

Synthesis, structures and applications of electron-rich polyoxometalates

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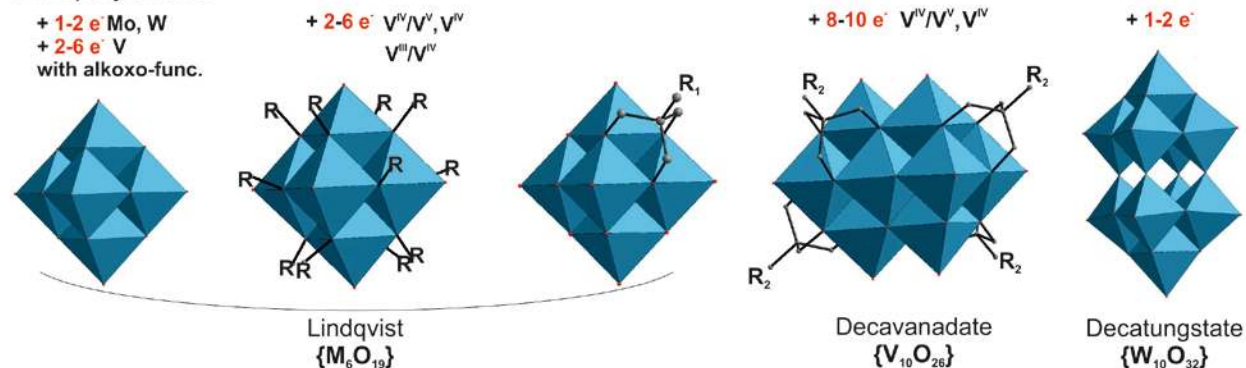
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Electron-rich polyoxometalates (POMs), known since the early discovery and development of POM chemistry, are POMs incorporating extra electrons upon reduction and comprise an emergent family of different archetypes, structural flexibility and functionality. Here, we describe synthetic strategies to obtain electron-rich POMs with important catalytic, electronic and magnetic properties and discuss their differences and advantages compared to their fully oxidized analogues. This is the first review summarizing the existing knowledge about polyoxometalate reduction, encompassing a comprehensive description of reduced compounds (over 200 structures are reviewed) and the influence the reduction causes on the structure, function and properties of this molecule class.

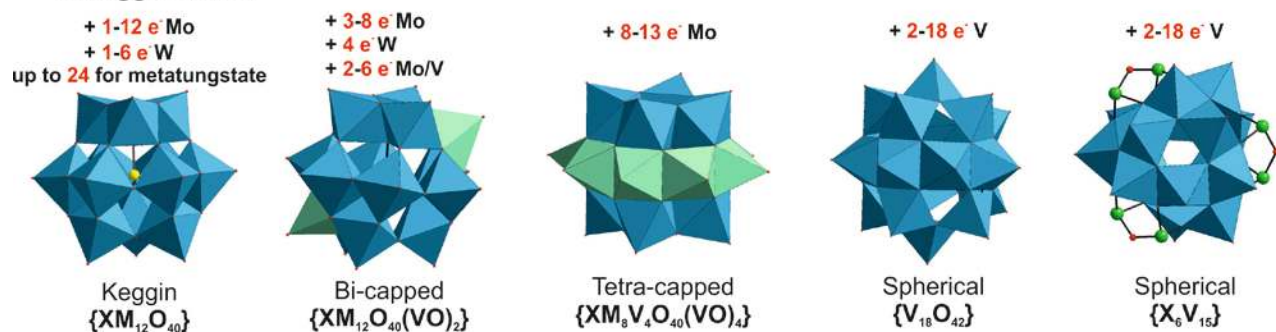
Polyoxometalates (POMs) are a large group of transformable discrete anionic polynuclear metal-oxo clusters. These compounds contain arrays of corner- and edge-sharing pseudo-octahedrally coordinated MO_6 ($M = V, Nb, Mo, W$) units, packed to form an ionic core, where the electronic configuration of the metal is usually d^0 or d^1 (metals in their highest oxidation states).¹ These metals are commonly called addenda atoms or peripheral elements and their ionic radii and charge are suitable for O^{2-} coordination. The coordination number of the addenda atoms can be increased from 4 to 6 upon acidification and they are able to form double bonds with unshared terminal oxygens in MO_6 octahedra through $p_\pi-d_\pi$ interactions. One of the most widely accepted classification of POMs divides them into two groups: 1) isopolyanions (IPAs), which consist of only one type of metal (M) atom, $[M_mO_y]^{q-}$, and 2) heteropolyanions (HPAs), with the general formula $[X_rM_mO_y]^{q-}$, where X is the so-called heteroatom. POMs have multiple applications in various areas, such as catalysis,^{2,3} bio- and nanotechnology,⁴ medicine,⁵⁻⁶ macromolecular crystallography,⁷⁻⁹ electrochemistry,¹⁰ material sciences¹¹ and molecular magnetism¹² and many of them are related to their redox properties. POMs are often recognized as electron reservoirs because of their strong capacity to bear and release electrons indicating their redox nature.¹³ POMs can be regarded as soft Lewis bases due to the abundant oxygen atoms that can donate electrons to electron acceptors. However, the addenda metal ions of the polyanion skeletons possess unoccupied orbitals that can accept electrons and thereby act as Lewis acids.²

The reduced, also called electron-rich, POMs typically retain the general structure of their parent molecule and are often characteristically deep blue in color comprising a very large group of complexes known as the “poly blues” or “heteropoly blues” (FIG. 1). Their blue color is the result of intense d-d electron transitions and intervalence charge-transfers.¹⁴

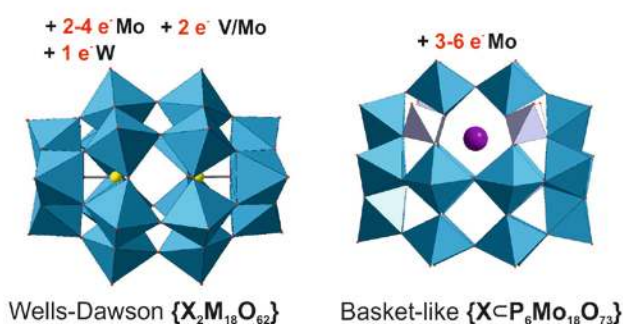
a Isopolyanions



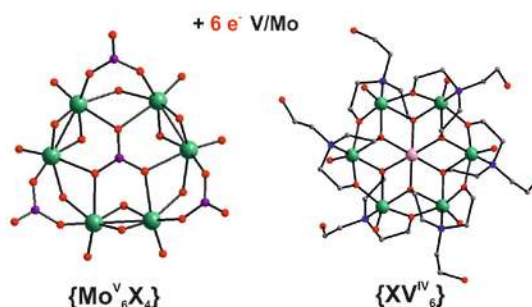
b Keggin based



c Dawson based



d Anderson-like



35

36 Figure 1 | **Conventional types of electron-rich POMs.** **a** | Isopolyanions: Lindqvist type isopolymolybdate, -tungstate $\{M_6O_{19}\}$
 37 ($M = Mo, W$) and organically functionalized vanadates $\{V_6O_n(OR)_{19-n}\}$ or $\{V_6O_{19-3n}((OCH_2)_3CR^1)_n\}$ ($R = -CH_3, -C_2H_5; R^1 = -CH_3, -$
 38 $C_2H_5, -CH_2OH, -NO_2$), decatungstate $\{W_{10}O_{32}\}$ and functionalized decavanadates $\{V_{10}O_{28-3n}((OCH_2)_3CR^2)_n\}$ ($R^2 = -C_2H_5, -CH_2OH$).
 39 Color code: MO_6 , blue polyhedra. **b** | Keggin based anions: classical Keggin anion $\{XM_{12}O_{40}\}$ (X – heteroatom, which is missing
 40 in metatungstate, $M = Mo, W$); bi- and tetra-capped pseudo-Keggin anions. Color code: MO_6 , blue polyhedra; VO_5 , green
 41 polyhedra. Examples of vanadium spherical anions $\{V_{18}O_{42}\}$ and $\{X_6V_{15}O_{42}\}$ ($X = As, Sb, Ge, and Si$). Color code: VO_n , blue
 42 polyhedra; X , green spheres. $\{V_{18}O_{42}\}$ is an isopolyanion, however based on the structural classification it is presented in the
 43 Keggin based anions section. **c** | Wells-Dawson based anions: classical $\{X_2M_{18}O_{62}\}$ (X – heteroatom, $M = Mo, W, V$) and basket-
 44 like $\{XCp_6Mo_{18}\}$ (X – alkali metal) archetypes. Color code: MO_6 , blue polyhedral; X – yellow or purple spheres. **d** | Anderson-
 45 like anions: left - $[(Mo^V_2O_4)_3(CO_3)_4(OH)_3]^{5-219}$; right - $XV^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6\}^{n+}$ ($X = Li, Na, Mg, Mn, Fe, Co, Ni\}^{206}$.
 46 Color code: V/Mo, green; M, pink; N, blue; C, violet; O, red.

47 The most prominent reduced POMs are the mixed-valence molybdenum blue $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ “giant wheels” based on $\{\text{Mo}_{154}\}$
48 units, which are obtained by partial reduction of Na_2MoO_4 with a reducing agent (e.g. N_2H_4 , NH_2OH , SnCl_2) in acidic
49 solutions.^{15,16} “Heteropoly ‘browns’” are polyoxotungstates (POTs) generated by spontaneous intraionic disproportionation of
50 the W^{V} atoms in the “blue” species under acidic conditions yielding more highly reduced $\text{W}^{\text{IV}}\text{O}_6$ octahedra.^{17,18}

51 The added electrons can be either localized on a metal ion or delocalized as “extra” electrons over a number of metal
52 ions leading to an increased electron density on the terminal oxygen ions of the POM. The delocalized electrons can be
53 considered either as thermally activated electrons hopping from one addendum ion to the next or as electron ground-state
54 delocalization. The latter presumably involves π bonding through bridging oxygens from the reduced metal ion M^{V} to its
55 oxidized neighbor addendum M^{VI} .¹⁴

56 The capacity to reduce a particular POM depends on the charge to nuclearity ratio and for heteropolyanions the kind
57 and oxidation state of the heteroatoms must be taken into consideration. In 1972, Pope¹⁹ divided all POMs into three types:
58 type I, which comprises polyanions in which each addendum atom has one unshared terminal oxo ligand, type II,
59 characterized by two unshared terminal oxo ligands per addendum atom, and type III, as a combination of the two former.
60 Pope predicted that only type I and III polyanions can be reversibly reduced. According to the molecular orbital theory of oxo-
61 type octahedral complexes, species with one unshared oxygen (type I) have one non-bonding t_{2g} orbital, which can
62 accommodate one or two electrons by reduction, however, anions with two unshared oxygens (type II) lack the non-bonding
63 t_{2g} orbital, because in the orbitals participate in the π -bonding.²⁰ Consistent with this early paradigm, up to date there is no
64 data about reduction of Anderson-type anions ($[\text{XMo}_6\text{O}_{24}\text{H}_x]^{n-}$, X = heteroatom; M = Mo, W; x = 0 – 6) or octamolybdates
65 ($[\text{Mo}_8\text{O}_{26}]^{4-}$), which belong to type II POMs. However, it is possible to reduce the heptamolybdate anion $[\text{Mo}_7\text{O}_{24}]^{6-}$ (type II
66 by Pope classification) photochemically through the formation of an intermediate complex bearing only one unshared oxygen
67 atom as in type I.²¹⁻²²

68 Polyoxomolybdates (POMs) are more readily reduced than their isostructural POTs, and therefore Mo ions are
69 preferentially reduced in mixed-metal Mo/W POMs.²³ The isostructural POMs have potentials that are about 400 mV more
70 positive than the corresponding POTs, for example, the one-electron reduction potential in acetone for $\alpha\text{-PW}_{12}$ is -895 mV,
71 whereas for $\alpha\text{-PMO}_{12}$ it is -468 mV.²⁴ In POMs exhibiting the common Keggin structure $[\text{XM}_{12}\text{O}_{40}]^{n-}$ (X = heteroatom, M = Mo,
72 W, Nb), which consists of 12 addenda atoms, the number of accepted electrons can vary from 1²⁵ to 12²⁶ for POMs, but for
73 the analogous POTs the maximum number of “blue” electrons is 6¹⁸ (TABLE 1). Vanadium addenda ions accept electrons even
74 better than molybdenum ions (one-electron reduction potential for $\alpha\text{-PVW}_{11}$ is 600 mV¹⁰). It has been demonstrated that in a
75 spherical $\{\text{V}_{18}\text{O}_{42}\}$ structure all vanadium ions are reduced to V^{IV} leading to an accepted number of 18 electrons.

76 POMs can be reduced in different ways, for example, photochemically,^{21, 27, 28} electrolytically¹ and in the presence of
77 reducing reagents (metals, B_2H_6 , NaBH_4 , N_2H_4 , NH_2OH , H_2S , SO_2 , SO_3^{2-} , $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$, SnCl_2 , MoCl_5 , MoOCl_5^{2-} , Mohr’s salt,
78 formic acid, ethanol, ascorbic acid, tartaric acid, thiourea, hydroquinone, D-glucose, sucrose, etc.). Under hydrothermal
79 conditions, Mo^{VI} and W^{VI} can accept one or two electrons¹ and thus the vast majority of reduced POMs are synthesized by the
80 hydrothermal method. Reduced POMs are often air-stable, whereas reduced POTs are typically air-sensitive.¹⁴ Various
81 oxidants, which contain O_2 or H_2O_2 , restore reduced POMs to the non-reduced ones. Since the reduction increases the
82 nucleophilicity of the POMs, transition metal ions act as electrophiles and stabilize the POMs through covalent attachments.²⁶

83 The characterization of reduced POMs can be challenging, especially in the case of mixed-metal compounds, where the
 84 usage of multiple complementary physical techniques is sometimes necessary just to determine the compound's formulation.
 85 A detection of the number and structural positions of the different metal centers can be achieved by single-crystal X-ray
 86 diffraction complemented by elemental analysis.

87

88 **Table 1.** Number of reduced electrons in POMs based on the Keggin structure XM_{12} (X = heteroatom; M = Mo, W)..

