray diffraction, FT-IR, UV-vis, NMR and ESI-MS spectrometry. Electronic structure and structure-stability correlations were evaluated by means of DFT calculations. The compounds exhibited multi-electron transfer and reversible photochromic properties by undergoing single-crystal-to-single-crystal (SC-SC) transformations accompanied with colour changes under light.

Polyoxometalates (POMs) are anionic molecular metal oxides constructed from W, Mo, V or Nb. They attract much attention due to their structures, electronic properties^[1] and applications in catalysis,^[2] magnetism,^[3] as well as medicine^[4] and molecular electronics.^[5] The first polyoxometalate compound was reported by Berzelius^[6] in 1826 but it was not until the 1930s that the X-Ray structure of this iconic compound, the Keggin ion, was first elucidated.^[6] This ion has a tetrahedral symmetry with the general formula $[XM_{12}O_{40}]^{n-}$, where X is a heteroatom (P, Si, S, Ge, As, Co, Fe)^[7] with four O atoms completing the tetrahedral geometry.

Investigations of the Keggin structure revealed four additional isomers, each resulting from the 60° rotation of the four basic $\{M_3O_{13}\}$ units, giving $\alpha, \beta, \gamma, \delta$ and ϵ isomers as reported by Baker and Figgis, see Figure 1.^[8] With the α and β -isomers, the four building blocks are linked together in a corner-shared fashion, whilst in the case of γ, δ and ϵ the corner-shared linkages are replaced by one, three and six edge-shared, respectively.^[9] Since the first report of the most common α - and β -Keggin isomers,^[10] many researchers have investigated their properties,^[11] whilst others reported families of transition metal substituted derivatives of α -, β - and γ - isomers.^[12] The first

Keggin species containing an ϵ -core was reported almost 60 years later as a Rh-substituted oxomolybdenum(V) complex,^[13] followed by the report of a mixed-valence Mo(V)/Mo(VI) isopolyanion^[14], the La and Ni-substituted oxomolybdenum ϵ -Keggin isomers^[15] and recently the Bi substituted vanadium-based ϵ isomer^[16], respectively. However, the only related δ -Keggin structures observed so far are not POM anions but cationic species e.g. the $[Al_{13}]$ cation^[17] and the “reverse-Keggin” ions incorporating either p-block elements (Sb^{5+}) or first row transition metal ions (Co^{2+}, Mn^{2+} or Zn^{2+}).^[18]

Herein, we report the synthesis and characterization of the first members of the δ -Keggin polyanionic isomers to be isolated, compounds **1** and **2**, with the general formula: $TEAH_pNa_q[H_2M_{12}(XO_4)O_{33}(TEA)]rH_2O$ where $p, q, r = [2,3,8]$ for **1** and $[4,1,4]$ for **2** [TEAH: $C_6H_{16}NO_3$ (N, O atoms fully protonated); M: $W^{VI}_4V^V_8$; X: V^V ; TEA: $C_6H_{13}NO_3$: hydroxyl groups fully deprotonated), respectively. The clusters were characterized in the solid state by X-ray diffraction and FT-IR analysis as well as in solution by electrospray ionization mass spectrometry (ESI-MS), UV-vis and Cyclic Voltammetry.

