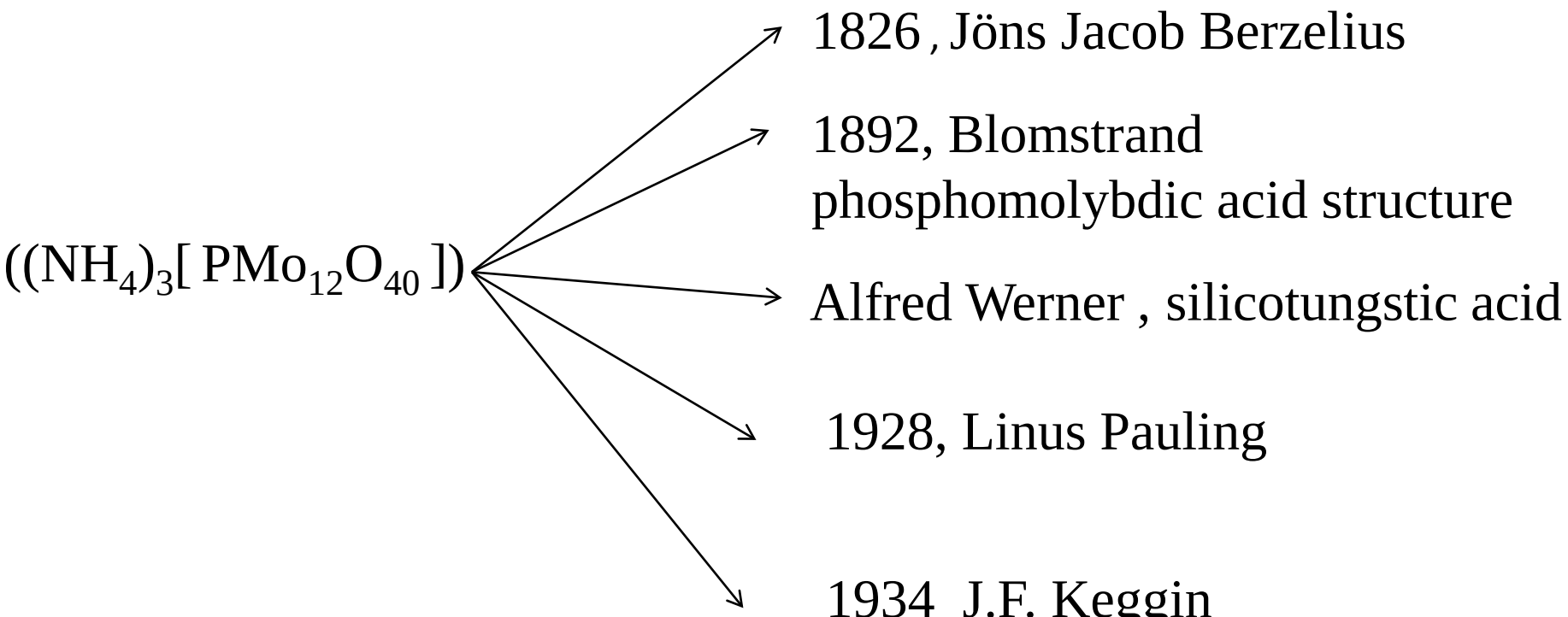
Structures & Synthesis

- “Keggin” structure
- “Lindqvist” structure
- “Dawson” structure
- “Anderson” structure
- “Silverton” structure
- “Allman-Waugh’’structure
- “nano-hedgehog’’ structure

