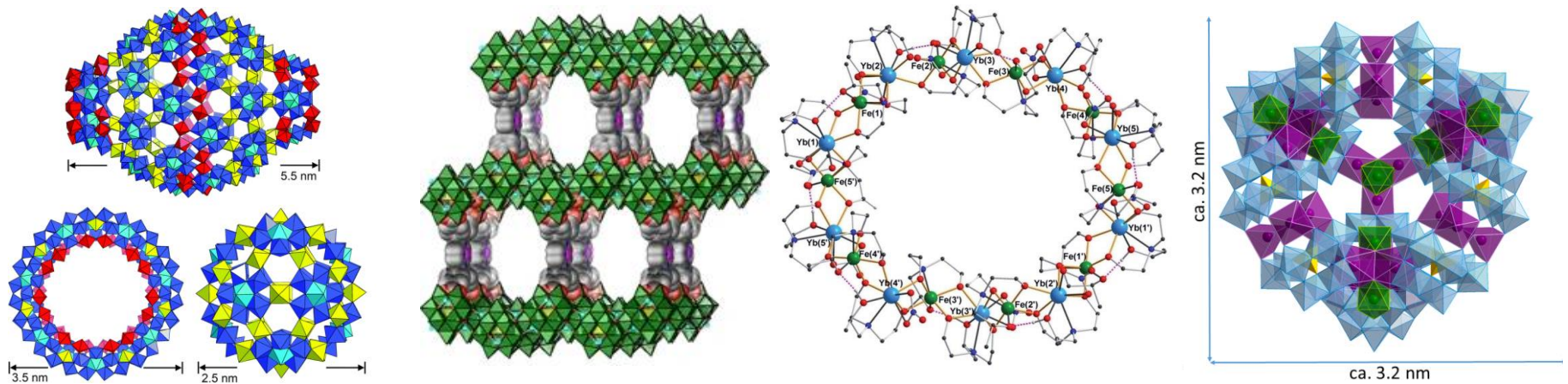


Advanced Functional Inorganic POMs, Coordination Clusters and Framework Materials

Dr. Masooma Ibrahim

Institute of Nanotechnology (INT)



Overview

- Coordination Clusters (CCs)
Prof. Annie Powell

- Polyoxometalates (POMs)
Dr. Masooma Ibrahim

- Polyoxometalate-Based Metal Organic Frameworks (POMOFs)
Dr. Masooma Ibrahim

Polyoxometalates (POMs)

■ General Introduction

- Background
- Synthetic Strategies
- Structural Principles
- Characterization Techniques

■ Emerging Properties and Applications

- Catalysis
- Magnetism
- Medical and Biological Applications
- Contrast Agents
- Electrochemical Applications

Polyoxometalates (POMs)

POMs are discrete polynuclear metal-oxo clusters specifically composed of the early transition metals (M) in their highest oxidation state (d^0 or d^1).

M= V^{5+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , and W^{6+} .