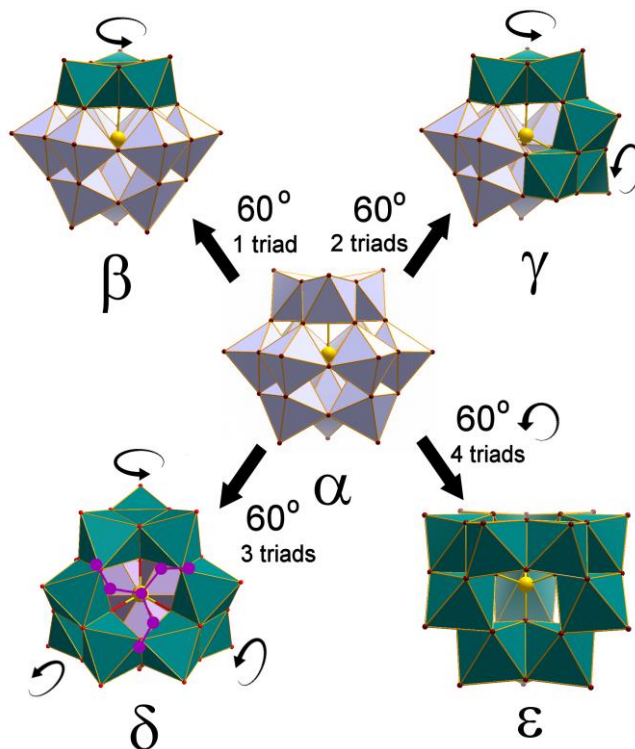


Figure 1. Polyhedral representation of the crystal structures of all the isomers of the Keggin anion: β, γ (top from the left), δ and ϵ (bottom from the left). The green polyhedra show the $\{M_3O_{13}\}$ units which have been rotated the 60° with respect to the α -isomer shown in the centre. The yellow spheres are the heteroatom templates, the small red spheres are the oxo-ligands. The purple ball and stick shows the coordinating ligand which allows the δ isomer to form.

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Crystallographic studies revealed that **1** crystallizes in the monoclinic system in $P2_1/c$ space group and the anion can be formulated as $[H_2W_4V_8(VO_4)O_{33}(C_6H_{13}NO_3)]^{5-}$ (**1a**). The anions exhibit a δ -Keggin structural motif and is derived from the α -Keggin isomer by 60° rotation of the three $\{M_3O_{13}\}$ subunits that are directly bonded to the top TEA tripodal ligand and edge-shared to each other, see Figures 1 and 2. The fourth $\{M_3O_{13}\}$ subunit remains at its original position and is located at the bottom cap opposite to the coordinated TEA ligand coinciding a C_3 axis and is corner-shared with the three neighbouring $\{M_3O_{13}\}$ subunits. Structure refinements revealed that the central XO_4 template and six metal centres that are directly bonded to the TEA tripodal ligand are fully occupied by vanadium atoms whilst the remaining bottom $\{M_3O_{13}\}$ and the three belt sites are occupied by four tungsten and two vanadium atoms disordered over the six positions. Crystallographic studies and BVS^[19] calculations have been carried out to establish the oxidation states of the metal centres. The tungsten atoms are found to be in the oxidation state VI (BVS_{av}=6.02) while all the vanadium atoms found to be in the oxidation state V (BVS_{av}=5.04).

The ‘capping’ triethanolamine ligand adopts a $\eta_2:\eta_2:\mu_3$ coordination mode, completes the octahedral coordination sphere of the upper “cap” vanadium centres, Figure S12, and appears to stabilize the δ -Keggin structure according to experimental evidence obtained from our control experiments. The vanadium atom in the VO_4 tetrahedron is coordinated to four μ_3-O^{2-} bridges, with the V–O bonds within the range of 1.679(9)–1.752(1) Å. Each V atom in the VO_6 octahedra exhibits one terminal oxo group, with a V=O bond length of 1.585(6)–1.690(6) Å, four $\mu-O^{2-}$ and one μ_4-O^{2-} bridges with V–O bonds spanning the range 1.785(5)–2.050(5) Å and 2.269(5)–2.372(5) Å, respectively.