Type of addenda ions	No. of accepted electrons	
	min	max
Keggin type XM_{12} (12 addenda ions)		
M = Mo	1 ²⁵	12 ²⁷
M = W	1 ¹²⁰	6 ¹⁸
M = Mo, W	2 ²⁶⁹	8 ¹⁰⁹
Bi-capped Keggin type XM_{12}V_2 (14 addenda ions)		
M = Mo	3 ¹²⁹	8 ¹³⁰
M = V, Mo	2 ¹³⁹	6 ¹⁴⁰
M = W	4 ¹⁴⁹	4 ¹⁴⁹
Tetra-capped Keggin type XM_8V_8 (16 addenda ions)		
M = Mo	8 ¹⁵⁷	13 ¹⁵⁸

89

90 To obtain the number of electrons and their location and degree of delocalization in the POMs is a more challenging
 91 approach. Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) can give insights into the
 92 valence of the metal centers, while magnetic measurements can indicate the number of unpaired electrons. In solution, redox
 93 titrations, electrochemistry, and UV-visible spectroelectrochemistry are most useful for determining the exact degree of
 94 reduction. Paramagnetic electron-rich POMs are predominantly studied by EPR spectroscopy, while diamagnetic ones are
 95 investigated by NMR spectroscopy in solution.²⁹ Computational chemistry has also become increasingly accurate and
 96 affordable for elucidating the electronic structure of reduced POMs.³⁰ The theoretical analyses based on the Anderson-
 97 Hubbard ideas using quantum-chemical density functional theory (DFT) and *ab initio* calculations or the parametric solution of
 98 exchange and delocalization problem provide a basis for further investigation of the multinuclear mixed-valence clusters.

99 As in the case of oxidized POMs reduced anions have been found the widest application as catalysts, due to their
 100 resistance to oxidative decomposition, high thermal stability, and sensitivity to light and electricity.^{27, 32-35} Almost all types of
 101 reduced POMs with different degree of reduction demonstrate electrocatalytic activity and have been applied as reductive
 102 and oxidative electrocatalysts. The outstanding photocatalytic activity of one-electron reduced decatungstate $[\text{H}^+\text{W}_{10}\text{O}_{32}]^{5-}$ also
 103 should be noted.²⁷ The magnetic susceptibility of a great number of electron-rich POMs was tested, but only some V^{IV} -
 104 containing Keggin-based anions were applied as qubits for molecular spintronics³⁵ or as molecular magnet³⁶. Unlike most
 105 nanoparticle-protecting ligands, electron-rich POMs can reduce metal cations to colloidal metal(0) particles, which are then
 106 stabilized by the oxidized POM anions, and thus the POMs play a dual role, acting as both reducing agents and stabilizing

107 anions. So far Keggin and Wells-Dawson electron-rich POMs with number of “blue” electrons from 1 to 8 were used as
108 protecting ligands for metal(0) nanoparticles.³⁷ Yamase group over the years tested isopolymolybdates (IPOMos) which can
109 be reduced within cancer cells as anti-cancer agents,^{38,39} the Lindqvist type POV inhibits Na⁺/K⁺-ATPase,⁴⁰ however application
110 of reduced POMs in biology is not elaborated enough and their role in this processes is not at all understood. The unique
111 stability of the Keggin structure allowing it to take up to 24 electrons makes it possible to use POMs based on this anion as
112 electron storage device.⁴¹

113 Despite the long history of “heteropoly blues” the present review is the first one that summarizes and gives an
114 overview of existing electron-rich POMs. The description of the reduced POMs is divided in two parts. The first section will
115 discuss isopolyanions, where one or more Mo, W or V atoms are in a lower oxidation state, whereas the second part will
116 describe reduced heteropolyanions based on their structural archetype, namely mixed-valence POMs based on Keggin
117 structure (anions with classical and capped Keggin structure), mixed-valence POMs with Wells-Dawson structure and their
118 derivatives (basket-like POMos and borophosphate POMos), Anderson-like fully reduced POVs and POMos and vanadium
119 cluster compounds based on the spherical {V₁₈O₄₂} archetype.. The reduced giant POMs developed by Müller *et al.*⁴² will be
120 left out due to existing reviews⁴³⁻⁴⁴ about these compounds. Furthermore, the use of POMs as electron-accepting moieties in
121 charge-transfer compounds developed by Hill⁴⁵ and Kochi⁴⁶, which are synthesized by co-crystallization with organic donors
122 such as substituted amides, aromatic amines, or tetrathiafulvenes and decamethylferrocene, are not discussed in this review.

123 **Reduced isopolyanions**

124 ***Isopolymolybdate s***

125 The existing data about reduced isopolymolybdates (IPMOS) are centered around the classical Lindqvist [Mo₆O₁₉]²⁻
126 archetype⁴⁷⁻⁵⁰ (FIG. 1 a) and heptamolybdate [Mo₇O₂₄]⁶⁻^{21,22} (FIG. 3 a), along with one-time synthesis of IPMOS with structures
127 that do not belong to one of the classical POM archetypes.⁵¹⁻⁵⁴ The photoreduction of alkylammonium polyoxomolybdates,²¹
128 namely hexa-, hepta and octomolybdates, is described by an example of heptamolybdate as the most extensive study. Up to
129 now seven reduced IPMOS, which accepted between one and twelve electrons, were crystallized and investigated by single-
130 crystal XRD (TABLE S1).

131 ***One-electron reduction of the Lindqvist anion [Mo^{VI}₆O₁₉]²⁻***. According to the Cambridge Crystallographic Data Centre (CCDC)
132 and Inorganic Crystal Structure Database (ICSD), up to date there are no data about crystal structures of reduced
133 isopolymolybdates with Lindqvist structure (FIG. 1 a). However, in 1979, Che and co-workers described the controlled
134 potential electrolysis of [Mo₆O₁₉]²⁻ in dimethylformamide, which yielded the brown [Mo^VMo^{VI}₅O₁₉]³⁻ ion.⁴⁸⁻⁵⁰ They showed
135 that the reduction step [Mo^{VI}₆O₁₉]²⁻ + e⁻ ⇌ [Mo^VMo^{VI}₅O₁₉]³⁻ is reversible and assumed that the structure of the parent oxidized
136 form is retained upon reduction. EPR measurements of [Mo^VMo^{VI}₅O₁₉]³⁻ indicate thermal delocalisation of the valence
137 electron with increasing temperature.^{48,49} The introduction of an electron which is localised on one molybdenum atom has a
138 perturbing effect on the Mo^V=O_t bond.⁴⁷

139 ***Mechanism of heptamolybdate [Mo^{VI}₇O₂₄]⁶⁻ reduction.*** According to Pope’s hypothesis¹⁹ the heptamolybdate anion
140 [Mo^{VI}₇O₂₄]⁶⁻ cannot be reduced due to the presence of two *cis*-dioxo groups within the MoO₆ octahedron (type II POM by
141 Pope classification). Thus, the reduction of [Mo^{VI}₇O₂₄]⁶⁻ has so far only been observed by irradiation with ultraviolet light

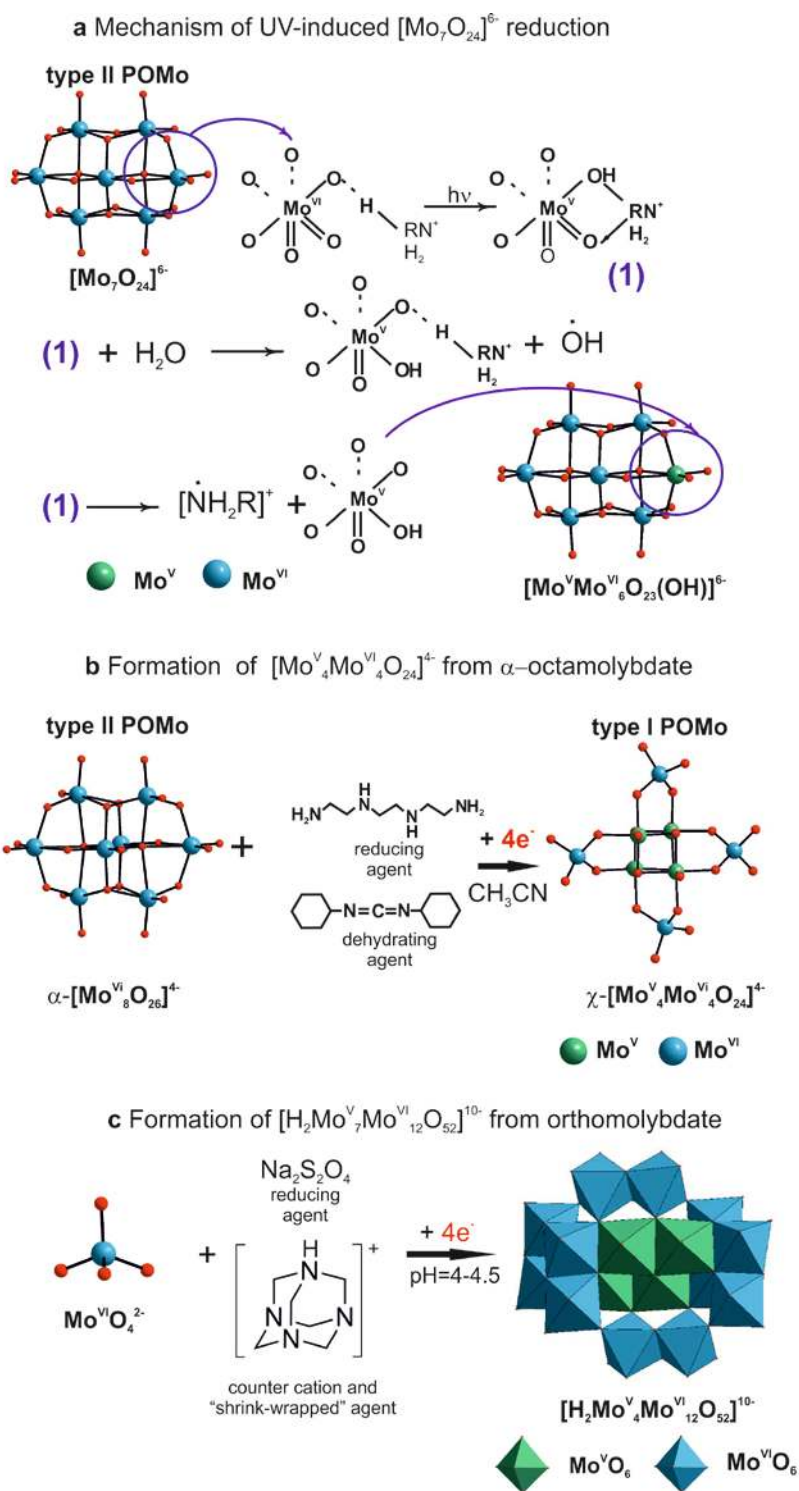
142 ($\lambda \geq 313$ nm) in aqueous solution²² or in the solid state²¹ in the presence of the $[\text{NH}_3^i\text{Pr}]^+$ ($i\text{Pr}$ – isopropyl) cation since the
143 proposed reduction mechanism involves an interaction between the heptamolybdate anion and the cation (FIG. 2 a). The
144 reduction of Mo^{VI} takes place through the formation of an intermediate complex with one unshared oxygen, which is
145 characteristic for type I POMs according to Pope (FIG. 2 a, reaction I). This intermediate enables the reduction reaction and
146 therefore does not contradict Pope's theory. The EPR spectra revealed a localized octahedral $\text{Mo}^{\text{V}}\text{O}_5(\text{OH})$ site resulting from
147 an electron transfer between the anion and the counterion via hydrogen bonding.^{21,22} The X-ray structure of UV-irradiated
148 single crystal of $[\text{NH}_3^i\text{Pr}]_6[\text{Mo}^{\text{VI}}_6\text{O}_{24}]$ is in agreement with the EPR by revealing the protonation of the bridged oxygen in the
149 $\text{Mo}^{\text{V}}\text{O}_5(\text{OH})$ octahedra (FIG. 3 a).²¹

150 **Electron acceptance as a key factor for the formation of new polymolybdate archetypes.** The reduction of type II IPOMos
151 (octa- and hepta-anions) in non-aqueous solvents leads to the formation of novel mixed-valent POMos with structures
152 different from the parent anions. α -Octamolybdate $(\text{Bu}_4\text{N})_4[\text{Mo}^{\text{VI}}_8\text{O}_{26}]$, a typical type II POM, was reduced to the crosslike
153 octamolybdate anion $[\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_4\text{O}_{24}]^{4-}$ by refluxing it with triethylenetetramine (TETA) and N,N' -dicyclohexylcarbodiimide
154 (DCC) in dry acetonitrile. The $[\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_4\text{O}_{24}]^{4-}$ anion has an unusual $\text{Mo}^{\text{V}}_4\text{O}_8$ cubane-like core and was termed χ -
155 octamolybdate due to its shape (FIG. 2 b).⁵²

156 Cronin *et al.*⁵⁴ obtained the novel mixed-valent “shrink-wrapped” anion $[\text{H}_2\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{12}\text{O}_{52}]^{10-}$ by the addition of
157 protonated hexamethylenetetramine (HMTAH^+ or $\text{C}_6\text{H}_{13}\text{N}_4^+$) as cation to the reaction solution that is typically used to for giant
158 Mo cluster systems (MoO_4^{2-} and hydrazine). The large organic cation prevents the rapid aggregation of metal-oxide-based
159 polyhedra to clusters with a stable uniform spherical topology. This novel compound contains an unusual platform-like Mo_{12}
160 core (FIG. 2 c).⁵⁴ The four Mo^{V} centers comprise two centrosymmetrically related Mo^{V}_2 groups (located in the central part of
161 the $[\text{H}_2\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{12}\text{O}_{52}]^{10-}$ cluster core) displaying a short Mo(2)-Mo(3) contact of 2.6427(4) Å, which is characteristic for
162 Mo – Mo single bonds.