“Keggin” structure

$[XM_{12}O_{40}]^{n-}$: X= P^{5+}, Si^{4+}, or B^{3+}

M= Mo ή W



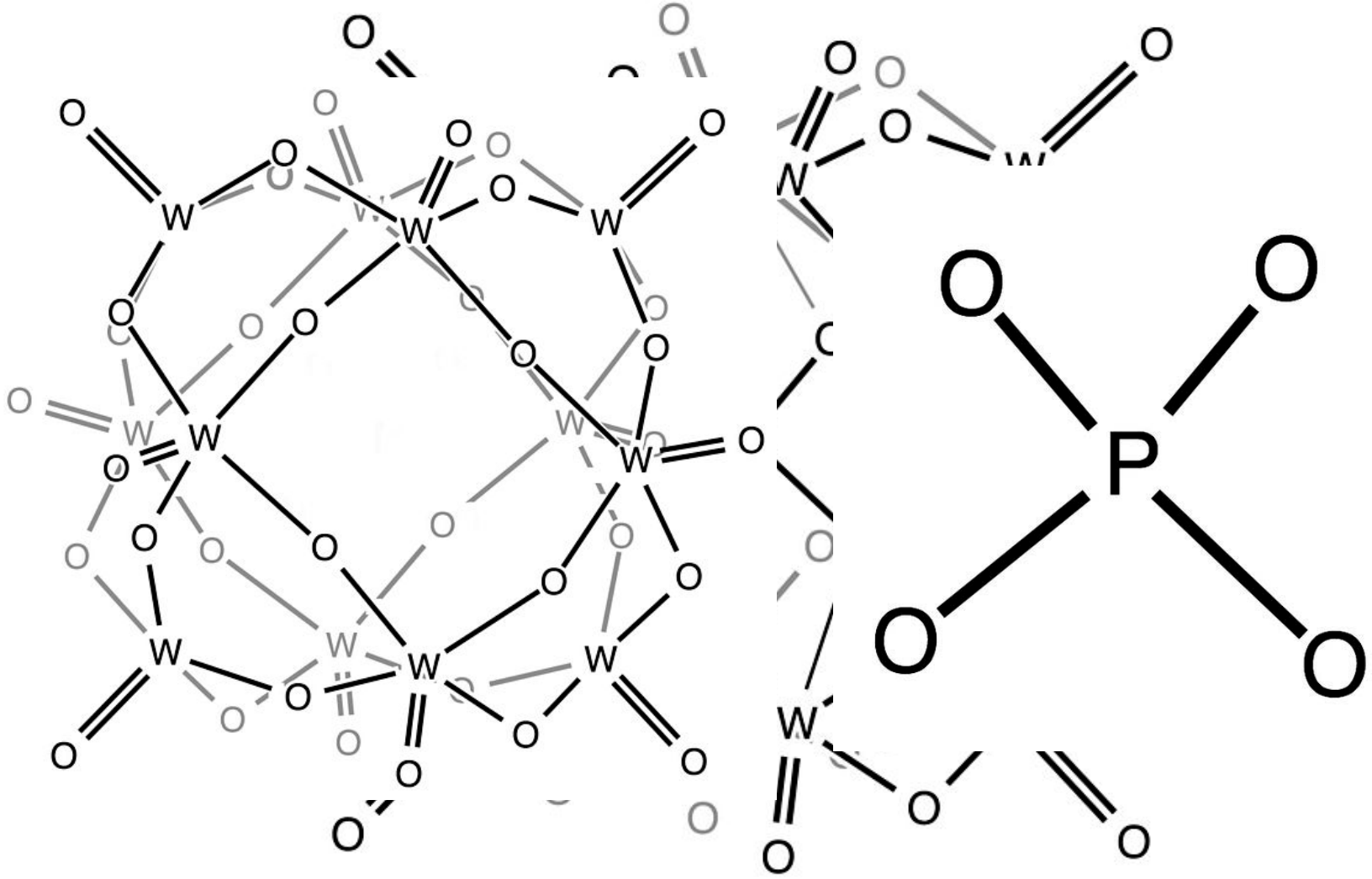
“Keggin” structure

$[XM_{12}O_{40}]^{n-}$: X= P^{5+}, Si^{4+}, or B^{3+}

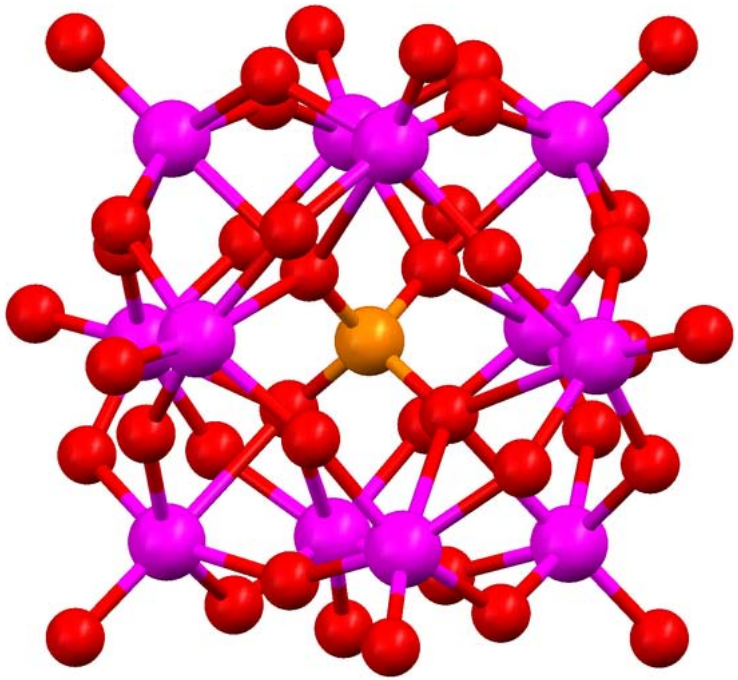
M= Mo ή W

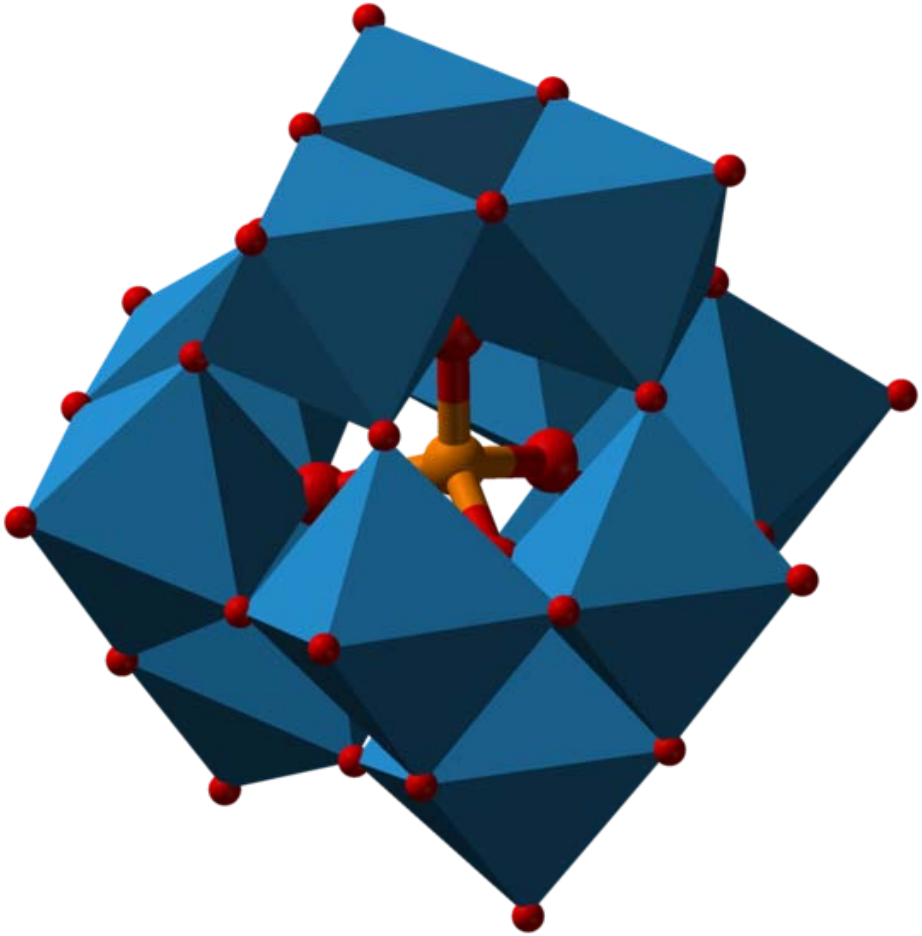
$12\ (NH_4)_2MoO_4 + H_3PO_4 + 21\ HNO_3 \rightarrow (NH_4)_3PMo_{12}O_{40}\downarrow + 21\ NH_4NO_3 + 12\ H_2O$