POMs are negatively charged

Possess predominantly O^{2-} ligands

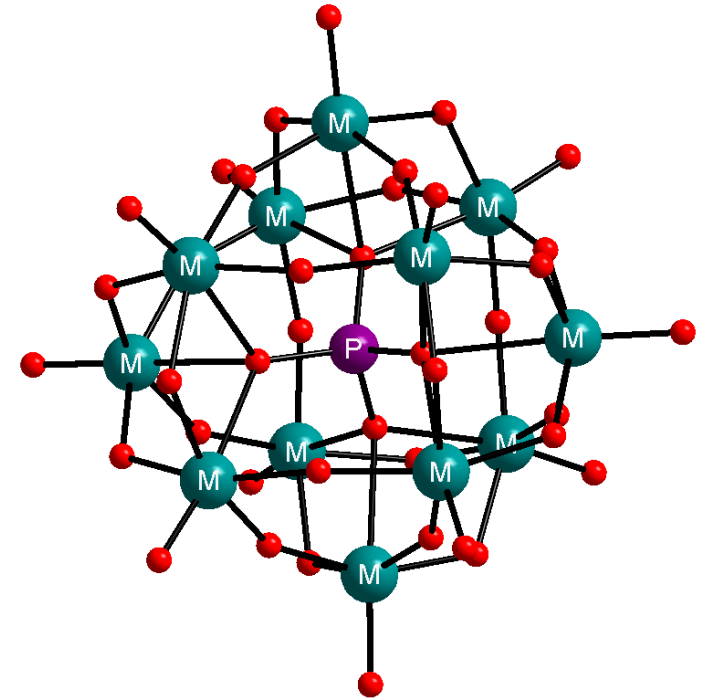
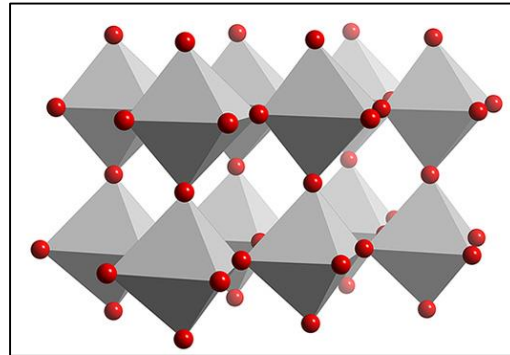
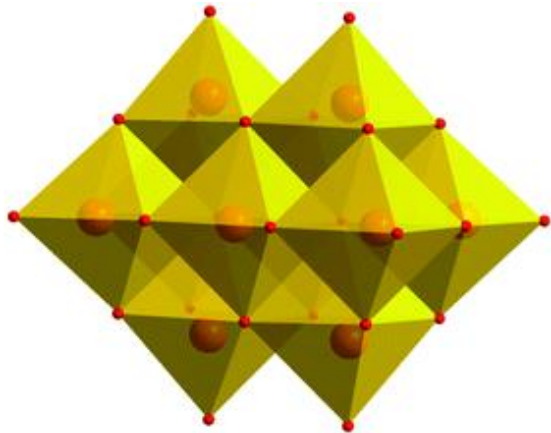
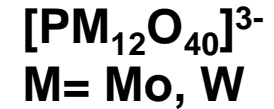
Polyoxometalates (POMs)

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POMs are negatively charged.

Possess predominantly O^{2-} ligands.



Polyoxovanadate $[V_{10}O_{28}]^{6-}$

WO_3 oxide

Polyoxomolybdates/polyoxotungstates

M. T. Pope Heteropoly and isopoly oxometalates; Springer-Verlag: Berlin ; New York, 1983.

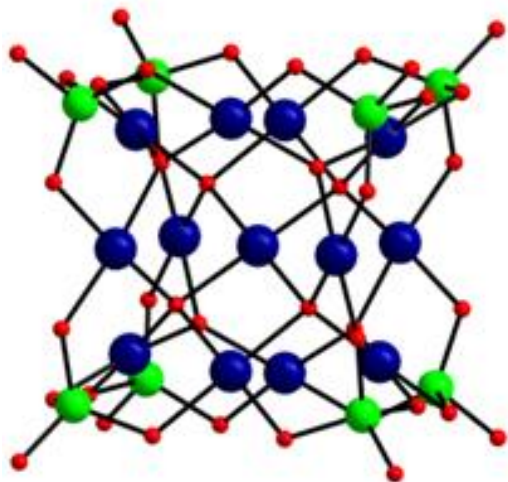
Polyoxometalate Type Structures

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period ↓																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac *	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				* 58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				* 90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

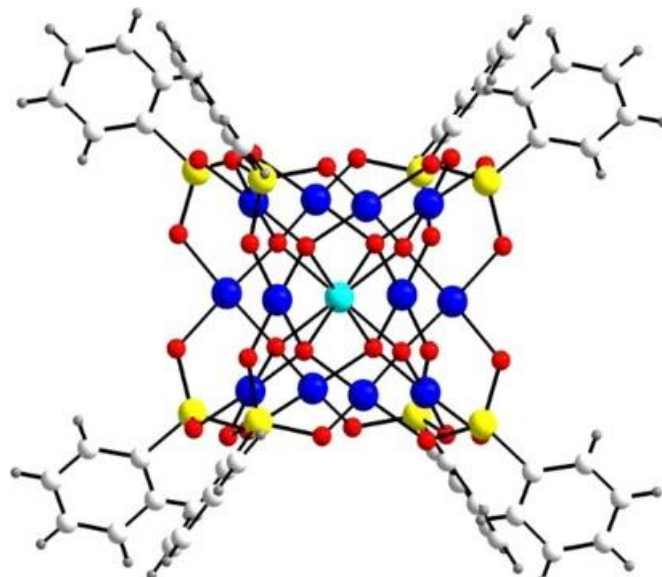
Classic POMs are Group V and VI polyanions in their highest oxidation state with a terminal and inert "yl" oxo group, which stabilizes the molecular form in water.