163 The reaction of the Lindqvist nitrosyl derivative $(^n\text{Bu}_4\text{N})_3[\text{Mo}^{\text{VI}}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}-(\text{MeOH})\}]$ with VCl_3 in methanol
164 yields the two electron reduced nitrosyl decamolybdate $[\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_7\text{O}_{25}(\text{OMe})_6(\text{Mo}^{\text{II}}\text{NO})]^-$ and the reaction of
165 $(^n\text{Bu}_4\text{N})_2[\text{Mo}^{\text{VI}}_5\text{O}_{18}(\text{NO})]$ with $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in a mixture of methanol and acetonitrile yields the four-electron reduced nitrosyl
166 decamolybdate $[\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_5\text{O}_{24}(\text{OMe})_7(\text{Mo}^{\text{II}}\text{NO})]^{2-}$.⁵¹

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170 Figure 2 | **Schematic representation of reduced isopolymolybdates formation.** **a** | UV-induced reduction of
 171 heptamolybdate.^{21,22} **b** | Formation of the reduced χ -type octomolybdate starting from α -octomolybdate.⁵² **c** | Formation of

172 the "shrink-wrapped" anion $[\text{H}_2\text{Mo}_4^{\text{V}}\text{Mo}_{12}^{\text{VI}}\text{O}_{52}]^{10-}$.⁵⁴

173

174 The structure of decamolybdate is closely related to that of the well-known decatungstate $[W_{10}O_{32}]^{4-}$ (FIG 1, a) and consists of
175 two halves of five edge-sharing octahedral connected through four quasi-linear Mo-O-Mo bridges. The Hückel calculations
176 demonstrate that the “blue” electrons are circulating around the eight equatorial molybdenum sites as the delocalization is
177 strongly favored by the quasi-linear M-O-Mo bridges.⁵¹

178 In 1993, Khan and co-workers were the first to obtain $[Me_2NH_2]_6[H_2Mo^V_{12}O_{28}(OH)_{12}(Mo^VI O_3)_4]$ by hydrothermal
179 synthesis starting from Na_2MoO_4 , MoO_3 , Mo, $C(CH_2OH)_4$, $(Et_4N)Cl$, Me_3NH and H_2O .⁵⁵ The high degree of reduction of the
180 central ϵ -Keggin (BOX 1) core $\{Mo^V_{12}O_{40}\}$ significantly increases the basicity of the oxygen atoms on the surface, which allows
181 the aggregation of four electrophilic $\{Mo^VI O_3\}$ units. The remarkable flexibility of the host ϵ -Keggin cage is demonstrated by
182 encapsulation of two protons. Later Yamase *et al.* showed that $[H_2Mo^V_{12}O_{28}(OH)_{12}(Mo^VI O_3)_4]^{6-}$ can also be formed by
183 reduction in tumor cells from heptamolybdate and confirmed their prediction by long-term photolysis of
184 $[PrNH_3]_6[Mo_7O_{24}] \cdot 3H_2O$ in aqueous solutions at pH 5–6 yielding the same electron rich anion.^{38,53}
185 $[H_2Mo^V_{12}O_{28}(OH)_{12}(Mo^VI O_3)_4]^{6-}$ depressed the proliferation of human cancer cells such as AsPC-1 ($IC_{50} = 175 \mu g \cdot ml^{-1}$)
186 pancreatic and MKN-45 ($IC_{50} = 40 \mu g \cdot ml^{-1}$) gastric cells *in vitro* and *in vivo*.³⁹ Considering the possibility of photoreduced
187 product formation in biological systems some of the anti-tumour activity of heptamolybdate can probably be traced back to
188 its reduced species.³⁹

189 The controlled hydrothermal oxidization of the triangular incomplete cuboidal $[Mo^IV_3O_4(H_2O)_9]^{4+}$ precursor in acidic
190 solution, which was synthesized according to Cotton procedure,⁵⁶ yielded the mixed-valence $Mo^{IV}-Mo^{VI}$
191 $[H_4Mo^{IV}_6Mo^{VI}_7O_{36}py_6] \cdot H_2py_3 \cdot 2H_2O$ (py – pyridine), in which the anion possesses a β -Keggin structure with two $[Mo^{IV}_3O_4]$
192 fragments.⁵⁷ The described anion exhibits Mo–Mo distances ranging from 2.5131(9) to 2.5318(9) Å, which is unusually short
193 for POMos. These short distances are unequivocally indicative of the existence of two Mo–Mo bonded $[Mo^{IV}_3O_4]$ units and in
194 agreement with bond distances in $[Mo^{IV}_3O_4(H_2O)]^{4+}$. The only known polyoxoanion with Mo^{IV} centres is $[H_4Mo^{IV}_6Mo^{VI}_7O_{36}py_6]^{2-}$
195 and it has six terminal pyridine groups stabilizing the six Mo^{IV} ions.⁵⁷

196 **Isopolytungstate s**

197 Among the highly diverse class of isopolytungstates, decatungstate $[W^{VI}_{10}O_{32}]^{4-}$ and metatungstate $[H_2W^{VI}_{12}O_{40}]^{6-}$ are most
198 susceptible to electron acceptance. Metatungstate demonstrated remarkable electron storage capacity as it can
199 accommodate up to 24 electrons.⁵⁸ Decatungstate can accept a maximum of two electrons. Up to now eight reduced
200 isopolytungstates (IPTs), which accepted between one and up to six electrons, were crystallized and investigated by single-
201 crystal XRD (TABLE S1).

202 **One-electron reduction of the Lindqvist anion $[W^{VI}_6O_{19}]^{2-}$.** Reduced IPTs of the Lindqvist-type anion with one accepted
203 electron $[W^V W^{VI}_5 O_{19}]^{3-}$ were synthesized hydrothermally in the presence of metallic V or Mo as reducing agent.⁵⁸ The
204 existence of the reduced tungsten sites was confirmed by manganometric titrations.⁵⁹ EPR analysis showed that the extra
205 electron in $[W^V W^{VI}_5 O_{19}]^{3-}$ is delocalized over all six W centers via intramolecular electron hopping between the metal centers
206 resulting in a rapid conversion of $-W^V-O-W^{VI}-$ into $-W^{VI}-O-W^V-$ and so on.^{48,59} Another procedure to obtain the reduced
207 Lindqvist-type IPT is the synthesis of the electron donor-acceptor complex $(CpFeCp)_3[W^V W^{VI}_5 O_{19}]$ ($CpFeCp = Fe(C_5H_5)_2$) from
208 orthotungstate WO_4^{2-} and ferrocene $Fe(C_5H_5)_2$ with no other reducing agent demonstrating that ferrocene acts as an effective
209 agent to reduce W^{VI} to W^V .⁶⁰

210 **Electron storage capacity of metatungstate $[H_2W_{12}O_{40}]^{6-}$.** Metatungstate $[H_2W_{12}O_{40}]^{6-}$ exhibits the α -Keggin structure (BOX 1)
211 with two non-exchangeable protons in a tetrahedral cavity, which is formed by four trinuclear capping units. In 1976, Launay
212 showed that metatungstate $[H_2W_{12}O_{40}]^{6-}$ can be reduced by controlled potential electrolysis to yield the brown form.⁵⁸ In
213 these brown compounds n (number of electrons introduced) is a multiple of 6, such as in the following species $H_8[H_2W_{12}O_{40}]^{4-}$
214 ($n = 6$), $H_{18}[H_2W_{12}O_{40}]$ ($n = 12$) and $H_{36}[HW_{12}O_{40}]^{5+}$ ($n = 24$), which could be isolated as solids.^{58, 61, 62} According to spectral and
215 electrochemical properties, it was suggested that the total reduction process involves the transfer of 6 electrons and 6
216 protons, which is consistent with the localisation of the accepted electrons within a single trinuclear cap W^{IV}_3 , where the
217 terminal oxo ligands are protonated to aqua ligands: $(W^{VI}=O)_3 + 6e^- + 6H^+ \rightarrow (W^{IV}\leftarrow OH_2)_3$.⁶³

218 Launay's suggestions⁵⁸ were confirmed by the synthesis of $Rb_4H_8[H_2W_{12}O_{40}]^{6-}$ ⁶⁴ and $[Bu_4N]_3H_9[H_2W_{12}O_{40}]^{6-}$ ⁶³
219 with the α -Keggin (BOX 1) anion $H_n\{[W^{IV}_3(OH_2)_3]W^{VI}_9O_{34}(OH)_3\}^{(5-n)-}$ ($n = 1, 2$) and ^{183}W -NMR¹⁷ and XPS investigations⁶¹. The
220 trinuclear caps W^{IV}_3 of the Keggin structure are proposed to be reduced sequentially.⁶³ The $6e^-$ reduced anion
221 $[H_2(W^{IV}_3(OH_2)_3)W^{VI}_9O_{34}(OH)_3]^{3-}$ can undergo condensation in aqueous solution between pH = 4 and 6.5 forming the highly-
222 nuclearity reduced species $[(XO_4)W^{IV}_3W^{VI}_{17}O_{62}H_x]^{y-}$ ($X = H_2^{2+}, B^{3+}$).⁶⁵

223 The 24-electron reduced POT $(NH_4)_6[H_2W_{12}O_{40}]$ yields a fuel cell electrocatalyst towards the oxidation of hydrogen in
224 acid electrolyte.⁶⁶ This activity may be caused by either the presence of 6d vacant orbitals similar to the conventional Pt
225 catalysts or reactivity of non-acidic protons in the structure. Moreover, electron-“tungsten brown” metatungstates with
226 reduced three W^{IV} caps exhibit some electrocatalytic activity.

227 **One and two-electron reduction in catalytic active decatungstates.** Decatungstate $[W^{VI}_{10}O_{32}]^{4-}$ is well-known for its high
228 photocatalytic activity.⁶⁷ The structure of $[W^{VI}_{10}O_{32}]^{4-}$ consists of two lacunary Lindquist $[W_5O_{14}]^{2-}$ fragments linked by four
229 corner-sharing oxygens with an unusually wide OWW angle of 178° (FIG. 1 a).⁶⁸ The one-electron-reduced complex
230 $[W^VW^VI_9O_{32}]^{5-}$ was prepared by controlled-potential electrolysis of $[W_{10}O_{32}]^{4-}$ in N,N-dimethylformamide (DMF).⁶⁹ Long-term
231 UV irradiation of the oxidized parent decatungstate leads to the formation of a mixture of protonated one- and two-electron
232 reduced species, namely $[HW^VW^VI_9O_{32}]^{4-}$ and $[H_2W^V_2W^VI_8O_{32}]^{4-}$, respectively.^{70,71} The unprotonated two-electron reduced
233 $[W^V_2W^VI_8O_{32}]^{6-}$ anion was prepared by controlled-potential electrolysis in the absence of protic media.⁷² The structure of the
234 decatungstate anion is obviously not changed by the reduction. Based on EPR⁷⁰ and ^{183}W NMR spectra⁷¹, it was concluded
235 that in both the one- and two-electron reduced anions, $[W^VW^VI_9O_{32}]^{5-}$ and $[W^V_2W^VI_8O_{32}]^{6-}$, respectively, the extra electrons
236 are principally located at the equatorial sites (four edge-shared within a plane octahedra) (FIG. 1 a).

237 Decatungstates have been successfully applied by Hill and co-workers^{27, 73, 74} during the homogeneous photocatalytic
238 oxidation of various organic substrates, such as alkanes, alkenes, alcohols, and amines due to the wide range of redox
239 potentials of $\{W_{10}O_{32}\}$, as well as the reversibility in their multielectron reductions. Mechanistic studies have shown that the
240 same one-electron reduced form of decatungstate $[HW^VW^VI_9O_{32}]^{4-}$ is formed during the catalytic oxidation, which may react
241 quantitatively with oxygen to form hydrogen peroxide and/or organic hydroperoxides as final products.⁷⁵⁻⁷⁷

242 **Isopolyvanadates**

243 Polyoxovanadates (POVs) appear to provide structures of sufficient flexibility to allow the existence of multiple oxidation
244 states while retaining structural integrity. The mixed-valent V^{IV}/V^V and fully-reduced V^{IV} ; V^{III}/V^{IV} isopolyvanadates (IPVs) consist

245 mostly of a variety of vanadium alkoxide structures. Up to now 22 reduced IPVs, which accept between one and six electrons,
246 were crystallized and investigated by single-crystal XRD (TABLE S1).

247 **Reduced and organically functionalized hexavanadates.** The Lindqvist vanadium core $\{V_6O_{19}\}$ (FIG. 1 a) is unstable due to the
248 high charge/volume ratio. The most high-valent (V^V), mixed-valent (V^{IV}/V^V , V^{III}/V^{IV}) or fully reduced (V^{IV} ; V^{IV}/V^{III}) hexavanadates
249 were obtained as alkoxo-derivatives, in which varying numbers of double bridged oxo groups of $\{V_6O_{19}\}$ are replaced by alkoxy
250 oxygen donors of polyol ligands (FIG. 1 a).⁷⁸ Zubietta *et al.* were successful in synthesizing a variety of hexavanadate
251 derivatives with the help of trisalkoxo μ -bridging moieties revealing a rich class of V^{IV}/V^V mixed valence compounds.⁷⁹⁻⁸¹ The
252 oxovanadium clusters can be formed under solvothermal conditions: 1) by a comproportionation reaction of precursors with
253 vanadium atoms in oxidation states +3 (V_2O_3) and +5 (VO_3^- , V_2O_5)⁸⁰; 2) by reducing the fully oxidized compound with reducing
254 agents (1,2-diphenylhydrazine, N_2H_5OH etc.)^{79,82}; 3) by reaction of $VO(OR)_3$ ($R = Me, Et, Bu$) with BH_4^- in methanol.⁸³⁻⁸⁷ The
255 solvothermal reaction of $VOSO_4$ with p-tert-butylcalix[4]arene in methanol under anaerobic conditions yielded the V^{III}/V^{IV}
256 hexavanadate $[V^{III}V^{IV}_5O_6(OCH_3)_8(calix)(CH_3OH)]^-$.⁸⁸ In each mixed-valence or fully reduced cluster six vanadium nuclei surround
257 one oxo anion forming a nearly regular octahedron (FIG. 1 a). EPR studies and DFT calculations showed that the d-electrons of
258 the V^{IV} nuclei can be extensively delocalized in the highly symmetrical $\{V_6O_{19}\}$ hexavanadate core.^{83,86} The magnetic exchange
259 interactions between unpaired d-electrons in the Lindqvist core-structure are prone to geometric spin frustration.⁷⁹ Recently,
260 Matson *et al.* reported the synthesis and characterization of iron-substituted Lindqvist type alkoxo-vanadates
261 $[V^{IV}_3V^V_2O_6(OCH_3)_{12}Fe^{III}X]$ ($X = Cl, OTf, OTf - trifluoromethylsulfonate$)⁸⁹, which are capable to accept up to four electrons while
262 remaining the +3 oxidation state of the iron atom.⁹⁰

263 Xu *et al.* have studied the influence of five functionalized hexavanadates, including one reduced IPVs
264 $[V^{IV}_3V^V_3O_{10}(OH)_3((OCH_2)_3CNO_2)_2]$ ⁹¹, on Na^+/K^+ -ATPase activity *in vitro*.⁴⁰ Dose dependent Na^+/K^+ -ATPase inhibition was
265 obtained for all investigated compounds, however, the obtained results indicate that the most potent inhibitor is the reduced
266 compound ($IC_{50} = (1.8 \pm 0.5) \cdot 10^{-5} \text{ mol} \cdot L^{-1}$).