$((NH_4)_3[\ PMo_{12}O_{40}\ ])$



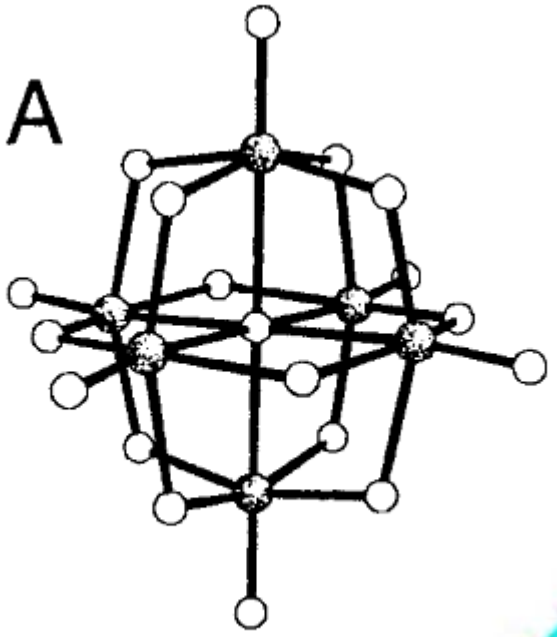
$((NH_4)_3[\ PMo_{12}O_{40}\ ])$

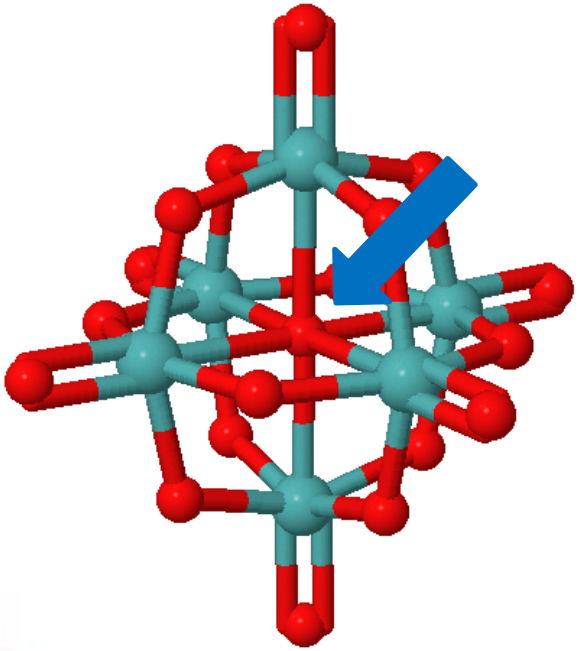


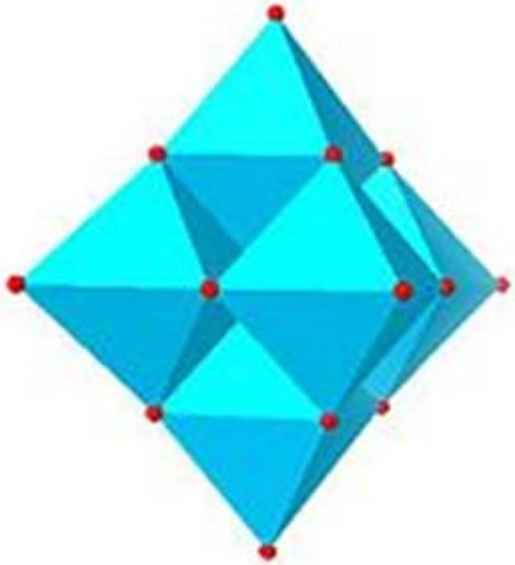


“Lindqvist” structure

$[M_6O_{19}]^{n-}$: M = Mo, W, Nb, Ta







“Lindqvist” structure

$[M_6O_{19}]^{n-}$: M = Mo, W, Nb, Ta

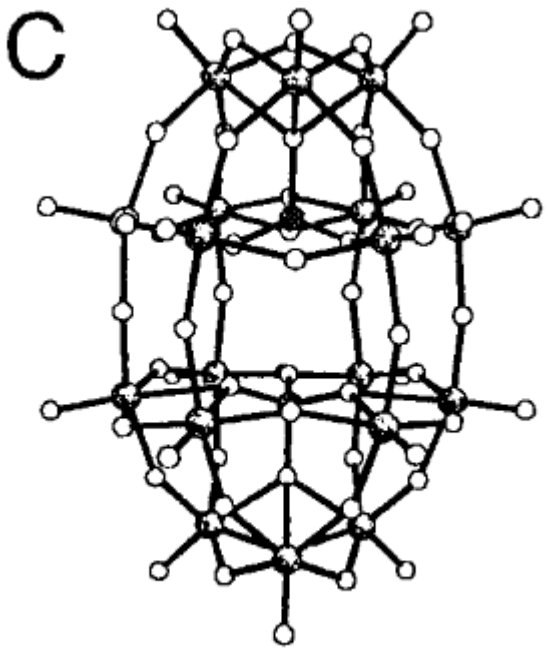
$6Na_2MoO_4 + 10HCl + 2(n\text{-}C_4H_9)_4NBr \rightarrow [(n\text{-}C_4H_9)_4N]_2[Mo_6O_{19}] + 10NaCl + 2NaBr + 5H_2O$