Polyoxopalladates

Angew. Chem. Int. Ed. **2008**, 47, 9542-9546.



Inorg. Chem. **2012**, 51, 24, 13214-13228

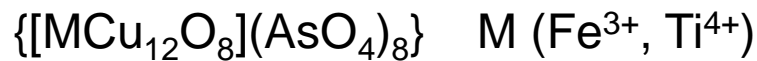
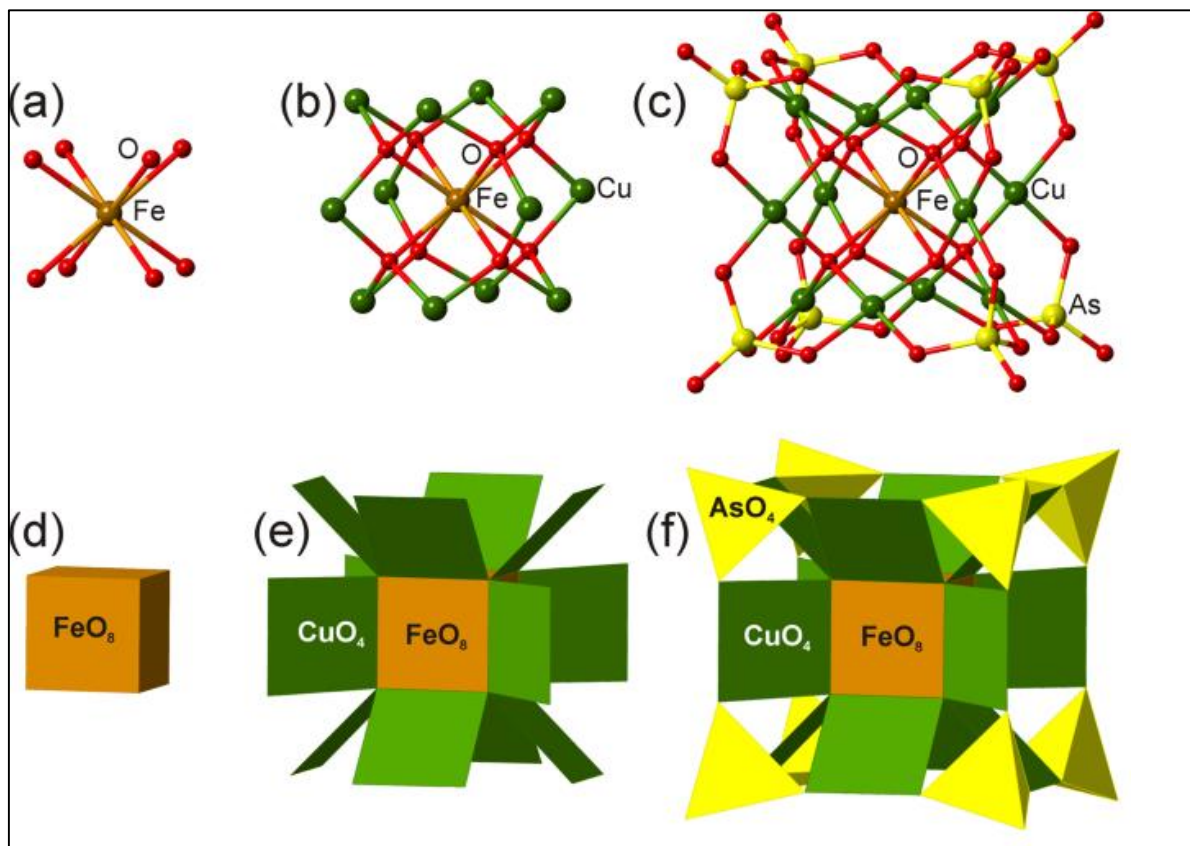


M (Sc^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Lu^{3+})

L (PhAsO_3^{2-} , PhPO_3^{2-} , SeO_3^{2-})