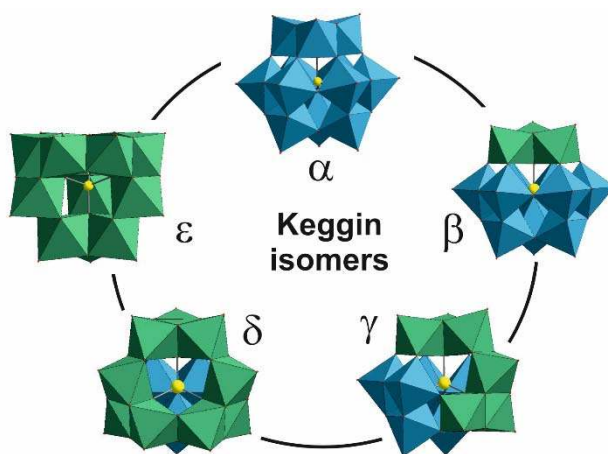
267 **Classically functionalized and "wheel"-type decavanadates.** Exploiting the hydrothermal synthetic procedure as in the case
268 of alkoxohexavanadates, Zubietta and co-workers obtained clusters based on the fully $\{V^{IV}_{10}O_{28}\}$ or partially $\{V^{IV}_8V^V_2O_{28}\}$
269 reduced cores with variable numbers of doubly and triply bridging oxo groups being replaced by the alkoxy oxygen donors of
270 tris-alkoxy ligands (FIG. 1 a).^{81,86}

271 In 1982, Heitner-Wirguin and co-workers firstly reported on the synthesis and structure of the mixed-valence wheel-
272 like decavanadate anion $[(V^{IV}O)_2V^V_8O_{24}]^{4-}$, which was obtained by the hydrolytic dissociation of $V^{IV}O(acac)_2$ in methylene
273 chloride or chloroform in the presence of $Cu^{II}(acac)_2$ or $Zn^{II}(acac)_2$.^{92,93} Later, an improved synthetic procedure, which does not
274 require the use of $Cu^{II}(acac)_2$ or $Zn^{II}(acac)_2$ anymore, was reported together with a magnetic susceptibility study by Baxter and
275 Wolczanski.^{94,95} The structure of $[(V^{IV}O)_2V^V_8O_{24}]^{4-}$ is absolutely different from d^0 decavanadate $[V^{IV}_{10}O_{28}]^{6-}$ and consist of the
276 macrocyclic $[V^VO_3]_8^{8-}$ ligand, which binds two vanadyl cations $[V^{IV}O]^{2+}$ at the center. The reaction of the macrocyclic $[V^VO_3]_8^{8-}$
277 ligand with Cu^{II} affords a heteropoly complex, namely $[Cu^{II}_2V^V_8O_{24}]^{4-}$, of which structure is similar to that of $[(V^{IV}O)_2V^V_8O_{24}]^{4-}$.⁹⁶
278 The second synthetic way to obtain the wheel cluster $[(V^{IV}O)_2V^V_8O_{24}]^{4-}$ is the condensation of $[V^V_5O_{14}]^{3-}$ upon irradiation with
279 visible light.^{97,98}

280 Reduced heteropolyanions

Box 1 | **Keggin structure and its isomers**

The Keggin structure was first reported in 1933 during the analysis of 12-tungstophosphoric acid²⁵⁵ and has become the *de facto* emblem of POM chemistry. The bulk of publications in this field are devoted to Keggin type anions. This ion has the general formula $[XM_{12}O_{40}]^{n-}$, where X is a heteroatom that is coordinated by four O atoms leading to its tetrahedral geometry, M = Mo or W, charges range from n = 2 (X = S^{VI} 256) to n = 7 (X = Cu^I 257). Investigations of the Keggin structure revealed five isomers, each resulting from 60° rotation of one, two, three and four $\{M_3O_{13}\}$ triad units, respectively, leading to the α , β , γ , δ and ϵ isomers as reported by Baker and Figgis.²⁵⁸ The arrangements of the M_3O_{13} triads affect the molecular orbital energies and the distances between metal centers, which also in turn affect the electrostatic repulsion. Thus, the stability of fully oxidized Keggin anions decreases in the order $\alpha < \beta < \gamma < \delta < \epsilon$. The reduced clusters behave differently. The β form becomes the most stable isomer after the acceptance of the second and fourth electron as the LUMO is lower than that in the α form.²⁵⁹ The γ isomer also has a low LUMO and gains stability upon reduction, but not enough to be competitive with the β isomer. The other isomers, δ and ϵ , are much more unstable than α or β in any reduction state and require transition metal support.²⁵⁹⁻²⁶¹ Remarkably, in reduced Keggin POMs resistance to addenda atom substitution can increase due to the additional energy factor of orbital overlaps for the delocalization of the added electrons. Also addenda substitution for a lower charged metal increases total negative charge of the already reduced anion, which can lead to its instability. A general way to stabilize the Keggin anions with higher negative charges after reduction is to introduce electrophilic capping groups such as $\{V^{VO}\}^{3+}$ or $\{V^{IV}O\}^{2+}$. The structures, which are formed after such capping, have become known as “pseudo-Keggin” structures.



282

283 **Electron accepting properties of Keggin-type polyoxomolybdates.** The synthesis of the heteropoly acid from orthophosphate
 284 PO_4^{3-} and molybdate MoO_4^{2-} under acidic conditions and its subsequent reduction to form an intensely coloured
 285 phosphomolybdenum blue $[P Mo_n^V Mo_{(12-n)}^{VI} O_{40}]^{(3+n)-}$ was firstly reported by Scheele in 1783. However, its discovery is widely
 286 attributed to Berzelius in 1826.¹⁵ Especially the molybdate blues have long been used for colorimetric determination of trace
 287 levels of elements that readily form Keggin anions, e.g. for analysis of phosphates and silicates.

288 So far seventeen reduced POMos of Keggin structure, which accept between one and up to twelve electrons, were
289 crystallized and investigated by single-crystal XRD (TABLE S2).

290 The redox behavior of Keggin-type POMos is highly acid-dependent.^{10,99} Launary *et al.* reported on the pH effect of the
291 first three reversible two-electron reductions of $[\text{SiMo}^{\text{VI}}_{12}\text{O}_{40}]^{4-}$. The two- electron waves are shifted to more negative
292 potential when the pH is higher and they are eventually split into one-electron waves. This takes place at pH 2.4 for the first,
293 pH 9.5 for the second and pH 13 for the third wave giving rise to the formation of $[\text{SiMo}^{\text{V}}\text{Mo}^{\text{VI}}_{11}\text{O}_{40}]^{5-}$, $[\text{SiMo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{10}\text{O}_{40}]^{6-}$ and
294 $[\text{SiMo}^{\text{V}}_3\text{Mo}^{\text{VI}}_9\text{O}_{40}]^{4-}$, respectively.^{48, 100}

295 The reduced α - and β -Keggin POMos can be synthesized electrochemically^{101,102} or by hydrothermal reactions^{21,105-112 25,}
296 ^{31, 103-107} Reduced POMos exhibiting the ϵ -Keggin structure can only be synthesized hydrothermally with the support of TM^{II} -
297 units (TM – transition metal, e.g. Ni^{II} , Co^{II}).^{26, 108-111} Organic ligands (e.g. 1,2-propanediamine) or reagents bearing a
298 heteroatom (e.g. As_2O_3)¹⁰⁹ can display reducing effects on the addenda atoms. A complex containing an ϵ -core is
299 $[\text{Na}(\text{Mo}^{\text{VI}}\text{O}_3)_4\text{Mo}^{\text{V}}_{12}(\text{OH})_{12}\text{O}_{28}]^{7-}$ possessing Mo-capping units and a central cavity, which is capable of accommodating protons
300 or metal cations.⁵⁵ This compound was obtained in aqueous solution from heptamolybdate and phenylphosphonic acid with
301 hydrazinium dichloride $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ as reducing agent. The magnetic properties of electron-rich Keggin-type POMos were
302 investigated and in the case of $[\text{GeMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{40}]^{12-}$ and $[(\text{As}^{\text{V}}\text{O}_4)\text{Mo}^{\text{V}}_8\text{W}^{\text{VI}}_4\text{O}_{33}(\mu_2\text{-OH})_3]^{8-}$ the negative Weiss constants
303 indicate the possible occurrence of weak antiferromagnetic interactions between the transition metal centers.¹⁰⁹ On the
304 other hand, the magnetic properties of the compound with fully reduced addenda atoms $[\text{Mo}^{\text{V}}_{12}\text{O}_{30}(\mu\text{-OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}_4(\text{H}_2\text{O})_{12}\}]$
305 (FIG. 3 a)²⁶ are dominated by exchange interactions between the four Ni^{II} centers, while the strong interactions between the
306 12 Mo ($4d^1$) centers result in six $\text{Mo}^{\text{V}}\text{-Mo}^{\text{V}}$ dumbbells with ~~two~~ single bonds as is the case
307 in $[\text{Na}(\text{Mo}^{\text{VI}}\text{O}_3)_4\text{Mo}^{\text{V}}_{12}(\text{OH})_{12}\text{O}_{28}]^{7-}$.⁵⁵

308 The Co^{II} -capped ϵ -Keggin anion $[(\text{Co}^{\text{II}}\text{bpy})_2(\text{PMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_8\text{O}_{40})]^{3-}$ has been checked for catalyzing water oxidation to
309 generate O_2 under visible light irradiation using $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer and $\text{S}_2\text{O}_8^{2-}$ as the sacrificial electron
310 acceptor.³¹ Although the stability of POMo under photocatalytic conditions was demonstrated by dynamic light scattering
311 (DLS), extraction experiment, and UV-Vis and FT-IR spectroscopy, it should be noted that bipyridine and $\text{Co}^{\text{III}}\text{Co}^{\text{II}}$ -oxide, which
312 can be formed under these conditions, are well established to be efficient water oxidation catalysts. A turnover number of up
313 to 49 sec^{-1} was observed by the authors,³¹ which shows that this reduced POMos could be an efficient visible light-driven
314 catalysts for water oxidation. The photocatalytic water oxidation activity of $[(\text{Co}^{\text{II}}\text{bpy})_2(\text{PMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_8\text{O}_{40})]^{3-}$ resembles that of
315 POMs with non- reduced addenda atoms.¹¹²

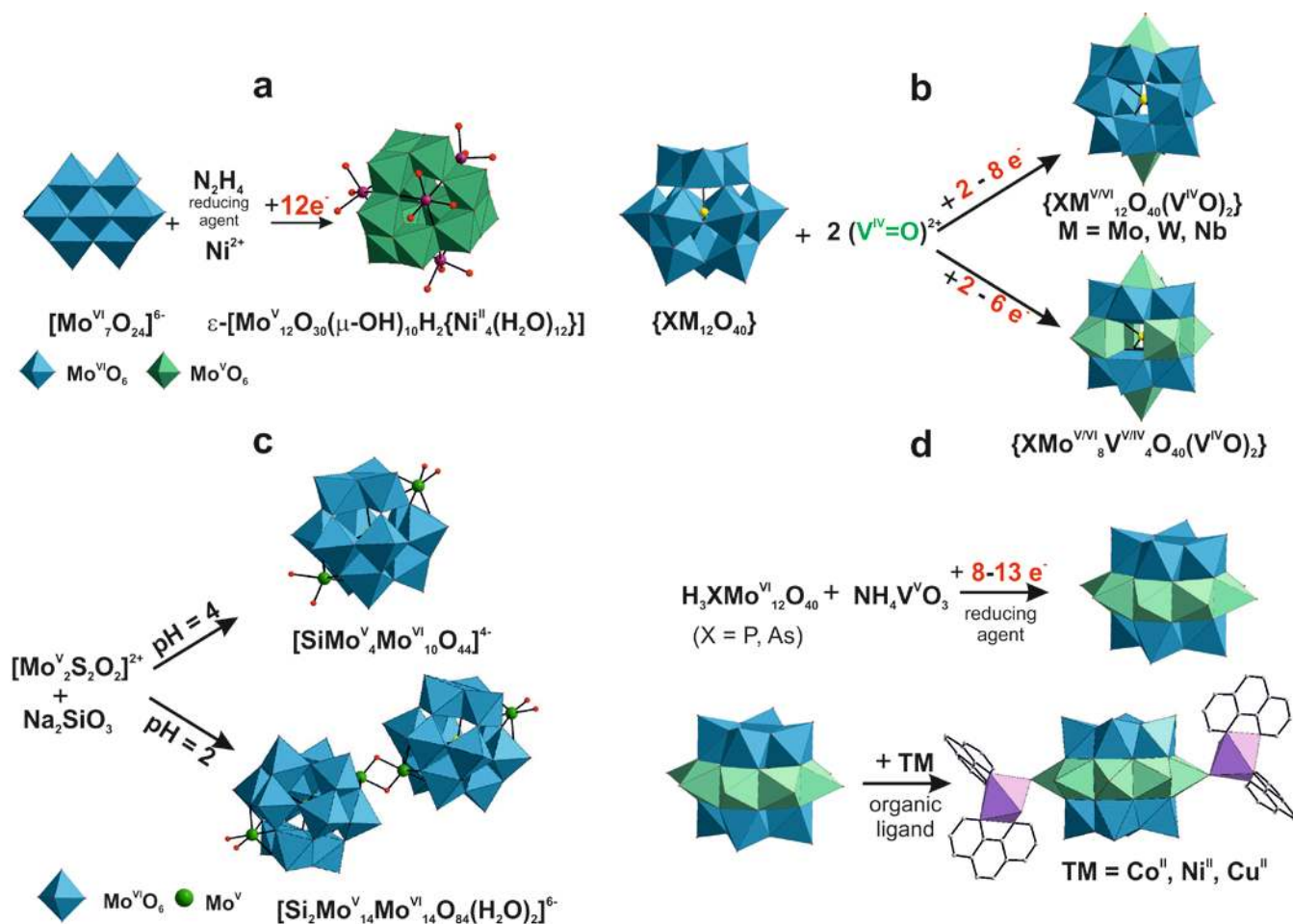
316 Nobel metal nanoparticles can be formed in water at room temperature in the presence of four electron-reduced
317 Keggin POMo $\text{H}_7[\beta\text{-PMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_8\text{O}_{40}]$ and are stable for several months.¹¹³⁻¹¹⁵ In this case the electron-rich POMos play the role
318 of the reductant and stabilizer.