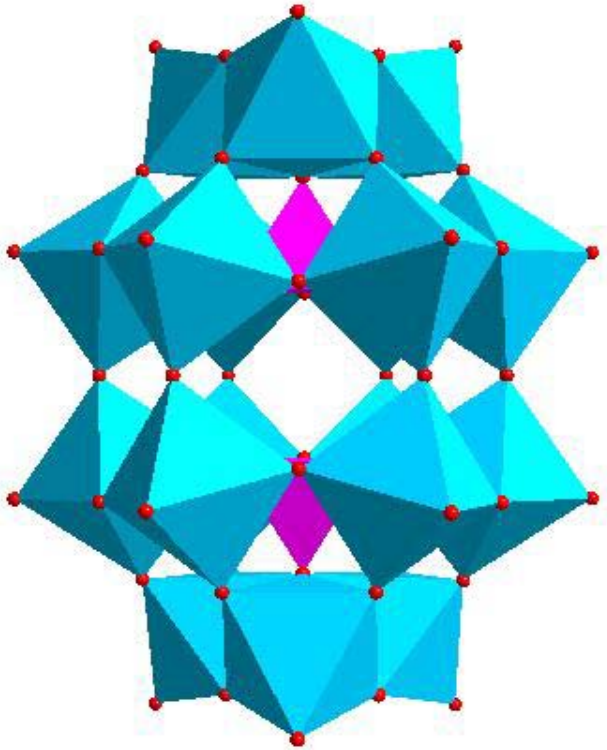
“Dawson” structure

A-α-XM_9O_{34} : two “Keggin” fragments

M = Mo, W

X = P, As, S

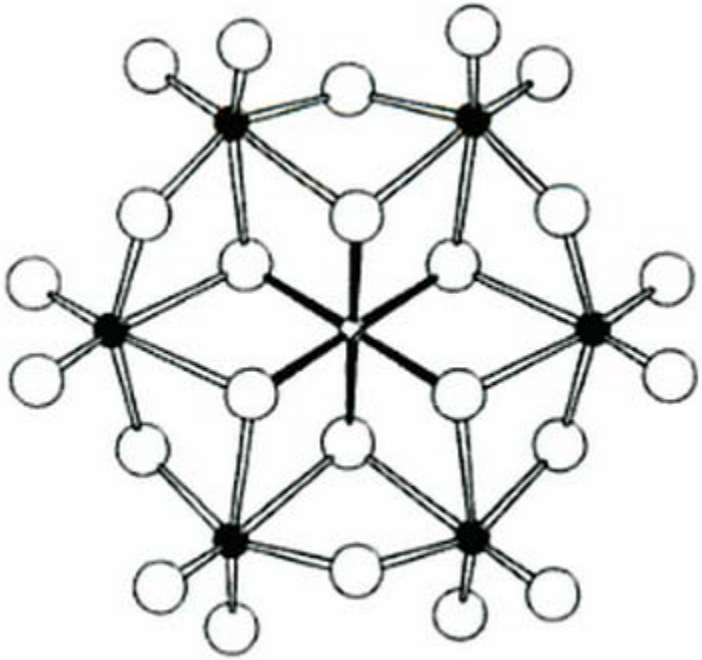


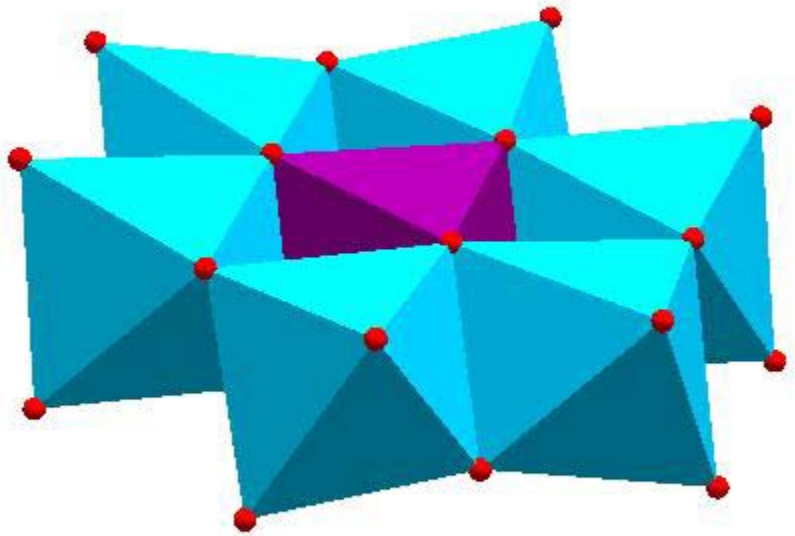


“Anderson” structure

$[XM_6O_{24}]^{n-}$: M = Mo, W

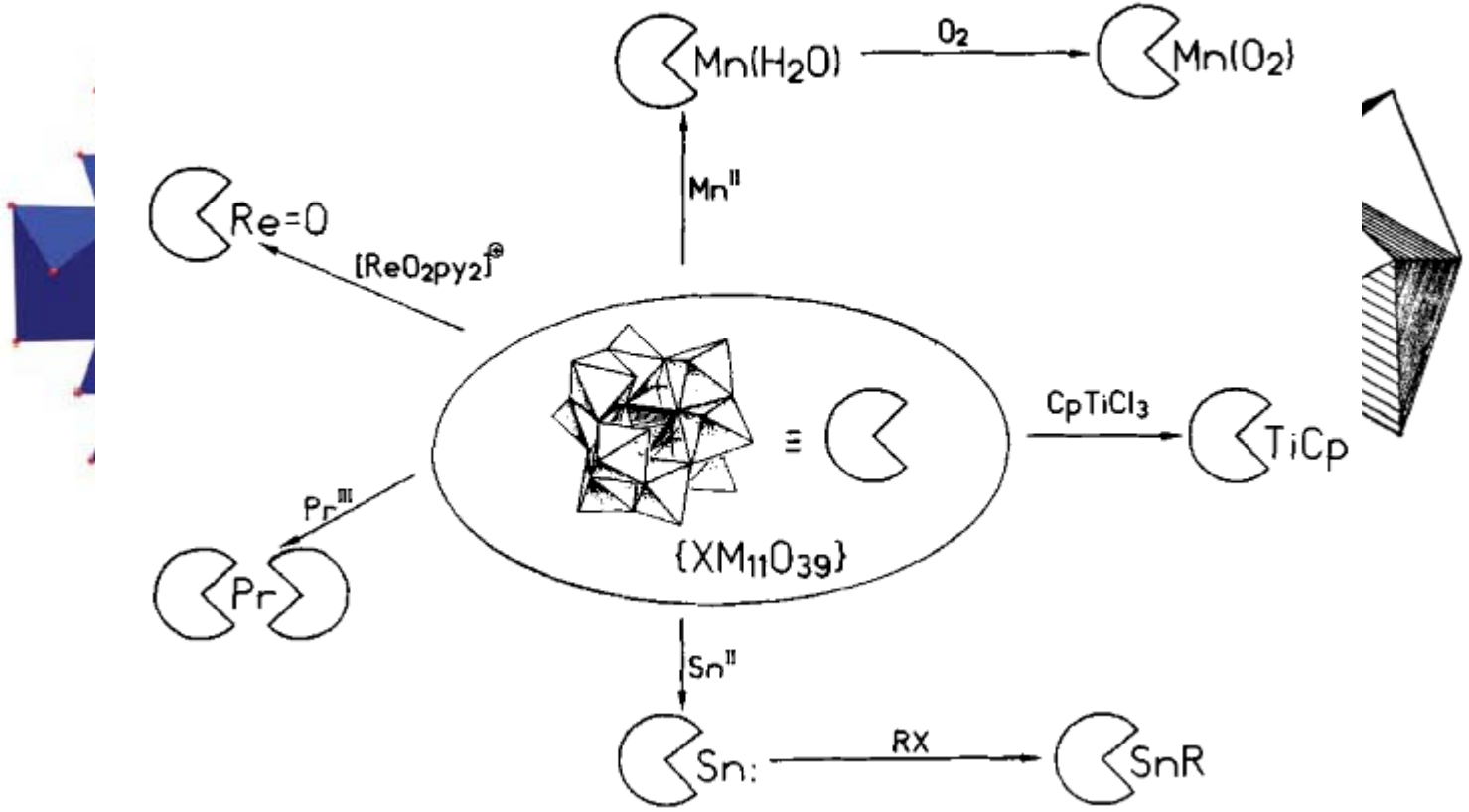
X = Cr^{3+},Mn^{4+},Co^{3+},Cu^{2+},Zn^{2+},Te^{4+},Pt^{4+},





“Silverton ”structure

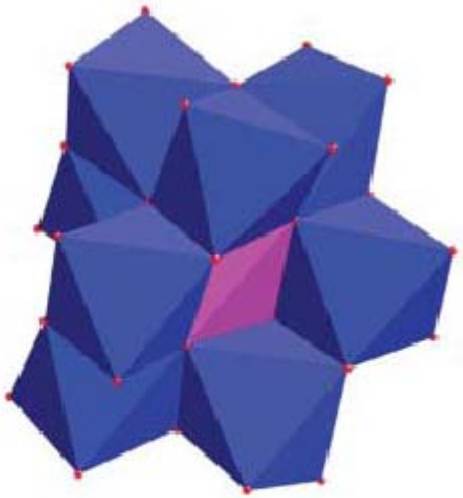
$[XMo_{12}O_{42}]^{9-}$: X = Ce^{III}, Gd^{III}