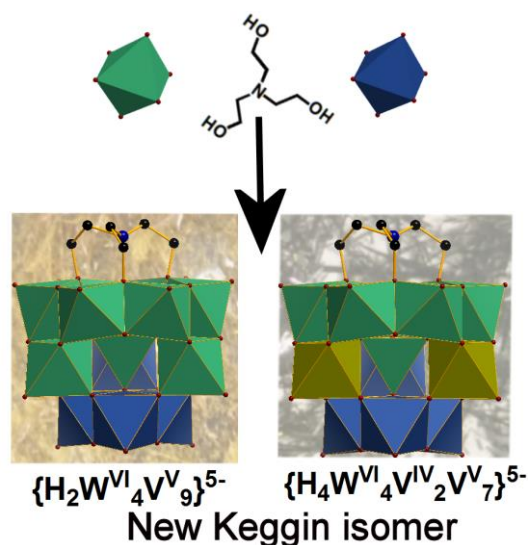


Figure 2. Polyhedral representations of the structure of the δ Keggin found in compounds **1** and **2**. The left and right images show the positions of the V^{VI} (green), W^{VI} (blue) centres and the V^{IV} (yellow: right) produced upon reduction resulting on irradiation. The coordinated tripodal ligand TEA is shown. Colour scheme: W^{VI} : blue, V^{IV} : green, V^{IV} : dark yellow, C: black, N: blue; Counterions have been omitted for clarity.

The remaining W atoms in the WO_6 octahedra support one terminal oxo group, with the W=O bond length in the range of 1.630(5)–1.679(6) Å, four $\mu-O^{2-}$ and one μ_4-O^{2-} bridges with W–O bond lengths in the range of 1.861(5)–1.938(5) Å and 2.305(5)–2.382(5) Å, respectively. Compound **1** was prepared under “one-

pot” conditions from a warm aqueous solution of $NaVO_3$, $Na_2WO_4 \cdot 2H_2O$, TEA·HCl and NaCl, where $Na_2S_2O_4$ was subsequently added, followed by the adjustment of the pH of the reaction mixture with HCl. Yellow needles of suitable quality for X-Ray diffraction analysis were isolated 2–3 weeks later, but both the purity and crystallisation time improved to under 5 days when excess TEA·HCl was used (see experimental section). However structural analysis revealed an isostructural species to compound **1** with the formula $(C_6H_{16}NO_3)_4Na[H_2W^{VI}_4V^{IV}_8(V^{IV}O_4)O_{33}(C_6H_{13}NO_3)] \cdot 4H_2O$ **2**. The structure crystallises in space group ($P2_1/m$) with a crystallographic mirror plane passing through the the centre of the cluster with the main difference being the TEAH⁺:Na⁺ ratio.

In order to determine the role and the impact of the reducing agent, $Na_2S_2O_4$, on the formation of the final product, the same experimental procedure was carried out in the absence of $Na_2S_2O_4$. Orange needles of (**1**) were isolated from an orange solution along with unidentified green precipitate after one week, indicating that the presence of the $Na_2S_2O_4$ is important for the purity and increased yield of the isolated product. It is worth noting that the crystallization time was also reduced from 2–3 weeks to 1 week. Further attempts to synthesize the δ -Keggin isomer in the absence of the TEAH ions have been unsuccessful, suggesting the crucial role of the tripodal ligand in the formation and stabilization of the final product. Additional control experiments showed that the absence of appropriate number of M_3O_{13} building blocks (mainly responsible for the isomerism in POM chemistry) where the TEA can coordinate to and “lock” the δ -Keggin, led to the formation of an α -Keggin instead, Figure S13. Reversing the $VO_3^- : WO_4^{2-}$ ratio to 3:7 generated more tungsten based M_3O_{13} building blocks with lower coordination affinity to the TEA ligand which inhibited the “locking” and isolation of the δ -isomer. When **1** and **2** were illuminated under a 150 W Xe lamp,^[20] the crystals underwent a colour change from yellow to green; observed at room temperature after 2 and 12 hours., respectively Under these conditions a single-crystal-to-single-crystal transformation occurs, whereby compounds **1** and **2** become dark green to give compounds **1'** and **2'** (Figures 2 and S8–S10). X-ray studies showed that the structure of compound **1'** and **2'** are identical to **1** and **2**, but a BVS analysis indicates the δ -Keggin shell is two electrons reduced and two additional oxygen atoms are now protonated (the source of the electrons appears to be the TEA in combination with the water content in the crystal lattice of **1** and **2**)^[21] while the M–O (M = W, V) distances of compounds **1'** and **2'** have changed, as expected for the reduced species (Table S1). If the compounds are left in air they slowly return back to their fully oxidized state (yellow coloured crystals) if kept under dark. In the presence of atmospheric oxygen **1'** converted back to **1** (8–9 months) and **2'** to **2** (4 months), respectively. Additionally, X-ray diffraction data of the single crystal samples were collected before and after the irradiation, confirming further the structural integrity and composition of the cluster.^[21]