319 The salt of doubly reduced $[\text{PMo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{10}\text{O}_{40}]^{5-}$ anion with benzimidazolium exhibited a dielectric anomaly, which was
320 caused by electric dipole relaxation.¹¹⁶ This dipole relaxation can be explained by a hopping process of the blue electrons and
321 a charge relaxation from a disproportionated structure to a fully delocalized structure due to distortion of the Keggin
322 framework by intermolecular interaction.

323 POM-molecular cluster batteries based on $[\text{PMo}^{\text{VI}}_{12}\text{O}_{40}]^{3-}$ anion exhibit a large capacity of ca. 270 (A h)/kg in a voltage
324 range between 1.5 – 4.0 V due to their ability to reversibly accept 24-electrons during charging/discharging process.⁴¹

325 **Electron accepting properties of Keggin-type polyoxotungstates.** In 1960-1970 Pope and co-workers laid the foundation for
 326 the investigation of the reduction processes in Keggin-type heteropolytungstates (HPT).^{117,118} and unveiled the formation of
 327 heteropoly “browns” with W in the oxidation state +4.^{17,18} They demonstrated that the electrons can be accepted by Keggin
 328 POTs $[XW_{12}O_{40}]^{n-}$ ($X = P^V, Si^IV, Fe^{III}, Co^{II}$) without protonation until the total charge of the reduced species is -6 in acidic media
 329 and -8 in neutral media. Further reduction is then always accompanied by protonation keeping the overall ionic charge at -6
 330 or -8. So far eleven reduced HPTs exhibiting the Keggin structure $\{XW^{V/VI}_{12}O_{40}\}$, which accept between one and up to six
 331 electrons, were crystallized and investigated by single-crystal XRD (TABLE S2).

332 Reduced Keggin type POTs could be so far synthesized electrochemically¹²³⁻¹²⁵ 117-119 or under hydrothermal
 333 conditions.^{106, 120-123} One-electron reduced POTs were obtained at pH = 4.3 – 5.5, whereas the higher reduced electron-rich
 334 Keggin POTs were obtained at higher pH. As previously noted the “blue” electrons do not alter the crystal structure of the
 335 parent POT anion. Detailed analysis of structural parameters of $\alpha-[Co^{II}W^{VI}_{12}O_{40}]^{6-}$ and $\alpha-[Co^{II}W^V_2W^{VI}_{10}O_{40}]^{8-}$ showed that
 336 except for a shortening of each central Co tetrahedral distance by 0.03 Å and a consequent corresponding increase in
 337 $W-O_{tetrahedra}$ distances, the reduction caused remarkably little change in the interatomic distances within the complex.¹²⁴



338

339

340 Figure 3 | **Synthesis of electron-rich POMs based on the Keggin anion.** **a** | Schematic representation of the formation process
 341 of fully reduced Ni^{II}-supported $[Mo^V_{12}O_{30}(\mu-OH)_{10}H_2\{Ni^{II}_4(H_2O)_{12}\}]$ anion.²⁶ **b** | General scheme of bivanadyl bi-capped Keggin

342 POMs formation. **c** | pH-depended formation of monomeric $[\text{SiMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{10}\text{O}_{44}]^{4-}$ and dimeric $[\text{Si}_2\text{Mo}^{\text{V}}_{14}\text{Mo}^{\text{VI}}_{14}\text{O}_{84}(\text{H}_2\text{O})_2]^{6-}$ bi-
343 capped anions.¹⁵² **d** | Schematic representation of the formation of transition metal supported tetra-capped anion (e.g.
344 $[\text{AsMo}^{\text{VI}}_6\text{Mo}^{\text{V}}_2\text{V}^{\text{IV}}_8\text{O}_{44}]^{5-}$ connected covalently with two $\{\text{Co}(\text{phen})_2(\text{H}_2\text{O})\}$).¹⁵⁵

345

346 Using ^{27}Al NMR Hill *et al.* demonstrated the defined electron exchange between a fully oxidized $\alpha\text{-}[\text{Al}^{\text{III}}\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{5-}$ and
347 the one-electron reduced $\alpha\text{-}[\text{Al}^{\text{III}}\text{W}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{6-}$.¹²⁵ The electron-rich $\alpha\text{-}[\text{Al}^{\text{III}}\text{W}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{6-}$ is stable with respect to
348 disproportionation, structural isomerization and hydrolysis (from pH 0 to 7). In addition, it remains unprotonated over a wide
349 pH range (pH 1.8 to 7.5) and is free of Na^+ ion pairing with Na^+ ($C > 1 \text{ M}$).

350 Stability of the $[\text{SiW}^{\text{IV}}_3\text{W}^{\text{VI}}_9\text{O}_{40}]^{10-}$ “brown” anion in acid solution depends on the nature of the Keggin isomer and
351 decreases in the order $\alpha > \beta > \gamma$, which can be correlated with the structural modifications induced by rotation of the
352 $\{\text{W}^{\text{IV}}_3\text{O}_{13}\}$ groups. The $4e^-$ blue anion $[\text{SiW}^{\text{V}}_4\text{W}^{\text{VI}}_8\text{O}_{40}]^{8-}$ is stable in acidic solution with the β -isomer being more stable than the
353 corresponding α and γ forms.¹²⁶

354 Coronado and co-workers investigated the influence of the electron transfer on the magnetic properties of the two-
355 electron reduced $\{\text{W}_4\text{O}_{16}\}$ fragment of the $\alpha\text{-}[\text{PW}^{\text{V}}_2\text{W}^{\text{VI}}_{10}\text{O}_{40}]^{5-}$ anion.¹²⁷ They showed that the electron transfer between edge-
356 sharing and corner-sharing WO_6 octahedra have very close energy values and induce a large energy gap between the singlet
357 ground state and the lowest triplet states. These data explain the diamagnetic properties of the mixed-valence Keggin ions
358 reduced by two electrons and can be used for other electron-rich POM archetypes.

359 Neumann and co-workers have recently shown that $\text{H}_5[\text{PW}^{\text{V}}_2\text{W}^{\text{VI}}_{10}\text{O}_{40}]$ is a photoactive electron and proton donor by
360 light-induced excitation of the intervalence charge transfer band.³² The reduced POT $\text{H}_5[\text{PW}^{\text{V}}_2\text{W}^{\text{VI}}_{10}\text{O}_{40}]$ was used to transfer
361 electrons to the di-rhenium catalyst that catalyzes the selective reduction of CO_2 to CO .

362 The study of reoxidation of photoreduced $[\text{PW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{4-}$ by hydrogen peroxide, peroxyacetic acid,
363 peroxymonosulfate, peroxydisulfate and dioxygen (O_2) in the presence of the model pollutant 2-propanol under various
364 conditions provide insight into POM-catalyzed redox reactions in water purification and selective redox applications.³³ A
365 unified chain reaction is proposed in which the rate-limiting step is outer-sphere one-electron transfer to oxidants yielding
366 $\cdot\text{OX}$ ($\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ or $\text{CH}_3\text{CO}_2^{\cdot}$). The chain includes a number of $[\text{PW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{4-}$ -regenerating steps that, with some bulk
367 oxidants, leads to further consumption of bulk oxidant and transformation of pollutant.

368 The conversions of the three types of olefins catalyzed by $\text{NaCu}^{\text{I}}_2(\text{tib})_4(\text{H}_2\text{O})_4[\text{H}_2\text{PW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}][\text{H}_2\text{PW}^{\text{VI}}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$ (tib –
369 1,3,5-tris(1-imida-zolyl)benzene), are 98.3% (1-hexene), 95.7% (cyclo hexene), and 97.1% (1-octene), indicating that this
370 compound can be used as an effective catalyst for epoxidation.¹²⁰

371 The photochemically reduced ($\lambda > 320 \text{ nm}$, propan-2-ol as a sacrificial reagent) tungstosilicate, $[\text{SiW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{5-}$, was
372 used to obtain fine metal nanoparticles of Ag, Au, Pd, and Pt, by simple mixing of the corresponding metal ions with reduced
373 polyoxometalates at room temperature.¹²⁸

374 **Capped Keggin polyoxometalates**

375 The surface modification of a classical Keggin anion with other groups may adjust or ameliorate the physicochemical
376 properties of the Keggin ion itself. Inorganic $\{\text{VO}\}$ capped Keggin-type derivatives (FIG. 1 b) have been synthesized by
377 hydrothermal technique. These compounds are mainly obtained as bi-capped and tetra-capped bivanadyl POMs, bi-capped

378 bivanadyl POTs and polyoxoniobates (PONs), and bi-capped bimolybdenum and biantimony POMos do also exist. (TABLE S3,
379 S4)

380 **Redox-properties of bi-capped bivanadyl Mo and mixed Mo/V polyoxometalates.** Highly reduced bi-capped bivanadyl mix-
381 valence molybdenum Keggin anions $\{XMo^{V/VI}_{12}O_{40}(V^{IV}O)_2\}$ (X = Si, P, Ge, As, V)^{104,105, 129-138} or molybdenum-vanadium anions
382 $\{XMo^{V/VI}_8V^{IV/V}_4O_{40}(V^{IV}O)_2\}$ (X = P, V)^{103, 139-147} were firstly presented by Hill *et al.*¹³¹ in 1996 and proved to be useful building
383 blocks to construct multi-dimensional extended solid materials that show oxidative resistance and act as catalysts in
384 homogeneous oxidation (FIG. 1 b; FIG. 3 b). 26 reduced bi-capped bivanadyl POMos and mixed POMo/Vs, which accept
385 between two and eight electrons, were crystallized and investigated by single-crystal XRD (TABLE S3) up to now.

386 A number of bi-capped Keggin-type structures have been synthesized by hydrothermal reactions, sometimes
387 supported by organic ligands (bipyridine, 1,10-phenanthroline etc) and transition metals (Co^{II},¹⁰⁵ Cu^I,¹³⁷ Zn^{II}¹³⁴ etc). Under
388 these conditions the reactions allow only little control over the stoichiometry or the degree of reduction.

389 Capping of the {VO} units on two opposite sides of α -Keggin POMs results in an asymmetrical negative charge
390 distribution and polarization of the POMo core making them attractive for asymmetric modification with transition metal
391 cations (e.g. Ni^{II},¹³³ Cu^I,¹³⁷ Co^{II}¹⁰⁵). Moreover, the steric orientations of the coordination sites for the capped Keggin POMos
392 are more flexible than those for the uncapped species.

393 The first reported bi-capped POMo, the $[PMo^V_6Mo^VI_6O_{40}(V^{IV}O)_2]^{5-}$ anion,¹³¹ can be best described as an α -Keggin core
394 $\{PMo_{12}O_{40}\}$ with {VO} units capping two opposite pits. Caps are formed through the ligation of four oxygen atoms originating
395 from two opposite $\{Mo_4O_4\}$ faces to each {VO} unit in a square pyramidal manner (FIG. 3 b). DFT calculations¹³² confirmed
396 Hill's suggestion that the metal centers in this reduced anion contain eight d electrons: six are accommodated in three
397 symmetry-adapted Mo orbitals, while the other two d electrons are in quasi degenerate linear combinations of the d
398 vanadium orbitals.

399 By using the Wells-Dawson-type POMo $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ and NH_4VO_3 as starting material in a hydrothermal reaction
400 it is possible to obtain another Mo-V bi-capped bivanadyl mixed Mo/V Keggin-type derivative, namely
401 $[PMo^VI_8Mo^V_2V^{IV}_4O_{42}]^{5-}$.^{147,148} The structure of $[PMo^VI_8Mo^V_2V^{IV}_4O_{42}]^{5-}$ is similar to that of $[PMo^V_6Mo^VI_6O_{40}(V^{IV}O)_2]^{5-}$.¹²⁵ In the case
402 of bi-capped molybdenum-vanadium anions $\{XMo^{V/VI}_8V^{IV/V}_4O_{40}(V^{IV}O)_2\}$ (X = P, V)^{103, 139-147} the α -Keggin core is based on a
403 central $\{XO_4\}$ tetrahedron surrounded by four corner sharing triads of $\{Mo_2VO_{13}\}$, which is composed of two $\{MoO_6\}$ octahedra
404 and one square $\{VO_5\}$ pyramid (FIG. 3 b).

405 Generally, variable-temperature magnetic susceptibility measurements showed the presence of antiferromagnetic
406 interactions among the reduced Mo^V ions plus a paramagnetic contribution from the V^{IV} ions in $\{XMo^{V/VI}_{12}O_{40}(V^{IV}O)_2\}$ (X = Si, P,
407 Ge, As).^{133,134,137,138} In addition, an antiferromagnetic interaction is possible between the cation (e.g. Co^{II}) and the V^{IV} ions,
408 which are directly linked through an oxygen bridge.