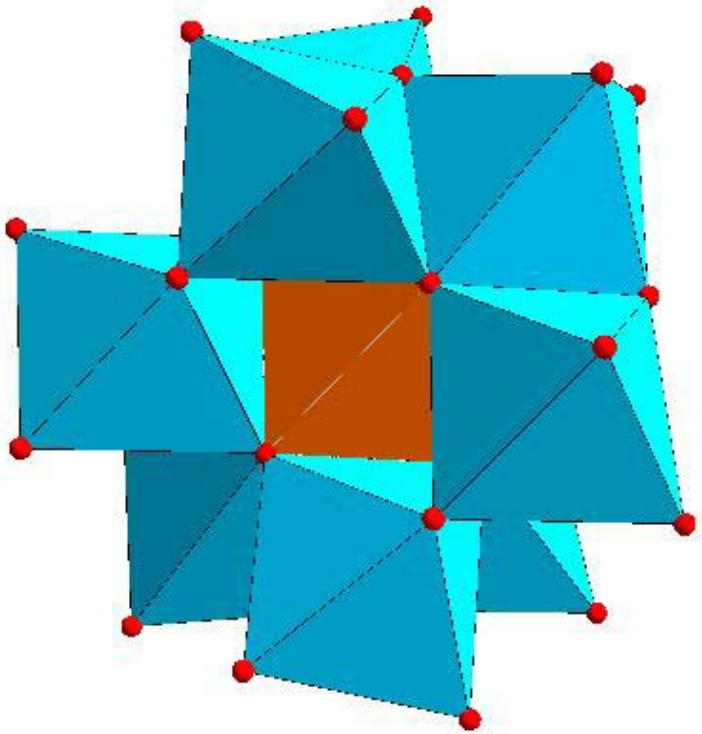
‘’Allman-Waugh’’structure

$XM_9O_{32}^{n-}$: M = Mo

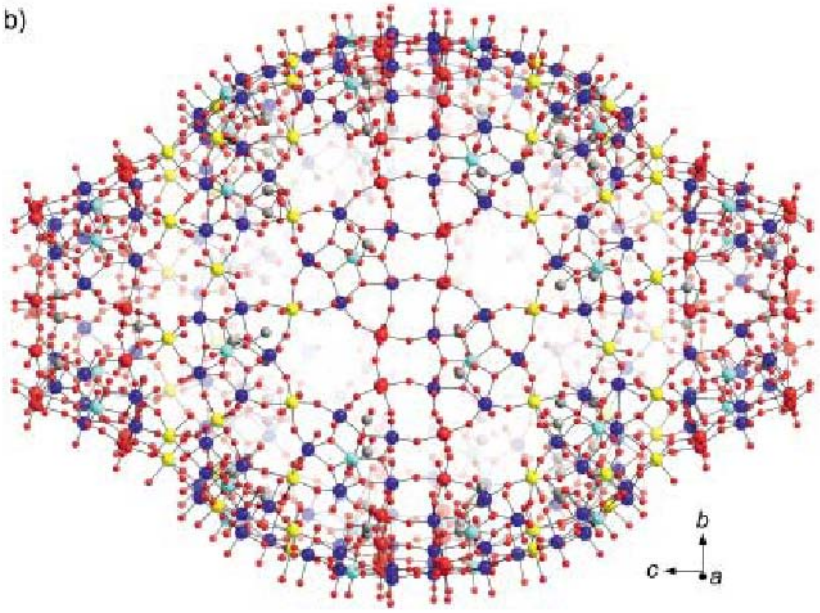
X = Mn^{IV}, Ni^{IV}

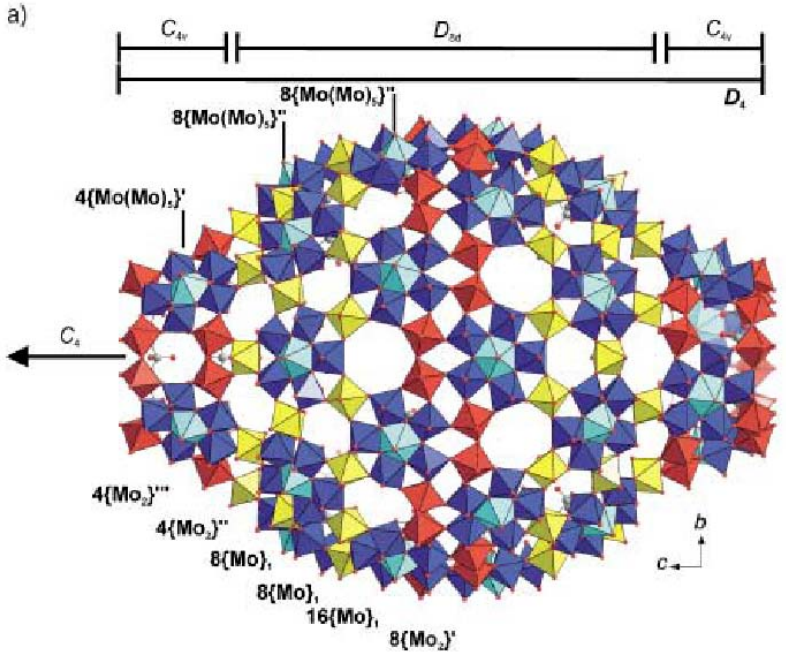


(d)

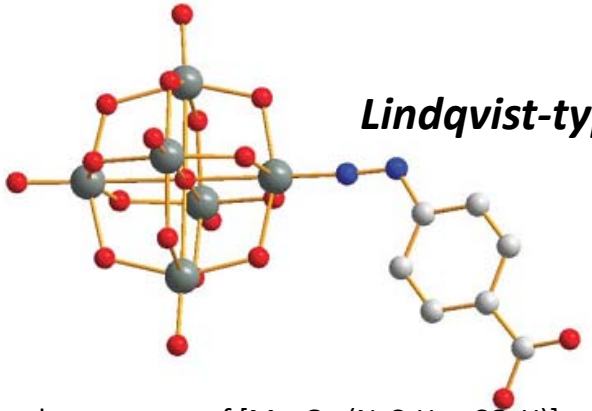


“nano-hedgehog’’ structure





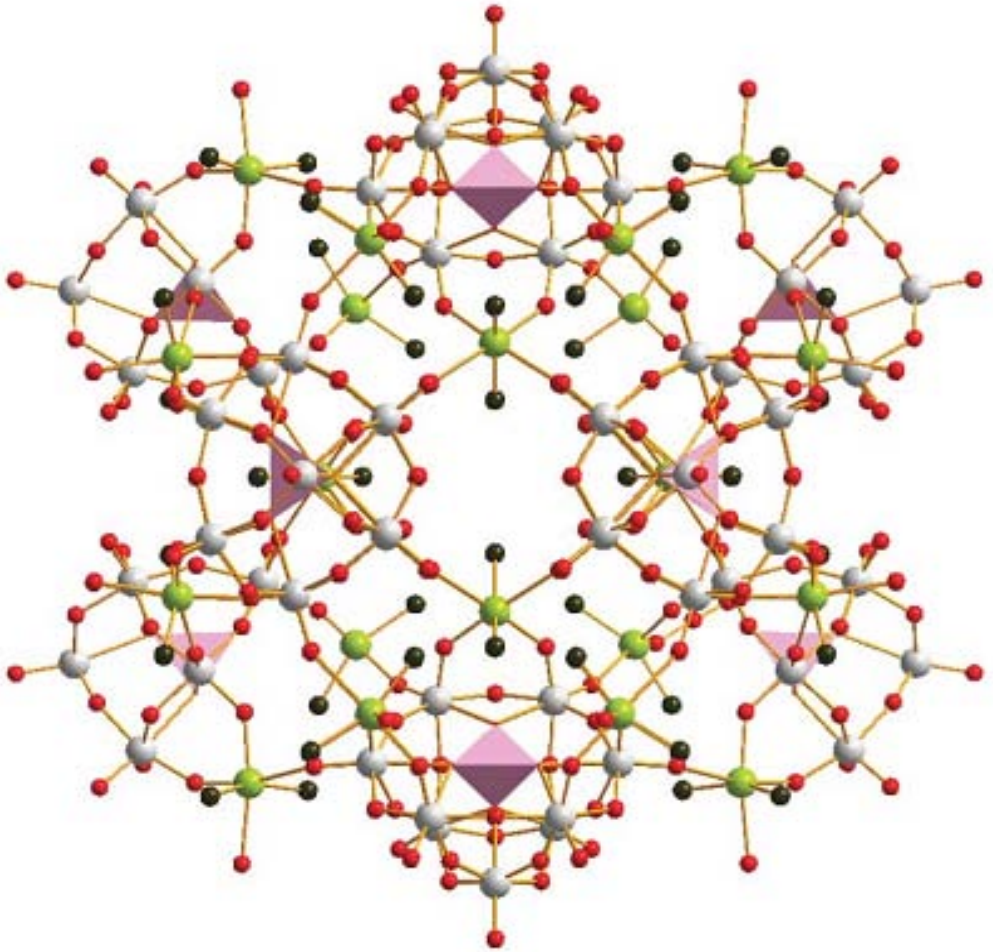
The **derivatisation** of POM frameworks by replacing/derivatising the oxo ligands is an important aim since this will allow a much greater degree of control