Polyoxometalate Chemistry at Volcanoes

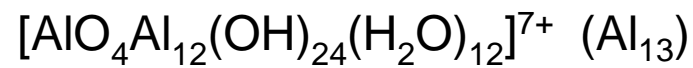
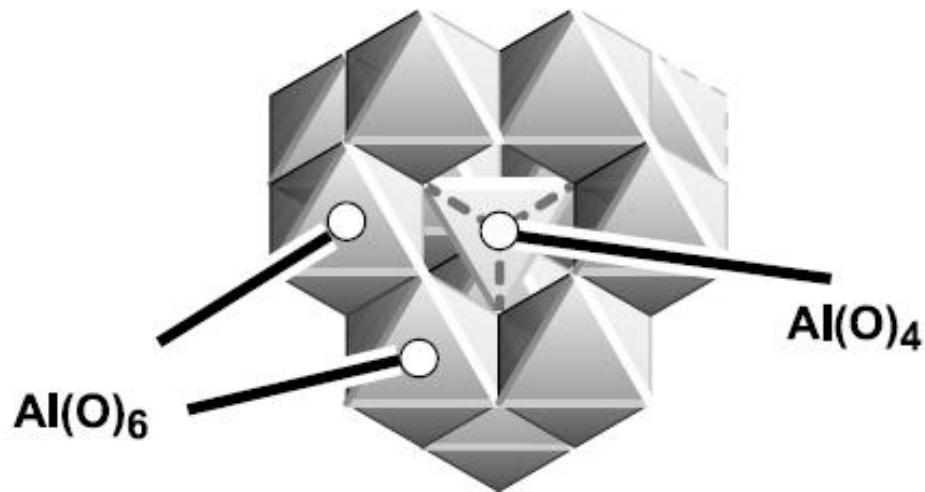
Sci Rep. 2020, 10, 6345