Further studies have been carried out in order to unambiguously identify the reduction state of the cluster. By conducting 1H NMR studies exploiting the Evans Method,^[22] it was possible to deduce that the compounds have been reduced by 2 electrons ($\mu_{eff} = 2.4$ and $S = 1.6$; $S =$ number of unpaired electrons). Also, in compounds **1'** and **2'**, V4 and V5 are likely to be in oxidation state V^{4+} , BVS_{av} = 4.3 and 4.2, respectively (see Figure 2). Also, a similar study for compounds **1** and **2** confirms the oxidized nature of the cluster shell of the δ -Keggin clusters (Figures S18 and S19).

The composition of **1** was verified further using high resolution electrospray ionization mass spectrometry^[23] (ESI-MS). The studies were performed in a mixture of H₂O/CH₃CN solvents. At the *m/z* range of 1364-2110, the observed distribution envelopes could be assigned to the anionic fragment of compound **1**, with the formula [W₄V₅V^{IV}₄O₃₇H₉(C₆H₁₃NO₃)(C₆H₁₆NO₃)(H₂O)]¹⁻ or even the anionic dimer and trimer of **1** species, formulated as {[W₄V₅V^{IV}₄O₃₇H₉(C₆H₁₃NO₃)]₂(C₆H₁₆NO₃)(H₂O)₂}³⁻ and {[W₄V₆V^{IV}₃O₃₇H₇(C₆H₁₃NO₃)]₃Na₄(C₆H₁₆NO₃)(H₂O)₉}⁴⁻, respectively. Moreover, the peak located at *m/z* = 969.2 corresponds to the fragment {[V₅V^{IV}₂O₂₅H₇Na₅(C₆H₁₃NO₃)](C₆H₁₆NO₃)₅(H₂O)₉}²⁻, whilst the peak centred at *m/z* = 835.7 could be assigned to the cluster fragment {[V₄V^{IV}₃O₂₅H₇Na₈(C₆H₁₃NO₃)](C₆H₁₆NO₃)₃(H₂O)₇}²⁻. Finally, peaks in the region *m/z* 1054-1209, correspond to the {[WV^VV^{IV}₆O₂₅H₈Na(C₆H₁₃NO₃)](C₆H₁₆NO₃)₆(H₂O)₅}²⁻ and {[WV^VV^{IV}₇O₂₅H₁₁(C₆H₁₃NO₃)Na](H₂O)₂}¹⁻ species (Figure 3). The observed fragmentation is due to the experimental conditions used during the ionization process of the species in the gas phase. The stability of the species in solution for at least a few hours has been verified by UV-vis spectroscopy prior to the ESI-MS studies.

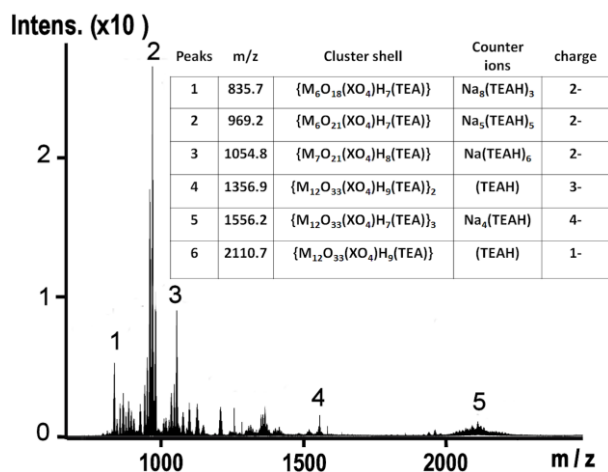


Figure 3. ESI mass spectrum in negative-mode of **1** in the *m/z* range of 800-2500 showing the major peaks of charged fragments.