Lindqvist-type

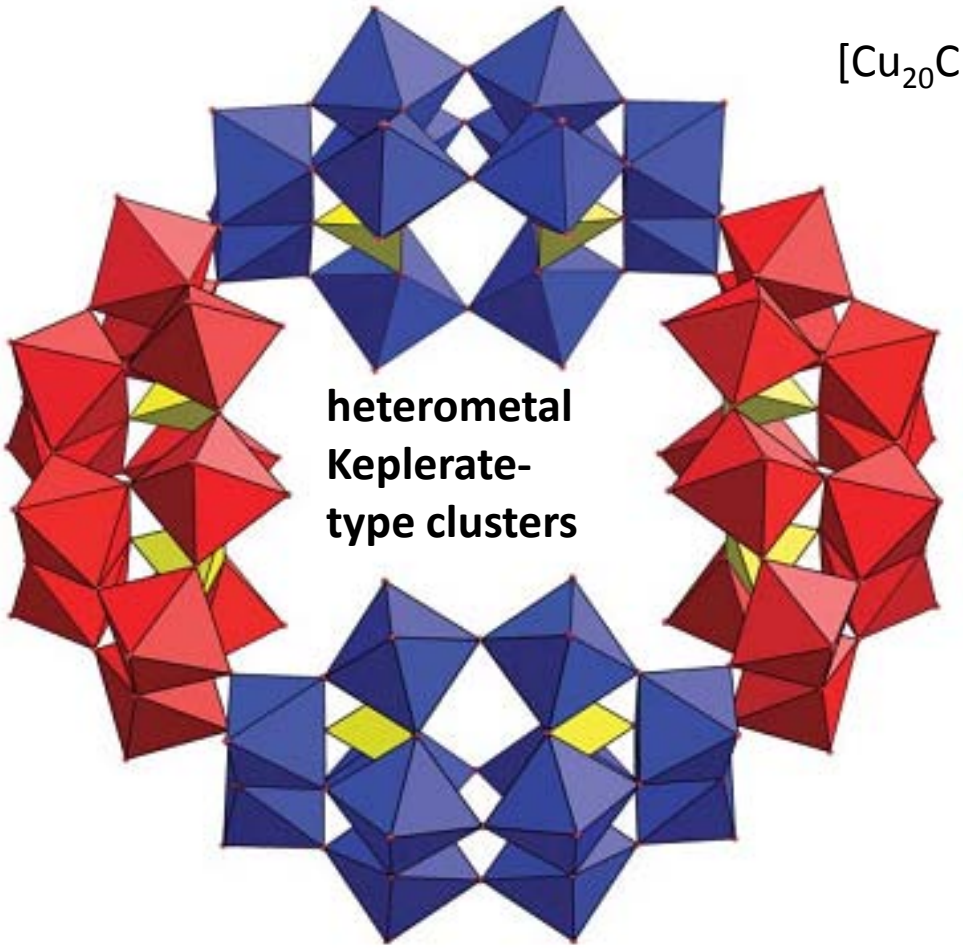
Molecular structure of $[Mo_6O_{18}(N_2C_6H\text{-}p\text{-}CO_2H)]_{32}$. Colour scheme: Mo - deep grey , O – red, N – blue, C – grey

Sythesis of Coordination Polymers



A representation of the structure of $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A\text{-}PW_9O_{34})_{12}]_{362}$. Colour scheme: W – grey, Sn – green. O – red, C – black. PO_4 moieties are shown as pink tetrahedra.

POM-based materials with magnetic and conducting properties

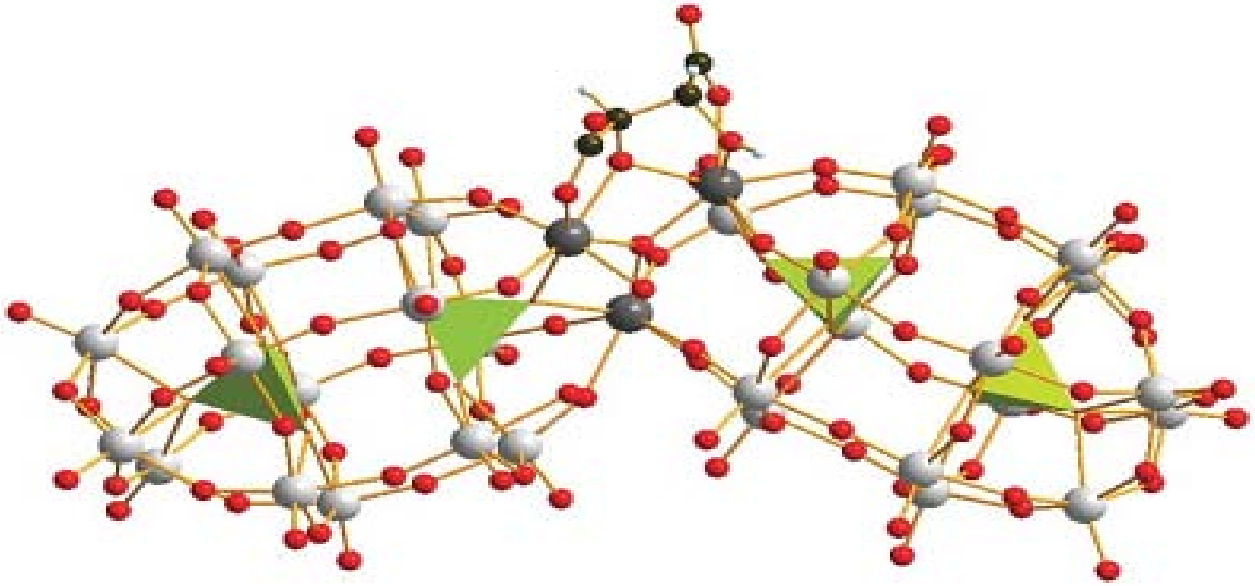


$[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$

The development of POM-based clusters incorporating paramagnetic centres is an interesting goal since it is possible to utilise existing building blocks/clusters to generate very large **magnetic molecules**.

Structure of the $\{W_{48}\}$ cluster showing the cavity in which the 20 copper(II) ions are complexed, the $\{W_{12}\}$ hexavacant buildingblocks are shown in blue and red and the copper(II) ions are omitted for clarity.