Discovery of polyoxocuprate nanoclusters in fumarolic minerals

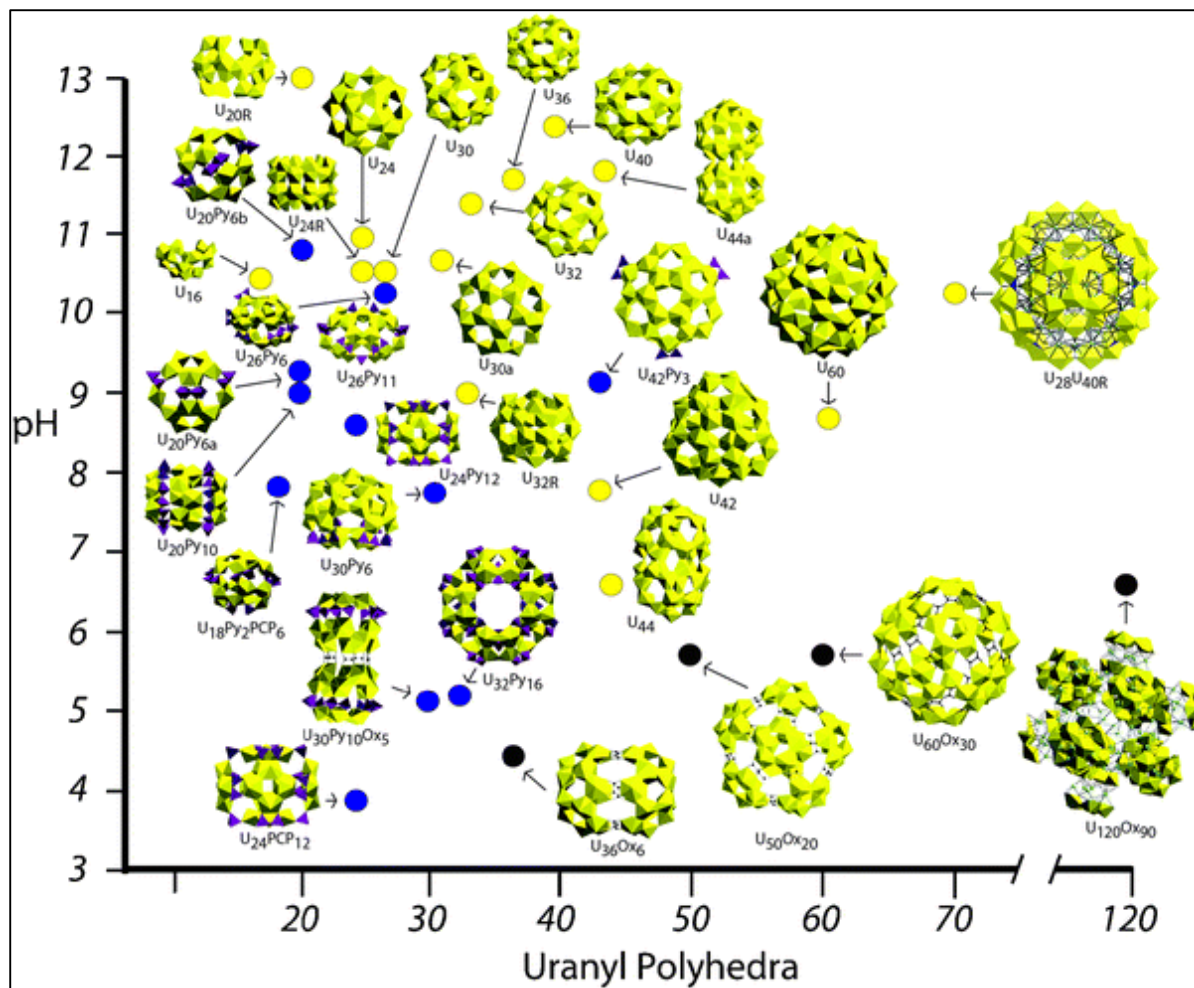
Aluminium Polyoxocation

Science, 2002, 297,2245-2247



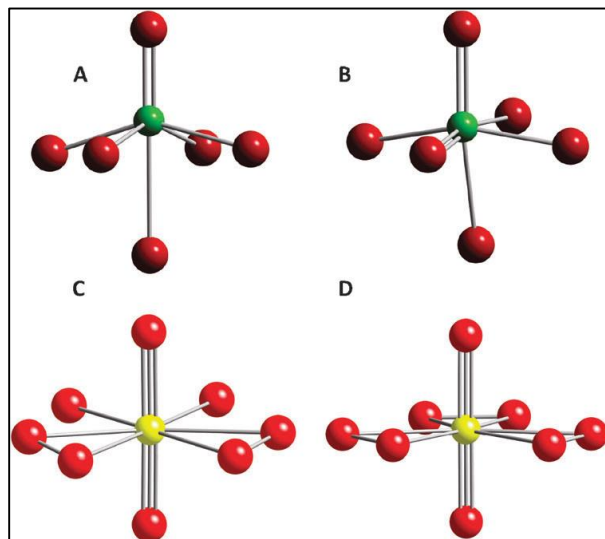
Uranyl Polyoxometalate

Chem. Soc. Rev. 2012, 41, 7354-7367

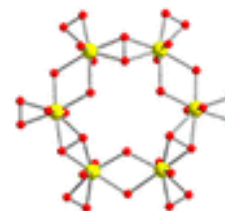
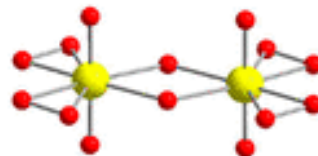
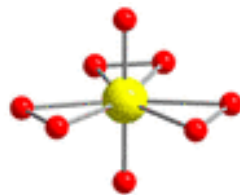


Uranyl Polyoxometalate

Chem. Soc. Rev. **2012**, *41*, 7354-7367



A & B. green spheres are d^0 Group V and Group VI transition metals V, Nb, Ta, Mo, W. A shows a distorted octahedron with a single yl-oxygen trans to a long M–O bond. B shows a distorted octahedron with two cis-yl-oxygen ligands.
C & D show the uranyl building blocks; yellow spheres are U^{6+} . C is uranyl cis-dihydroxidediperoxide and D is uranyl triperoxide