409 Studies of the electrochemical properties of compounds with $\{XMo^{V/VI}_{12}O_{40}(VO)_2\}$ (X = Si, P, Ge, As)^{134,135,139} structure
410 revealed similar redox behavior to the parent Keggin $\{XMo_{12}O_{40}\}$, that is, they undergo three two-electron reversible
411 reductions of molybdenum. The $V^{IV}O^{2+}$ caps have a slight effect on the electrochemical properties and no redox waves of V^{IV}
412 can be observed.¹³⁴

413 Bi-capped anions $[PMo^{V/VI}_{12}O_{40}(V^{IV}O)_2]^{n-}$ with two localized spins have been proposed as qubits for molecular
414 spintronics.³⁵ Here, the molybdenum core acts as a reservoir for a variable number of delocalized electrons and exhibits weak

415 magnetic coupling with the two $(VO)_2^+$ units. Through electrical manipulation of the molecular redox potential, the charge of
416 the core can be changed, thus two-qubit gates and qubit readout can be implemented.³⁵

417 The $[HPMo^{VI}_8V^V_4O_{40}(V^{IV}O)_2]^{2-}$ -carbon paste electrode (CPE) exhibits bifunctional electrocatalytic activities, namely
418 reduction of iodate IO_3^- and oxidation of ascorbic acid with electrocatalytic efficiency (CAT) of 57% and 43%, respectively,
419 which are considerably higher than the CAT values for $HPMo^{VI}_{12}O_{40}^{2-}$ -CPE (16% and 1%).¹³⁹ Here and throughout it should be
420 noted, that CPEs are quite unstable and some of POM electrochemical features can involve the CPE components.

421 **Redox-properties of bi-capped bivanadyl polyoxotungstates and polyoxoniobates.** The only two examples of reduced bi-
422 capped bivanadyl polyoxotungstates, $[V^{IV}W^V_2W^{VI}_{10}O_{40}(V^{IV}O)_2]^{2-}$ ¹⁴⁹ and $[As^VW^V_4W^{VI}_6V^{IV}_4O_{42}]^{7-}$,¹²² have been reported recently
423 (TABLE S3). Photocatalytic studies indicate that the compound $[Ni^{II}L_4V^{IV}W^{VI}_{10}W^V_2O_{40}(V^{IV}O)_2]$ (L = 1,4-bis(imidazol-1-
424 ylmethyl)benzene) not only serves as an active photocatalyst for the degradation of dye molecules but also exhibits selective
425 photocatalytic activity for the degradation of cationic dyes in aqueous solution.¹⁴⁹ Furthermore, two bi-capped bivanadyl
426 structures are known for polyoxoniobate: fully-oxidized $[V^V Nb^V_{12}O_{40}(V^VO)_2]^{9-}$ and the three-electron reduced
427 $[V^{IV}Nb^V_{12}O_{40}(V^{IV}O)_2]^{11-}$.^{150,151} They were synthesized under similar hydrothermal conditions but for the synthesis of the
428 reduced anion ethylenediamine was presented in the reaction mixture.

429 **Redox-properties of bi-capped bimolybdenum and biantimony polyoxomolybdates.** The formation of molybdenum-capped
430 anions is also possible if no vanadium compound is present in the reaction mixture. Six reduced bimolybdenum and
431 biantimony POMos, which accept between four and eight electrons, were crystallized and investigated by single-crystal XRD
432 (TABLE S3).

433 Polyoxoanion $[SiMo^V_4Mo^{VI}_{10}O_{44}]^{4-152}$ which was synthesized by reaction of the oxothio precursor
434 $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]^{4-}$ with hydrochloric acid, silicate anions, and tetramethylammonium hydroxide under hydrothermal
435 conditions, is capped by $\{Mo^V O_2\}$ subunits sharing two O atoms to form a dimer. At high temperature and low pH, a
436 hypothetical five-electron reduced-Keggin structure with two $\{Mo^V O_2\}$ capping units is obtained. This electron-rich species
437 dimerizes to form $[Si_2Mo^V_{14}Mo^{VI}_{14}O_{84}(H_2O)_2]^{6-}$ (FIG. 3 c).¹⁵²

438 The $[AlMo^V_4Mo^{VI}_8O_{40}(Mo^{VI}O_2)]^{5-}$ ¹⁵³ and $[(As^V O_4)Mo^VI_6Mo^V_6O_{35}(Mo^VO_2)]^{-}$ ¹⁵⁴ anions also demonstrate bi-capped Keggin
439 structures. The attachment of capping units to the Keggin-type polyanion can be described as a Lewis-type interaction
440 between the four-electron-reduced $\{XMo^{IV}_4Mo^{VI}_8O_{40}\}$ species, acting as a base, and the $\{Mo^{VI}O_2\}$ as Lewis acid, which exhibit a
441 structure stabilizing effect.

442 The catalytic property of $[(As^V O_4)Mo^VI_6Mo^V_6O_{35}(Mo^VO_2)]^{-}$ ¹⁵³ has been explored showing that it is able to convert
443 styrene to benzaldehyde (85.2%). In the same time the catalytic properties of $[AlMo^V_4Mo^{VI}_8O_{40}(Mo^{VI}O_2)]^{5-}$ ¹⁵³ were evaluated
444 in the oxidation of cyclohexanol to cyclohexanone. A conversion rate of 26.7% with a high selectivity of 98.5% for the
445 conversion to cyclohexanone was reported. It has to be noted that a blank reaction without POMo gives only 4.2 % of
446 conversion.

447 POMs containing antimony oxide units often play an important role in heterogeneous oxidation catalysis. Moreover,
448 antimony cations also have a stabilizing effect on polyoxometalates at high temperatures.¹⁵⁴ The bi-capped antimony α -
449 Keggin anion $[PMo^V_5Mo^{VI}_7Sb^{III}_2O_{40}]^{2-}$ can be synthesized either under hydrothermal conditions in the system of
450 $Sb_2O_3 - (NH_4)_6Mo_7O_{24} - H_3PO_4 - en - H_2O$ ^{155,156} or by reduction of $(Bu_4N)_3[PMo_{12}O_{40}]$ with six mole-equivalents of Na/Hg

451 amalgam in the presence of two mole-equivalents of SbCl_3 following to the scheme:¹⁰⁴
452 $[\text{PMo}_{12}\text{O}_{40}]^{3-} + 2 \text{SbCl}_3 + 6e \rightarrow [\text{PMo}_{12}\text{O}_{40}\text{Sb}_2]^{3-} + 6\text{Cl}^-$.

453 **Redox-properties of tetra-capped pseudo-Keggin polyoxoanions.** In contrast to bi-capped Keggin systems tetra-capped
454 structures of electron-rich POMs are known only for mixed Mo/V systems with the general formula $\{\text{XMo}_8^{\text{V/VI}}\text{V}_8^{\text{V/IV}}\}$, X = P, V,
455 As (FIG. 1 b; FIG. 4 d).^{103, 122, 157-165} 19 reduced tetra-capped pseudo Keggin polyoxoanions, which accept between eight and
456 thirteen electron, were crystallized and investigated by single-crystal XRD so far (TABLE S4).

457 All tetra-capped compounds are synthesized in a similar fashion. When applying hydrothermal synthesis, the
458 heteropolyacids $\text{H}_3\text{XMo}_{12}\text{O}_{40}$ (X = P, As) and $\text{NH}_4\text{V}^{\text{V}}\text{O}_3$ are often used as the starting material. Wang and coworkers pointed out
459 that the use of NH_4VO_3 as precursor in the transformation reaction of the Keggin into the pseudo-Keggin structure may
460 increase the negative charge density on the external oxygen atoms leading to a more reactive POM anion.¹⁵⁹ Using
461 $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ during the synthesis not only decreases the pH of the reaction system but also can act as a reducing agent.¹⁵⁷

462 $[(\text{XO}_4)\text{Mo}^{\text{V/VI}}_8\text{V}^{\text{IV}}_8\text{O}_{40}]^{n-}$ is structurally based on the α -Keggin $\{(\text{PO}_4)\text{Mo}^{\text{V/VI}}_8\text{V}^{\text{IV}}_4\text{O}_{36}\}$ (FIG. 1 b) archetype containing four
463 additional five-coordinated terminal $\text{V}^{\text{IV}}\text{O}^{2+}$ units. One distorted and disordered XO_4^{3-} (X = P, V, As) tetrahedron lies inside the
464 host cavity. The Mo ions are all six-coordinated resulting in an octahedral geometry. Each vanadium ion possesses a distorted
465 $\{\text{VO}_5\}$ square pyramidal geometry with eight vanadium ions forming the central belt by sharing edges of $\{\text{VO}_5\}$ square
466 pyramids. There are two $\{\text{Mo}_4\text{O}_{18}\}$ rings by common edges above and below the V_8 belt. The assignments of the oxidation
467 state for the molybdenum and vanadium ions are consistent with their coordination geometry and confirmed by bond
468 valence sum calculations. In most of the cases the transition metal (Co^{II} , Ni^{II} or Cu^{II}) complexes do covalently link to the anion
469 via terminal capping $\text{V}^{\text{IV}}=\text{O}$ groups (FIG. 3 d).

470 An Ab Initio and DFT study of $[\text{PMo}^{\text{V}}_2\text{Mo}^{\text{VI}}_6\text{V}^{\text{IV}}_4\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_4]^{5-}$ shows that six of ten accepted electrons are delocalized
471 over the V_8 -ring, whereas the remaining electrons are delocalized over the Mo centers.¹⁶⁶ As with bi-capped anions, variable-
472 temperature magnetic susceptibility measurements were performed and show the presence of antiferromagnetic
473 interactions between the reduced Mo(V) and V(IV) atoms.¹⁵⁷⁻¹⁶⁰

474 **Wells-Dawson-type polyoxometalates**

475 So far eight reduced POMs, two reduced POTs and three mixed-metal (Mo/W and V/Mo) POMs of Wells-Dawson
476 structure, which accept between one and up to five electrons, were crystallized and investigated by single-crystal XRD so far
477 (Table S5).

478 **Polyoxomolybdates exhibiting the Wells-Dawson structure.** The one- and two electron reduction of α - $[\text{P}_2\text{Mo}^{\text{VI}}_{18}\text{O}_{62}]^{6-}$ in
479 acetonitrile leads to α - $[\text{P}_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{17}\text{O}_{62}]^{7-}$ and α - $[\text{P}_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{17}\text{O}_{62}]^{8-}$, which were confirmed by EPR and ^{31}P NMR studies.¹⁶⁷
480 The magnitudes of the EPR g values suggest that the odd electron is either delocalized or is rapidly hopping between a mirror-
481 plane-related pair of equatorial Mo atoms.¹⁶⁷ Electrolytic reduction of $[(\text{P}_2\text{O}_7)\text{Mo}^{\text{VI}}_{18}\text{O}_{54}]^{4-}$ at 0.11 V in acetonitrile solution
482 yielded the green one-electron reduced species $[(\text{P}_2\text{O}_7)\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{17}\text{O}_{54}]^{5-}$ and the blue two-electron-reduced species
483 $[(\text{P}_2\text{O}_7)\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{54}]^{6-}$, of which formation was confirmed by ^{31}P NMR and EPR studies.¹⁶⁸ Four compounds contain two or
484 three electron reduced Wells-Dawson anions $\{\text{As}_2\text{Mo}_{18}\text{O}_{62}\}$, which are capped by a certain number of Cu^{II} or As^{III} species on
485 different coordination positions. These compounds were hydrothermally synthesized by altering of the pH and the organic
486 ligand within the reaction system.¹⁶⁹

487 Reduction by two or more electrons produces highly basic forms that have been isolated as protonated
 488 polyoxometalate salts.¹⁷⁰ The dependence of the EPR line width on temperature for $[\text{Bu}_4\text{N}]_5[\text{H}_3\text{S}_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{17}\text{O}_{62}]$ is consistent
 489 with the intermolecular thermal delocalization of the odd electron over the entire molecular framework in the temperature
 490 range from 77 to 253 K.¹⁷¹ By reaction of $[\text{Bu}_4\text{N}]_4[\text{H}_3\text{S}_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{18}\text{O}_{62}]$ with triphenylphosphine in acetonitrile the four-electron
 491 reduced α -Wells-Dawson compound $[\text{Bu}_4\text{N}]_5[\text{H}_3\text{S}_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{12}\text{O}_{62}]\cdot 4\text{MeCN}$ was prepared.¹⁷² The most significant structural
 492 alterations, compared to the parent structure, are an increase in the Mo–Mo distances between corner-sharing MoO_6 units in
 493 the equatorial belt by 0.066 Å and a decrease in the Mo–O–Mo bond length connecting the two halves of the anion.
 494 $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{17}\text{O}_{62}]\cdot\text{CH}_3\text{CN}$ was used to fabricate a modified carbon paste electrode (CPE) which exhibits five redox
 495 peaks in the potential range from –300 mV to 700 mV exhibiting more positive first redox potentials than the $[\text{P}_2\text{Mo}^{\text{VI}}_{18}\text{O}_{62}]^{6-}$
 496 ion and in addition higher stability and electrocatalytic activity towards the reduction of nitrite, chlorate, bromate and
 497 hydrogen peroxide in acidic (1 M H_2SO_4) aqueous solution.³⁴