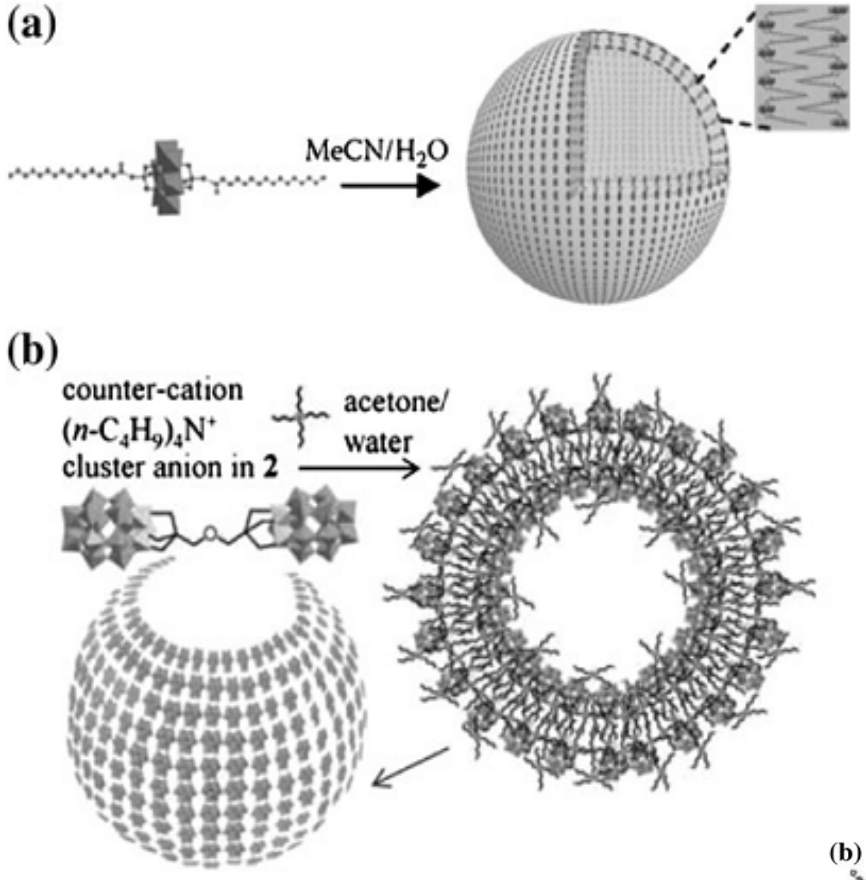
Chiral and biologically active polyoxometalates



A representation of the structure of $\{a\text{-}P_2W_{15}O_{55}(H_2O)[Zr_3(m_3\text{-}O)(H_2O)(tartH)[a\text{-}P_2W_{16}O_{59}]\}^{15-}$. Colour scheme: W – grey, Zr - deep grey, O – red, C – black, H – light blue. The PO_4 moieties are shown as green tetrahedra

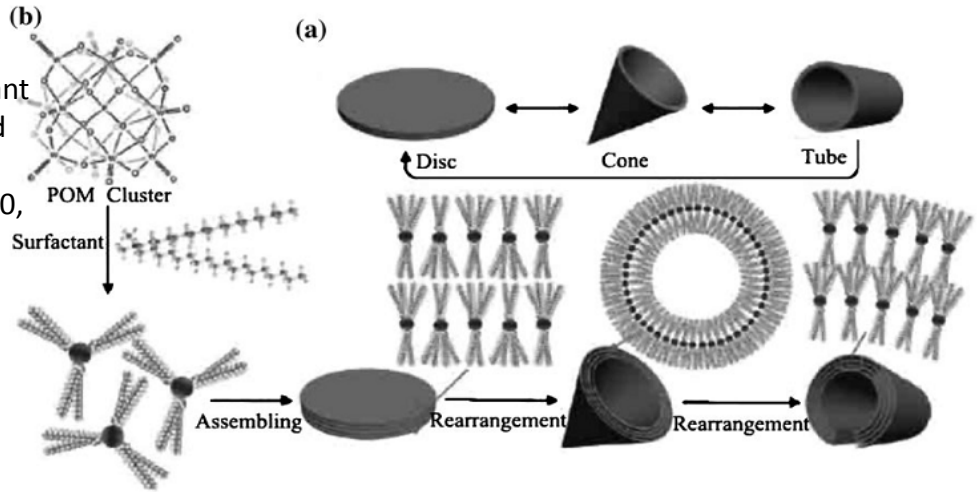
Perhaps one of the most extraordinary areas of application of polyoxometalate chemistry **lies in biology**

the wide variety of structures, water solubility, anionic nature, electrochemical activity, and recent realisation that large inorganic clusters can penetrate cell walls. Recent investigation of anti-tumor, -viral, and-bacterial activities of POMs shows **induced cell apoptosis**, **inhibition of virus binding to a receptor**, and the enhancement of P-lactam antibiotics, **inhibition of bacterial growth**, herbicidal action, as well as **regulation of insulin levels**



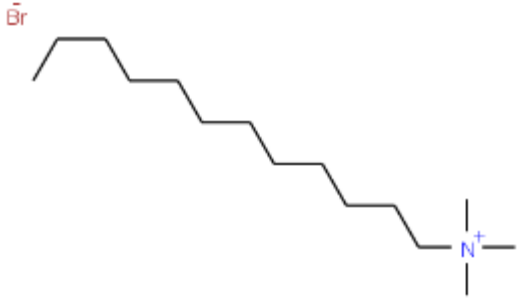
a **hybrid** ‘‘**surfactant**’’ with a large hydrophilic POM cluster as its polar head group,$[n\text{-}Bu_4N]_3[MnMo_6O_{18}\{(OCH_2)_3\text{-}CNHCO\text{-}(CH_2)_{14}CH_3\}_2]$ (Mn-Anderson-C_{16}) that can <u>self-assemble</u> into vesicle structure in the water/MeCN mixed solvents

In oil, the hybrid ‘‘surfactant’’ Mn-Anderson-C (n = 6, 16) assembled into reverse-vesicular structures

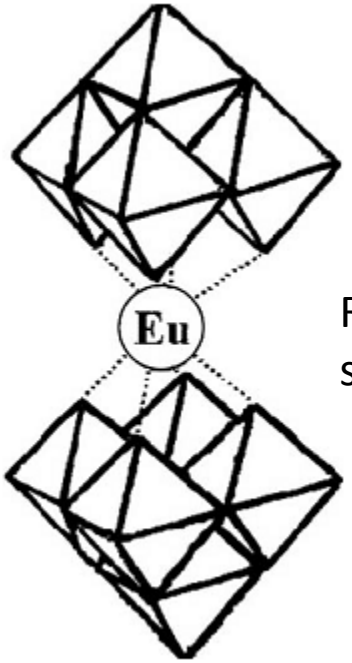


Schematic illustrations of a the Mn-Anderson-C_{16} hybrid surfactant and their vesicle formation from water/MeCN mixed solvent and b vesicle formed from V_3-capped Wells–Dawson-type cluster $TBA_5H_4[P_2V_3W_{15}O_{62}]$ (Reprinted from J. Am. Chem. Soc. 2008, 130, 14408–14409. and Angew. Chem. Int. Ed. 2009, 48, 8309-8313)