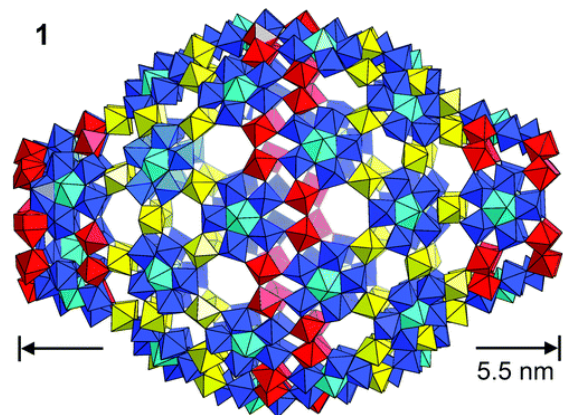


Structure Size



Inorg. Chem. **2020**, *59*, 3, 1633–1641

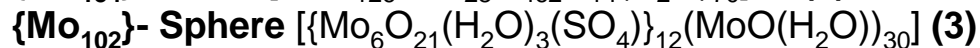
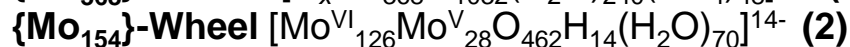
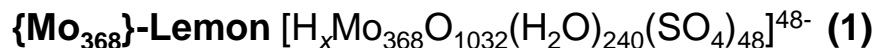
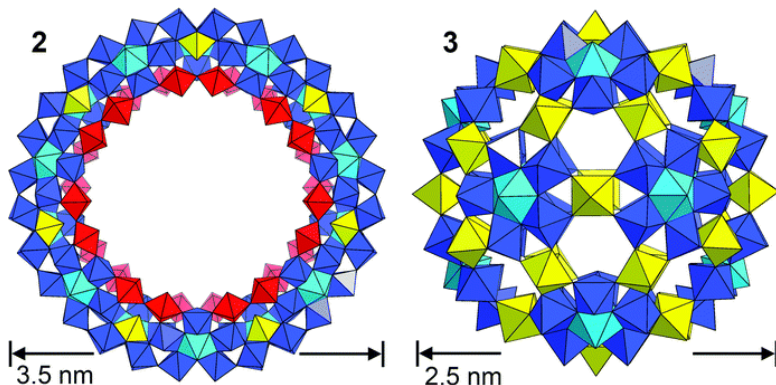
Molybdenum Blue as Polyoxomolybdate nanostructures



A special class of polyoxomolybdates:
Molybdenum blue structural types

Solutions of molybdenum blues (MBs) was
first mentioned by Scheele in 1783

C. W. Scheele, ed. Martin Sändig, Niederwalluf/Wiesbaden
(reprint: original 1793), Vol. 1, 1971.



A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem. Int. Ed.*, 1995, 34, 2122-2124.

A. Müller, E. Beckmann, H. Bögge, M. Schmidtman and A. Dress, *Angew. Chem. Int. Ed* *Angew.* 2002, 41, 1162-1167.

A. Müller, B. Botar, S. K. Das, H. Bögge, M. Schmidtman and A. Merca, *Polyhedron*, 2004, 23, 2381-2385.

History

The first Polyoxometalate (POM)

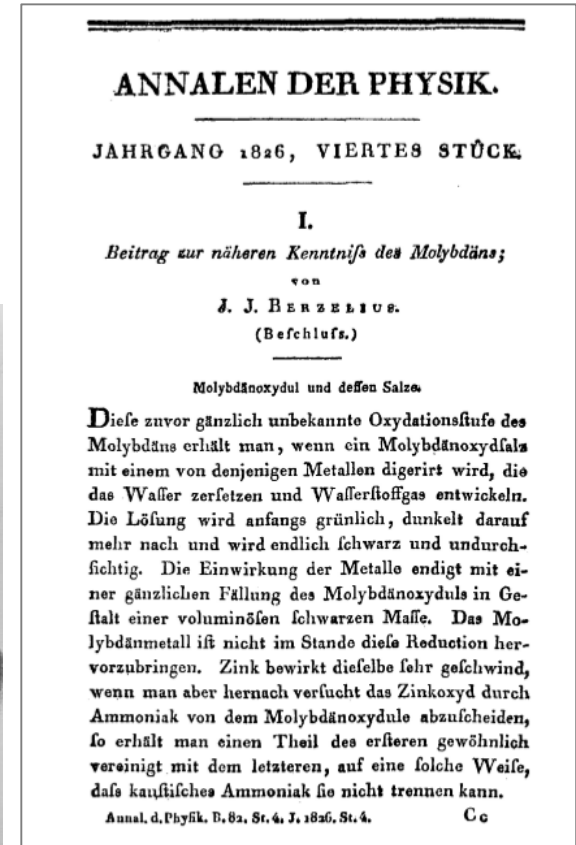
A phosphomolybdate, was reported by the Swedish scientist Jöns Jakob Berzelius in 1826 by reaction of $(\text{NH}_4)_2\text{MoO}_4$ with phosphoric acid.