In order to investigate the electronic structure of the clusters, we performed density functional theory (DFT) analysis to elucidate the most favourable positions of the two crystallographically disordered over 6 positions vanadium (V^{IV}) centres and consequently the location of the two unpaired electrons injected in the cluster shell. Figure 4 shows the relative energies with respect to the most stable positional isomer for the parent compound, [W^{VI}₄V^V₈(V^{VO}₄)O₃₃(C₆H₁₃NO₃)]⁷⁻ and the two electron reduced species, [W^{VI}₂V^{IV}₂V^V₆(V^{VO}₄)O₃₃(C₆H₁₃NO₃)]⁹⁻. Note that we have omitted the protons in the {M₁₂} cage, therefore the negative charge of the cluster increased accordingly. For the parent compound the relatively most stable geometries are δK-1, with one vanadium in the bottom cap and the second one in the belt, and δK-2 with two vanadium atoms in the bottom cap. Nevertheless, the relative small energy difference (3.5 kcal mol⁻¹) with respect to geometries δK-3 and 4 makes this results rather inconclusive, since the average method error is around 1–2 kcal mol⁻¹ (<5%).^[24] Fortunately, results of the two electron reduced species show a promising

energy difference within isomers. In this case, the most stable isomer is δK-3, being +4 kcal mol⁻¹ relatively more favourable compared to δK-1, 2 and 4. In δK-3 both V(IV) atoms are in the belt region and three, of the four tungsten atoms, form a triad [M₃O₁₃]. Previous knowledge in relation to the formation mechanism of POM clusters has shown that triads can be considered as structural *building blocks* which is in agreement with our energy calculations.^[25] Therefore our preliminary results allows us to propose that the most plausible positional isomer is the δK-3, with the two unpaired electrons residing in the belt position of the shell; however further theoretical and experimental analysis will be necessary to validate this hypothesis.

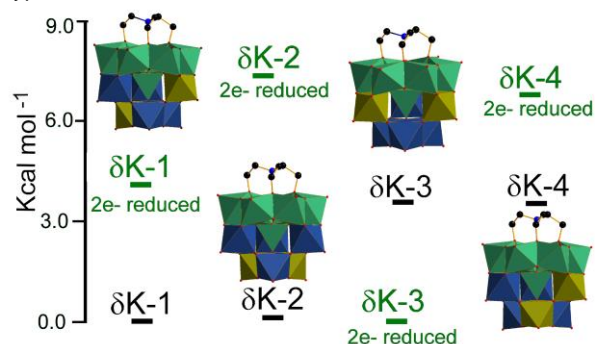


Figure 4. Theoretical relative energies with respect to the most stable positional isomer (δK-1 to δK-4), with the formula [W^{VI}₄V^V₈(V^{VO}₄)O₃₃(C₆H₁₃NO₃)]⁷⁻, black lines and its two electron reduced analogues, [W^{VI}₄V^{IV}₂V^V₆(V^{VO}₄)O₃₃(C₆H₁₃NO₃)]⁹⁻, green lines. These results helped us to determine the more favourable positions of the two V^{IV} atoms. W: Indigo, V^V: green, V^{IV}: dark yellow, C: black, N: blue.

In conclusion, the isolation and complete characterization in solid state and solution of the elusive polyanionic δ-Keggin isomer, with the formula [H₂W^{VI}₄V^V₈(V^{VO}₄)O₃₃(C₆H₁₃NO₃)]⁵⁻, was synthesized under one-pot conditions utilising a tripod ligand which appears to lock the δ- isomer via coordination of the TEA ligands. The compound type was shown to undergo a cation modulated photochemical two electron process upon illumination observed as SC-to-SC transformation studied by X-ray diffraction. Future work will focus on investigating further the electronic properties as well as attempting to finely tune the variables and the effect of the isomerism that controls the solid state electron transfer processes in polyoxometalate systems.