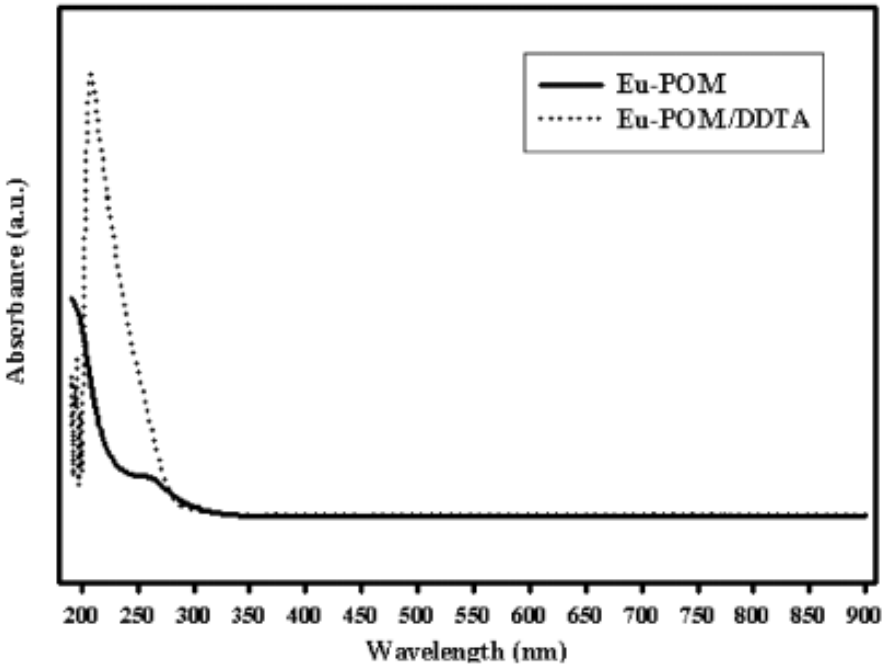
Photoluminesence



Dodecyltrimethylammonium (DDTA)

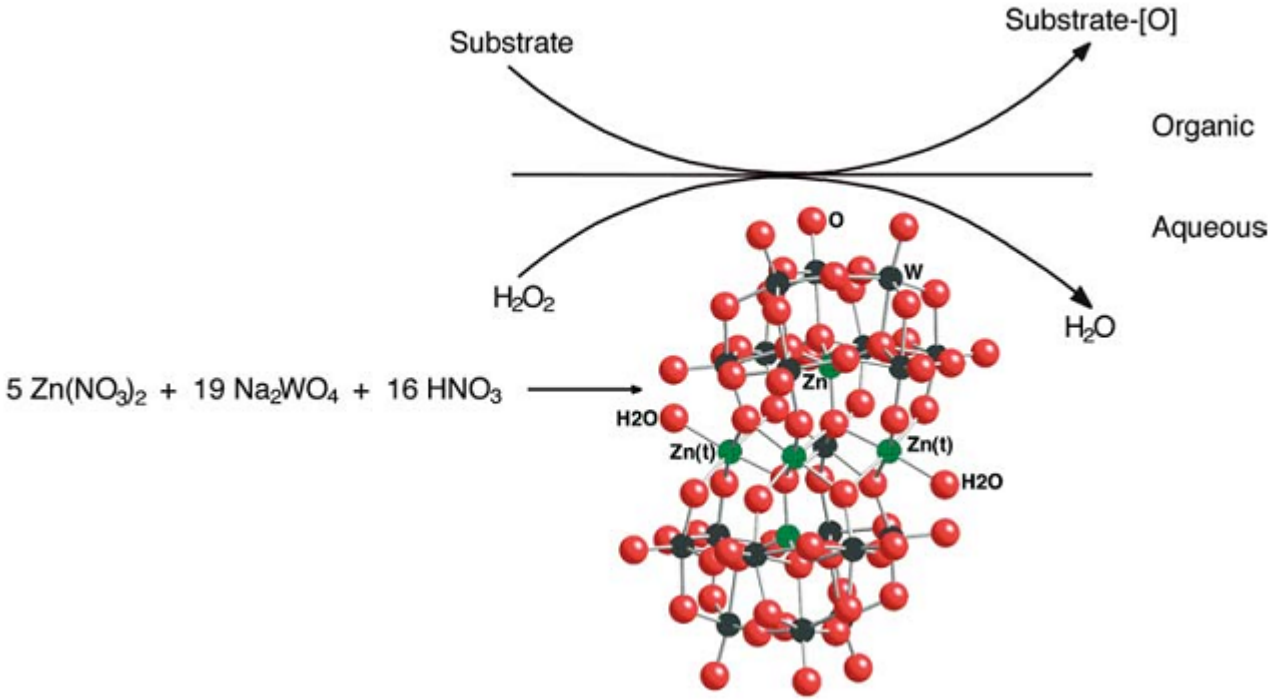


Representation of structure $EuW_{10}O_{36}^{9-}$

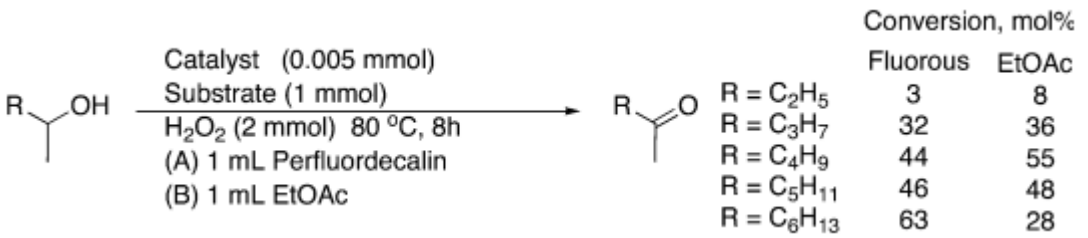


Absorption spectra of Eu-POM (in distilled water) and Eu-POM/DDTA (ethanol)

Eu-POM solution and the reaction mixture was refluxed under a nitrogen atmosphere at hot temperature (80^0 C) for 24 h



The assembly the $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$. polyoxometalate catalyst and a representation of aqueous biphasic oxidation



	Conversion, mol%	
	Fluorous	EtOAc
$R = C_2H_5$	3	8
$R = C_3H_7$	32	36
$R = C_4H_9$	44	55
$R = C_5H_{11}$	46	48
$R = C_6H_{13}$	63	28

Oxidation of aliphatic alcohols catalyzed by $(RFN^+)_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$

A Survey of Applications of Polyoxometalates

Dimitris E. Katsoulis

Dow Corning Corporation, Central Research and Development, Midland, Michigan 48686

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Dimitris E. Katsoulis was born in Athens, Greece in 1955. He received a B.S. degree in Chemistry from University of Athens in 1977. He subsequently joined the research group of Prof. Michael T. Pope at Georgetown University and obtained a Ph.D. degree in 1985. He continued with a postdoctoral assignment at Georgetown University, and in 1988 he joined the Science and Technology function of Dow Corporation in Midland Michigan. He is currently an Associate Research Scientist in the Rigid Materials Science Expertise Center (Central R&D) in Dow Corning. His research interests include hybrid materials, with focus on siloxane-polyoxometalate compositions, sol–gel chemistry, silsesquioxanes, gel systems, polymer matrix composites, and nanocomposites.