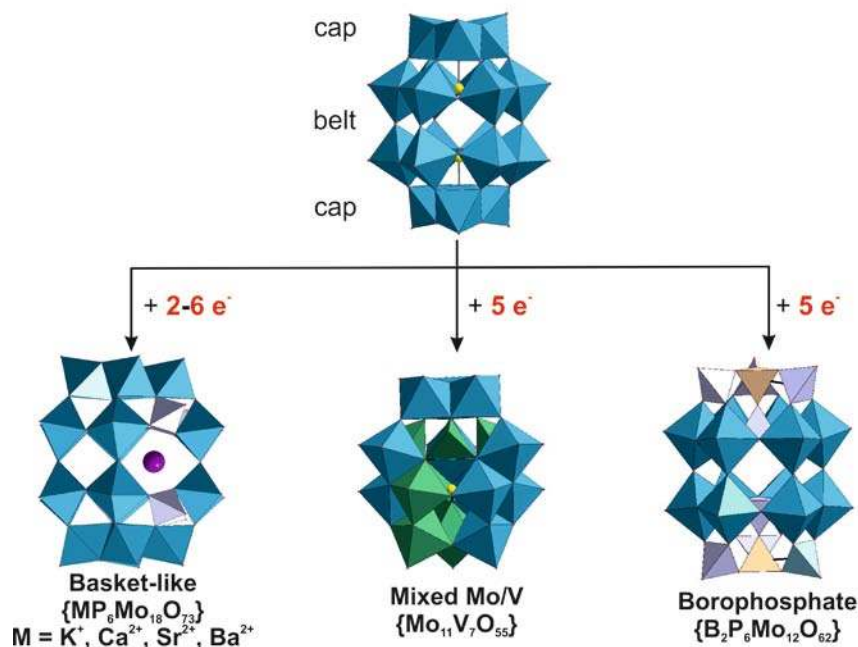
498 $\alpha\text{-}[(\text{SO}_3)_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{54}]^{6-}$, which incorporates the pyramidal sulfite anion, was synthesized in the presence of an
 499 excess of triethanolamine (TEA) at pH 4.0 with $\text{Na}_2\text{S}_2\text{O}_4$ not only acting as reducing agent but also as the source for the
 500 incorporated SO_3^{2-} .¹⁷³ The electrochemistry of these two-electron rich anion has been investigated in aqueous media using
 501 cyclic and rotated disk voltammetry at glassy carbon electrodes and bulk electrolysis with a focus on the pH-dependence for
 502 the oxidation to $\alpha\text{-}[\text{Mo}^{\text{VI}}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$.¹⁷⁴ In buffered media at $\text{pH} \geq 4$, the cyclic voltammetric response for $\alpha\text{-}$
 503 $[(\text{SO}_3)_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{54}]^{6-}$ reveals two partially resolved one-electron oxidation processes corresponding to the sequential
 504 generation of $\alpha\text{-}[(\text{SO}_3)_2\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_{17}\text{O}_{54}]^{5-}$ and $\alpha\text{-}[(\text{SO}_3)_2\text{Mo}^{\text{VI}}_{18}\text{O}_{54}]^{4-}$.¹⁷⁴ $\alpha\text{-}[(\text{SO}_3)_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{54}]^{6-}$ was obtained during simple
 505 one-pot reaction because $\alpha\text{-}[\text{Mo}^{\text{VI}}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$ is slightly easier to reduce than the β -form. Furthermore, on a much longer
 506 bulk electrolysis timescale, $\beta \rightarrow \alpha$ isomerisation occurs showing that the reduced forms of the α -isomer are
 507 thermodynamically favoured over the β forms, which was shown by Cronin and co-workers.¹⁷⁵ In aprotic acetonitrile $\beta\text{-}$
 508 $[\text{Mo}^{\text{VI}}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$ is retained on the voltammetric timescale upon one- and two-electron reduction. $\alpha\text{-}[(\text{SO}_3)_2\text{Mo}^{\text{VI}}_{18}\text{O}_{54}]^{4-}$
 509 undergoes reduction slightly easier than the β form.

510

Box 2 | Wells-Dawson structure

In 1892, Kehrman described the synthesis of a Wells–Dawson-type phosphotungstate for the first time.²⁶¹ However, Dawson published the first crystallographic study of this structure 60 years later.²⁶² The general formula of the Wells–Dawson anion is $[(\text{XO}_4)_2\text{M}_{18}\text{O}_{54}]^{n-}$; M = Mo, W and X = main-group element. The classical Wells-Dawson structure incorporates two tetrahedral anions such as PO_4^{3-} ,²⁶² AsO_4^{3-} ,²⁶³ SO_4^{2-} ,¹⁷⁰ or ClO_4^- .¹⁷⁸ There are only a few examples of $\{\text{M}_{18}\}$ Wells-Dawson-like clusters that host non-tetrahedral anions, for example, a single pyramidal anion BiO_3^{3-} ,²⁶⁴ AsO_3^{3-} ,²⁶⁵ or SO_3^{2-} ,¹⁷³ in each $\{\text{M}_9\}$ unit, presumably due to size restrictions. A ditetrahedral anion – $\text{P}_2\text{O}_7^{4-}$,¹⁶⁸ (two tetrahedral sharing one corner) was also observed in the centre of the structure. The structure, known as α -Wells-Dawson isomer, possesses two identical “half units” of the central atom surrounded by nine octahedral units XM_9O_{31} linked through oxygen atoms. The isomeric β -Wells-Dawson structure originates from the rotation of one half unit by $\pi/3$ around the axis connecting both heteroatoms. Similarly to many heteropolyanions, the Wells–Dawson structure can be chemically manipulated to generate lacunary units by removing up to six MO_6 octahedra, which gives X_2M_{12} anion. The redox properties of Wells-Dawson

polyoxometalates in aqueous media have received limited attention because of their low solubility and their instability under basic conditions.²⁶⁶⁻²⁶⁸



Color code: MoO₆, blue octahedral; PO₄, lilac tetrahedra; VO_n, green polyhedra; S, yellow sphere.

511

512 **Polyoxotungstates exhibiting the Wells-Dawson structure.** α -[(SO₃)₂W^{VI}W^{VI}₁₇O₅₄]⁵⁻ was obtained as Pr₄N⁺ (Pr = propyl)
513 salt by reducing the so-called “Trojan Horse” [(SO₃)₂W^{VI}₁₈O₅₆(H₂O)₂]⁸⁻ cluster¹⁷⁶ via a template orientation transformation.
514 Cyclic voltammetry of α -[(SO₃)₂W^{VI}₁₈O₅₄]⁴⁻ and α -[(SO₃)₂W^{VI}W^{VI}₁₇O₅₄]⁵⁻ in CH₃CN produces evidence for an extensive series of
515 reversible one-electron redox processes that are associated with the tungsten-oxo framework of the POT cluster.¹⁷⁷ The
516 encapsulated sulfite anions in the “Trojan Horse” [W^{VI}₁₈O₅₆(SO₃)₂(H₂O)₂]⁸⁻ cluster¹⁷⁶ act as embedded reducing agents and are
517 oxidized to sulfate when heated to over 400 °C according to the following reaction scheme: [(S^{IV}O₃)₂W^{VI}₁₈O₅₆
518 (H₂O)₂]⁸⁻ → [(S^{VI}O₄)₂W^V₄W^{VI}₁₄O₅₄(H₂O)₂]⁸⁻ + 2 H₂O.

519 The only example of a Wells-Dawson-type anion with ClO₄²⁻ as heteroatom was observed in [ⁿBu₄N]₃[Cl₂W^VW^{VI}₁₇O₆₂],
520 which was obtained under UV irradiation from monomeric WO₄²⁻.¹⁷⁸ The powder EPR spectrum of reduced
521 tungstoperchlorate indicates the presence of W^V and suggests that the unpaired electron may be delocalized over the W
522 atoms in the anion network due to thermally activated electron hopping.

523 The potential photocatalyst for oxidative decomposition of methylene blue dye contains [As₂W^V₂W^{VI}₁₆O₆₂]⁸⁻, which is
524 connected to eight copper ions and synthesized under hydrothermal conditions.¹⁷⁹

525 **Addenda priority for electron acceptance in mixed-metal Wells-Dawson polyoxometalates.** Baker and co-workers
526 investigated mixed Mo/W electron-rich anions and the derivatives of parent [P₂Mo_nW_{18-n}O₆₂]⁶⁻ (n = 1 – 6) in aqueous solution
527 using ³¹P and ¹⁸³W NMR as well as EPR in the 1980s.¹⁸⁰⁻¹⁸³ In 1983, Pope reported the synthesis of Wells-Dawson lacunary
528 polyoxotungstates and vanadyl sulfate one-electron reduced anions [P₂V^{IV}V^VW_{18-n}O₆₂]⁽⁸⁺ⁿ⁾⁻ (n = 1, 2).¹⁸⁵ The electrochemistry
529 of mono-substituted V^{IV} Wells-Dawson anions V{X_kV^{IV}Mo^{VI}_nW^{VI}_{17-n}O₆₂} (X = P, As; k = 1,¹⁸⁵ 2;¹⁸⁷⁻¹⁸⁹; n = 0,¹⁸⁷⁻¹⁸⁹ 2¹⁸⁶) were
530 investigated by Nadjo *et al.* These anions are efficient as electrocatalysts for the reduction of NO₂⁻, oxidation of L-cysteine and

531 as stabilizing agents for the preparation of Pd⁰ nanoparticles.¹⁸⁷⁻¹⁸⁹ However, so far no single crystal structure of this kind of
532 Wells-Dawson anion is reported.

533 Cronin and co-workers recently reported a new structural type that is related to the Wells-Dawson archetype in terms
534 of the cage geometry but with seven of the metal centres having been changed to hetero-metals like in the case of
535 (NH₄)₇[(SO₃)Mo^{VI}₁₁V^V₅V^{IV}₂O₅₂].12H₂O, where 7 Mo atoms were changed to V^{IV/V}.¹⁹⁰ The V^V is partially reduced to V^{IV} by sulphite,
536 which also acts as a heteroanion. The distorted egg-shaped capsule of the molybdovanadate-sulfite anion is built up of two
537 different hemispheres. In the upper hemisphere, three edge-sharing MoO₆ octahedra form the cap, which is connected to the
538 belt via vertexes of alternating V^VO₄ tetrahedra and MoO₆ octahedra. The {M₆} belt at the bottom hemisphere is made of
539 three sets of edge-sharing MoO₆/VO₆ octahedra interconnected within the framework to give three Mo–O–V moieties
540 arranged in a ring-like structure. Finally, the {M₃} cap at the bottom of the cluster contains two Mo and one V position,
541 respectively (BOX 2).

542 **Reduced Basket-like polyoxomolybdates.** As a unique class of unclassical POM, the basket-like archetype
543 {M₆CP₆Mo^{VI}₁₈O₇₃} (M = alkali metal, C - covalently incorporated) represents mixed valence molybdates, which are obtained
544 by two or more electron reductions from the corresponding Mo^{VI} of orthomolybdate MoO₄²⁻¹⁹¹⁻¹⁹⁶ or heptamolybdate
545 Mo₇O₂₄⁶⁻¹⁹⁷⁻²⁰¹ (BOX 2). So far 31 reduced Basket-like polyoxoanions, which accept between two and six electrons, were
546 crystallized and investigated by single-crystal XRD up to date (TABLE S6).

547 All basket-like POMos were obtained by hydrothermal synthesis using potassium^{191,192} or alkaline earth metals¹⁹³⁻²⁰¹
548 (Ca, Sr, Ba) as template agents to stabilize and induce polyanions formation. The organic ligands play an important role as
549 reducing agents to reduce the Mo^{VI} to Mo^V centers in one pot reactions including {Mo} (MoO₃/Mo, Na₂MoO₄ or
550 (NH₄)₆Mo₇O₂₄), H₃PO₄, MCl₂ (M = Ca, Sr, Ba) or KH₂PO₄ and H₂O leading to different dimensions or packing arrangements in
551 the final hybrid materials.^{196,198-201}

552 The basket-like polyoxoanion consists of two parts: the “handle” {P₄Mo₄} unit and the “basket body” {P₂Mo₁₄} segment
553 (BOX 2). The lower {P₂Mo₁₄O₄₆} part is a tetravacant lacunary derivative of the Wells–Dawson anion [P₂Mo₁₈O₆₂]⁶⁻ formed by
554 removal of four “belt” Mo octahedra, in which each of the fourteen Mo atoms has only one terminal, double-bonded oxygen
555 atom and thus meets the criteria for receiving “blue” electrons.¹⁴ The upper part {P₂Mo₄O₂₇} is the handle of the basket
556 formed by four MoO₆ octahedra and four PO₄ tetrahedra, in which each of the four Mo atoms has two terminal, double-
557 bonded oxygen atoms. The {P₄Mo₄} and the “basket body” {P₂Mo₁₄} moieties are connected together through edge- and
558 corner-sharing modes. The entire basket-shaped cluster possesses C_{2v} symmetry. The Mo–O bonds between {P₄Mo₄} and
559 {P₂Mo₁₄} have longer distances and smaller bond orders in comparison to classical Wells-Dawson anion. As a result, the
560 negative void formed by nine oxygen atoms of the two parts is large and can accommodate either alkali or alkaline earth
561 metals.

562 Another example of Wells-Dawson derivative encapsulating alkali metal [Na(SO₃)₂(PhPO₃)₄Mo^V₄Mo^{VI}₁₄O₄₉]⁵⁻ was
563 synthesized from Na₂MoO₄, Na₂S₂O₄ and phenylphosphonic acid.²⁰² Electrochemical investigations of
564 [Na(SO₃)₂(PhPO₃)₄Mo^V₄Mo^{VI}₁₄O₄₉]⁵⁻ showed three redox couples, in which the electrons were mainly delocalized over eight
565 Mo sites.²⁰³

566 The compositions of carbon paste electrodes (CPE) with basket-like POMs have been checked for electrocatalytic
567 activity on reduction of nitrite NO₂⁻, hydrogen peroxide H₂O₂ and oxidation of dopamine. In the series of experiments with

568 $[\text{Sr C P}_6^{\text{V}}\text{Mo}^{\text{V/VI}}_{18}\text{O}_{73}]^{n-}$ it has been noted that catalytic activities were enhanced with increasing extent of the anion
569 reduction.^{194,199} The basket-like POMos demonstrated superiority over other POM archetypes as catalysts in
570 photodegradation reaction due to their special structure, which makes electrons and holes migrate rapidly to the surface of
571 the basket cage, thus improving the photocatalytic activities significantly.²⁰⁰

572 **Five-electron reduced Wells-Dawson-like borophosphate polyoxomolybdates.** In 2002, Sevov and co-workers reported
573 synthesis and structure of a new type of reduced borophosphate POMos. (TABLE S6).²⁰⁴ The polyanion $[\text{B}_2\text{P}_8\text{Mo}_{12}\text{O}_{59}(\text{OH})_3]^{8-}$ is
574 structurally very closely related to that of the α -Wells-Dawson anion $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and consist of two crystallographically
575 equivalent hemispheres of $[\text{BP}_4\text{Mo}_6\text{O}_{31}\text{H}_{1.5}]^{4-}$ that are linked together by six shared oxygen atoms (BOX 2).