Experimental Section

Synthesis of (C₆H₁₆NO₃)₂Na₃[H₂W₄V₈(VO₄)O₃₃(C₆H₁₃NO₃)]·8H₂O **1** : **Method A:** NaVO₃ (0.854 g, 7 mmol), Na₂WO₄·2H₂O (0.990 g, 3 mmol), TEA·HCl (0.464 g, 2.5 mmol) and NaCl (0.117 g, 2 mmol) were dissolved in deionised water (10 ml) giving a cloudy yellow solution. The reaction mixture was heated at 80-90 °C for 1 hour, during which time the cloudy yellow solution changed to clear orange. After cooling the reaction mixture down to room temperature, Na₂S₂O₄ (0.087 g, 0.5 mmol) was added to the reaction mixture resulting to dark brown solution and the pH was adjusted to 2.0-2.5 by addition of 37% HCl followed by a colour change to dark green. The reaction mixture was filtered and the filtrate was left undisturbed to crystallize at 18 °C. Orange needles suitable for X-ray diffraction analysis obtained after 2-3 weeks. Yield: 80 mg (8.1% based on W). MW: 2448.48 g·mol⁻¹. IR (cm⁻¹): 3410.2 (b), 1627.9 (m), 1384.9 (m), 1211.3 (m), 1064.7 (m), 975.9 (s), 891.1 (s), 833.25 (m), 775.4 (s), 636.5 (w), 551.6 (w). Elemental analysis calcd for C₁₈H₆₃N₃Na₃O₅₄V₉W₄: C 8.83, H 2.59, N: 1.72, Na 2.82, V 18.73, W 30.04%. Found: C 9.04, H 2.19, N 1.69, Na 3.00, V 19.66, W 28.24%.

Method B: The above synthetic procedure was repeated in the absence of Na₂S₂O₄. The reaction mixture was filtered and the filtrate was left undisturbed to crystallize at 18 °C. Orange needles suitable for X-ray diffraction analysis obtained after 1 week. Yield: 150 mg (15.2% based on W). The obtained spectroscopic and crystallographic data of the isolated compound are identical to 1.

Synthesis of (C₆H₁₆NO₃)₄Na[H₂W₄V₈(VO₄)O₃₃(C₆H₁₃NO₃)]·4H₂O **2**: The compound **2** was synthesized as compound **1** (method A) using an increased amount of TEA·HCl (1.857g, 10 mmol) instead. Orange needles suitable for X-ray diffraction analysis obtained after 5 days. Yield: 120 mg (12.1% based on W). MW: 2630.83 g·mol⁻¹. IR (cm⁻¹): 3354.2 (b), 1627.9 (m), 1384.9 (m), 1213.2 (w), 1066.6 (m), 970.2 (s), 891.1 (s), 831.3 (m), 777.3 (m), 624.9 (w), 547.8 (w). Elemental analysis calcd for C₃₀H₈₇N₅NaO₅₆V₈W₄: C 13.70, H 3.33, N: 2.66, Na 0.87, V 14.43, W 27.96%. Found: C 13.40, H 3.09, N 2.63, Na 0.67, V 17.06, W 25.45%.

Computational method: Geometry optimizations performed using B3LYP method as implemented in TURBOMOLE V6.3.1 package.^[26] TZVP basis set was used on all atoms. To allow for solvation effects, the conductor-like screening model (COSMO) method was used with ionic radii of the atoms, which define the dimensions of the cavity surrounding the molecule, are chosen to be (in Å) 2.23 for W and V, 2.0 for C, 1.8 for N, 1.72 for O, 1.3 for H.

Keywords: keggin isomers • polyoxometalates • assembly • photochromism • supramolecular chemistry

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