576 There are two phosphate groups inside the cluster, which are situated near the centres of the molybdenum belts. The
577 other six phosphate groups are part of the POM cage (addenda) sharing two vertexes with two edge-sharing molybdenum
578 octahedra and one vertex with a borate tetrahedra. The two borate groups of the anion (one in each hemisphere) share all
579 corners with three outer and one inner phosphate groups. The magnetic measurements indicate only one unpaired electron,
580 so the five electrons from these atoms are delocalized over the cluster and four of them are paired. The substitution of the six
581 terminal oxygen and hydroxyl groups of the outer phosphates in $[\text{B}_2\text{P}_8\text{Mo}_{12}\text{O}_{59}(\text{OH})_3]^{8-}$ ²⁰⁴ with phenyl groups leads to
582 $[(\text{BPO}_4)_2(\text{O}_3\text{P-Ph})_6\text{Mo}_5^{\text{V}}\text{Mo}_7^{\text{VI}}\text{O}_{30}]^{5-}$ formation.²⁰⁵

583 **Anderson-like polyoxometalates**

584 While classical Anderson-type structure for POMos and POTs cannot be reduced as they contain type II POMs, one-pot
585 solvothermal reaction with organic ligands and reducing agent leads to formation of fully reduced Anderson-like
586 functionalized POVs and POMos. In these anions V or Mo ions form double bonds only with one terminal oxygen and thus
587 have free orbital to accept extra electron (FIG. 1 d). Up to now fourteen reduced Anderson-like POVs²⁰⁶⁻²¹² and seventeen
588 POMos²¹³⁻²²⁹, which accept six electrons, were crystallized and investigated by single-crystal XRD so far (TABLE S7).

589 In 1987 Huang *et al.* reported the first synthesis of hexanuclear oxovanadium (IV) anion $[(\text{V}^{\text{IV}}\text{O})_6(\text{CO}_3)_4(\text{OH})_9]^{5-}$ from
590 VOCl_2 and NH_4HCO_3 under CO_2 atmosphere.²¹¹ The $[(\text{V}^{\text{IV}}\text{O})_6(\text{CO}_3)_4(\text{OH})_9]^{5-}$ is consolidated by bridging hydroxo and carbonato
591 groups, one of which is situated in the centre of the anion. Khan *et al.* synthesized a series of POVs polyoxocations
592 $[\text{MV}^{\text{IV}}\text{O}_6\{(\text{OCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\}_6]^{n+}$ (M = Li, Na, Mg, Mn, Fe, Co, Ni).²⁰⁶ The cyclic fragment $\{\text{MV}_6\text{N}_6\text{O}_{18}\}$ adopts the
593 Anderson-type structure:²³⁰ by exhibiting a ring of six VO_5N octahedral linked to a central MO_6 (M = Li, Na, Mg, Mn, Co, Ni)
594 unit (FIG. 1 d).

595 Four Anderson-like alkoxo-POVs anions $[\text{V}^{\text{IV}}\text{O}_6(\text{OCH}_3)_9(\mu_6\text{-SO}_4)(\text{COO})_3]^{2-}$ can serve as 3-connected second building units
596 that assemble with dicarboxylate or tricarboxylate ligands to form a new family of metal organic tetrahedrons
597 $\{[\text{V}_6\text{O}_6(\text{OCH}_3)_9(\text{SO}_4)_4(\text{L})_6]^{8-}$ (L = BDC, BDC-NH₂, BDC-Br).²¹⁰ The similar behaviour demonstrated vanadium(V)-centered anion
598 $[\text{V}^{\text{V}}\text{O}_6(\text{OCH}_3)_9(\text{V}^{\text{VO}}\text{O}_3)(\text{H}_2\text{O})(\text{COO})_3]^{-}$, adopting discrete truncated tetrahedral cage geometry.²⁰⁹

599 The synthesis of new families of functionalized POMos with cyclic cores of Mo^{V} and localized Mo–Mo bonds was
600 initiated by Haushalter and Lai²¹³⁻²¹⁷ and developed by several groups. The fully-oxidized class with the general formula
601 $\{\text{X}_4\text{Mo}_6^{\text{V}}\text{E}_6\}$ (FIG. 1 d) can accommodate various central and peripheral X groups such as $\{\text{PO}_4\}$, $\{\text{C}_6\text{H}_5\text{PO}_3\}$, $\{\text{C}_6\text{H}_5\text{AsO}_3\}$ and
602 $\{\text{CO}_3\}$. The system was later extended to the oxothio chemistry by the synthesis of anions such as $[\text{X}_4\text{Mo}_6\text{S}_6\text{O}_6(\text{OH})_3]^{5-}$
603 (X = HPO_4 , HAsO_4)^{220,221} where six sulfur atoms were inserted in the bridging positions of the dimolybdenum pairs.

604 The hydroxyphosphate anions $[\text{Mo}_6^{\text{V}}\text{P}_4\text{X}_{31}]^{9-}$ ($\text{X} = \text{O}, \text{OH}$) tend to form dimers through joined metal ions (Na ,^{214,218,222},
605 Mn^{II} ²²³, Co^{II} ²²⁴, Ni^{II} ^{225,226}, Zn^{II} ²¹⁵, Fe^{III} ,²¹⁶ Cd^{II} ,^{219,226}). The Mo^{V} centers of the $\{\text{Mo}_6^{\text{V}}\text{O}_{24}\}$ core exhibit strongly interacting pairs
606 leading to an alternating pattern of short and long $\text{Mo}\cdots\text{Mo}$ contacts, characterized by distances of 2.58 and 3.58 Å,
607 respectively.²¹⁸ These anions exhibit reversible redox behaviour and are active catalysts for the reduction of Fe^{III} in solution,²²⁶
608 nitrite, hydrogen peroxide and ascorbic acid²²⁴ and for the oxidation of acetaldehyde with H_2O_2 .²²³

609 The hydrothermal synthesis of the molybdenum transition metal phosphate system can not only lead to the formation
610 of the $\{\text{P}_4\text{Mo}_6^{\text{V}}\}$ family but also to wheel-like structures $\{\text{Mo}_x^{\text{V}}\text{M}_x\text{P}_{26}\}$ ($x = 16 - \text{M} = \text{Co}^{\text{II}}$ ²²⁷, Ni^{II} ²²⁸; $x = 14 - \text{M} = \text{Ni}^{\text{II}}$ ²²⁹) with a
611 diameter of ~ 19 Å, which contain $\{\text{Mo}_4\}$ tetramers linked by transition metal trimers and tetramers. Co^{II} and Ni^{II} centres show
612 strong $\text{M}^{\text{II}}-\text{M}^{\text{II}}$ antiferromagnetic interactions (for Ni^{II} $g = 2.25$ and $J = -24.3 \text{ cm}^{-1}$ ²²⁸).

613 ***Vanadates of the $\{\text{V}_{18}\text{O}_{42}\}$ archetype***

614 The mixed-valence vanadium isopolyanions form a structurally unusually versatile cluster family due to the variation in the
615 amount of V^{IV} and V^{V} and the coordination geometries of the V centers (tetrahedral V^{V} , tetragonal-pyramidal $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$, and
616 octahedral $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$). The formation of supramolecular host-guest complexes with interesting topologies is possible by linking of
617 $\text{O}_4\text{V}=\text{O}$ square pyramids sharing corners and edges *via* their basal oxo groups, which was demonstrated by the structures of
618 $\{\text{V}_{18}^{\text{IV}}\text{O}_{42}\}$ and $\{\text{V}_{15}^{\text{IV/V}}\text{O}_{36}\}$ (FIG. 1 d).²³¹⁻²³⁴ These compounds demonstrate a very strong antiferromagnetic coupling via the μ -
619 oxo groups, while their frontier orbitals strongly interact with the single-occupied molecular orbitals of the involved vanadyl
620 groups ($S = 1/2$) and thus act as very efficient superexchange ligands.²³⁵ However, excited multiplet magnetic states can only
621 be populated significantly at very high temperatures at which the related compounds might already decompose, thus
622 inhibiting their experimental characterization. To partially overcome this obstacle the introduction of non-magnetic spacer
623 groups connected to the POV can be applied. Since the discovery of the arsenato-polyoxovanadate compound
624 $\text{K}_6[\text{As}_6\text{V}_{15}^{\text{IV}}\text{O}_{42}(\text{H}_2\text{O})]\cdot 8\text{H}_2\text{O}$ ²³⁶ a great number of As, Sb, Si and Ge derivatives of the isopolyoxovanadate $\{\text{V}_{18}\text{O}_{42}\}$ archetype
625 were reported.²³⁷⁻²⁴⁶

626 In this review we provide a brief overall picture of this type of POVs. The structural aspects, key properties and
627 synthetic routes of Si-POVs, Ge-POVs, As-POVs and Sb-POVs, of which central structural motifs are typically derived from the
628 $\{\text{V}_{18}\text{O}_{42}\}$ archetype, were reviewed recently.²⁴⁷

629 A typical example for host systems for small guests are polyvanadate cluster anions with an approximately spherical
630 $\{\text{V}_{18}\text{O}_{42}\}$ shell, which can be synthesized under relatively mild conditions applying an inert atmosphere.^{232,234} Interestingly, the
631 $\{\text{V}_{18}\text{O}_{42}\}$ shell can exist as two different structural types: either with a distorted rhombicuboctahedron or a so-called
632 pseudorhombicuboctahedron (the “14th Archimedean body”) geometry (FIG. 1 d). The first type has T_d symmetry and can be
633 regarded as an enlarged Keggin ion, in which all square planes of the rhombicuboctahedron are spanned by the 24 innershell
634 μ_3 -oxygen atoms, which in turn are capped by $\{\text{VO}\}$ units. The second type has an idealized D_{4d} symmetry.²³⁴

635 The spherical $\{\text{V}_{18}\text{O}_{42}\}$ shell principally represents a kind of container that can incorporate different species below a
636 critical size such as H_2O , halides, formate or nitrite. The type of encapsulation can depend on the pH value: in a highly basic
637 medium (pH 14) only a H_2O molecule is enclosed, whereas at lower pH values anionic species are preferentially
638 encapsulated.^{232, 234, 248, 249}

639 There are three types of $\{X_{2x}V_{18-x}O_{42}\}$ structures with x being 2, 3 or 4. The first described $[As^{III}_6V^{IV}_{15}O_{42}(H_2O)]^{6-}$ anion²³⁶
640 as well as other $\{X_6V_{15}\}$ ($X = Sb,$ ^{237,238} $Ge,$ ²⁴⁰ and Si ²³⁷) derivatives have crystallographic D_3 symmetry and consist of 15 distorted
641 tetragonal VO_5 pyramids and 6 trigonal XO_3 pyramids (FIG. 1 d). The 15 VO_5 pyramids are linked *via* vertices and edges to each
642 other and are connected to the XO_3 groups solely through vertices. Two neighboring XO_3 groups are joined via an oxygen
643 bridge forming a handle-like X_2O_5 moiety. The structure of the clusters can be regarded as consisting of three different layers:
644 {six corner- and edge-sharing VO_5 square pyramids} – $\{V_3X_6O_{28}\}$ – {six corner- and edge-sharing VO_5 square pyramids}.

645 The structures of $\{X_4V_{16}\}$ and $\{X_8V_{14}\}$ ($X = As,$ ^{239, 241} $Sb,$ ^{242, 243} $Ge,$ ²⁴⁶ and Si ^{244,245}) are built on the same principal as
646 $\{V_{15}X_6\}$, that is, by replacing two diagonal VO_5 square pyramids with two X_2O_5 groups.

647 The geometrically frustrated structure of $\{V^{IV}_{15}As^{III}_6\}$ exhibits highly interesting magnetic and redox properties. The
648 $\{As^{III}_6V^{IV}_{15}\}$ cluster with an ~ 1.3 nm diameter exhibits a structure with layers of different magnetizations: a large central V^{IV}_3
649 triangle is sandwiched by two smaller V^{IV}_6 hexagons (FIG. 1 d). The 15 spins ($S = 1/2$) are coupled by antiferromagnetic super-
650 exchange and Dzyaloshinsky–Moriya interactions *via* different pathways, which results in a collective low spin ground state
651 with $S = 1/2$.³⁶ Studies of the adiabatic magnetization and quantum dynamics show that the $\{As^{III}_6V^{IV}_{15}\}$ cluster can act as a
652 qubit with relatively long coherence lifetimes and exhibits phonon bottleneck-induced magnetization hysteresis.^{36, 235, 250, 251}

653 Conclusions and outlook

654 The majority of studies in the area of electron-rich POMs has hitherto been focused on bulk synthesis and
655 characterisation, however, great progress has been made recently in investigating their potentials as catalysts (see e.g. ref
656 ^{27,31-34}) and magnetic materials (see e.g. ref ^{35, 36}). Significant challenges exist for the experimental chemist to understand the
657 electrochemistry of POMs and thus the synthesis of POMs with defined numbers of “blue” electrons. The development of
658 new computational methodologies to investigate and understand the mechanisms of POM reduction is gaining
659 momentum.^{132, 166, 252} There is considerable interest in the integration of electron-rich POMs into biological systems as they
660 were shown to exhibit enhanced biological activity in comparison to their oxidized parent structures. For example, tuning of
661 redox state of Keggin mixed-metal Mo/V POMs is a dominating factor in the functionality of chemical and biological self-
662 detoxifying materials.²⁵³ Gaining real-time information about the properties of the different redox states (e.g., their optical
663 properties via spectro- electrochemical methods) is of high interest.

664 Despite a number of crucial challenges at both the fundamental and applied levels, the structural characteristics of
665 reduced POMs are highly advantageous and an enormous future potential exists to revolutionize a number of research fields
666 such as electro- and photocatalysis, magnetochemistry, nanochemistry and biology, amongst others.

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 1115 $\text{X} = \text{Cl}\cdot\text{H}_2\text{O}; \text{M} = \text{Mg}, \text{X} = 2\text{Br}\cdot\text{H}_2\text{O}; \text{M} = \text{Mn}, \text{Fe}, \text{X} = 2\text{Cl}; \text{M} = \text{Co}, \text{Ni}, \text{X} = 2\text{Cl}\cdot\text{H}_2\text{O}$) *Inorg. Chem.*, **43**, 5850–5859 (2004).
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