Ammonium Phosphomolybdate



Jöns Jakob Berzelius



First Structural Characterization

Timeline of speculations and discoveries

1783	C. W. Scheele	Reports reduced molybdenum oxides: "Molybdenum blue"
1826	J. J. Berzelius	Reports reaction of molybdate and phosphate
1862	M. C. Marignac	Isolates and reports various polyoxotungstates and polyoxomolybdates
1907	A. Miolati A. Rosenheim	Suggest corner-sharing tetrahedra as a structural motif Miolati-Rosenheim structural hypothesis
1909	A. Werner	Suggests highly linked polyhedra, based on his theory of coordination
1929	L. Pauling	Suggests corner-sharing octahedra based on ionic radii
1933	J. F. Keggin	Structural characterisation of 12-phosphotungstic acid

Some of the most famous chemists, e.g. Scheele (1742-1786), Berzelius (1779-1848), Werner (1866- 1919) and Pauling (1901-1994), were interested in this field

L'actualité chimique, **2006**, 315-318, 1952.

Linus Pauling Attempts

Dear Professor Bragg,
Oct 22, 1928

I am very pleased to have that you had
found the structure of these and that I recommend the
one I suggested. The letter came just about the time my
paper appeared, so that I could make no reference to
Vasthink. I have not yet tried applying the rules
governing deformation to all other the atoms you
can with what's meant.

The last of August I sent two papers to the Journal
of the American Chemical Society. One of them are
on the structure of complex crystals
I believe that nothing I have done is slightly
original - in particular was I qualified to read
- your letter a statement of the rules governing
the ordering of polyhedra atoms. I have written
the letter asking whether and how papers will appear
- November when I have for her I'll show you a
- to the same rules are included in a paper in
- your field's text-book, which will appear in
- December.

I am pleased with the clarity that the study
of crystals has introduced into the very complex
- paper in your and my field in papers.

Letter from Linus Pauling to W.L. Bragg. October 22, 1928.

Linus Pauling attempts

Dear Professor Bragg:

I was very pleased to learn that West had found the structure of topaz, and that it approximates the one I suggested. Your letter came just about the time my paper appeared, so that I could make no reference to West's work. I have not yet tried applying the rules governing deformation to see whether the atomic positions agree with West's or not.

The last of August I sent two papers to the Editor of the Journal of the American Chemical Society. In one of them are rules governing the structures of complex crystals. I realize that nothing I have done is highly original - in particular was I gratified to read in your letter a statement of the rule governing the sharing of polyhedron elements. I have written the Editor asking whether or not these papers will appear in December. When I hear from him I'll drop you a note. The same rules are included in a paper in Sommerfeld's Festschrift, which will appear in December.

I am pleased with the clarity that the study of crystals has introduced into the very complex tungsten and molybdenum compounds. Mr Craxton has begun the study of these crystals with X-rays.

I have suggested a structure for the rare-earth sesquioxides in place of Zachariasen's improbable one. A copy of the manuscript is included. It is interesting that on starting out with octohedra deformation led to 7-cornered polyhedra.

It is impossible to predict the slope of the coordinated polyhedrom about large cations; and even their coordination number is uncertain. Your mention of diopside has served to excite my curiosity immensely - I'd like very much to know what the structure is like. I have no doubt that there are strings of si tehahedra (possibly in the direction) or perhaps rings as in beryl. I'd like to know too whether Taylor's structure for rillimanite and mullite agrees with my predictions in regard to the amount of sharing, and whether he has found another structure for cyassite. My vacation and my book on line spectra have prevented me from doing as much work as I'd like recently.

Sincerely,
Linus Pauling

Linus Pauling Attempts

July 15, 1929

Professor W. L. BRAGG,
Physical Laboratory,
University of Manchester,
Manchester, England.

Dear Professor Bragg:

I was decided definitely to stay in Pasadena now, although I am very much interested in the possibility of going to Harvard. But staying here means that I shall lose the opportunity of coming to Manchester for a few months. In the last few days early in March, 1929. It will still be necessary for me to spend a week in Berkeley next I have a discussion with the University of California regarding that I give lectures in chemistry and physics for a week every year. Some or such series in Manchester would about the end of April. I suppose you close up sometime in July, or perhaps June. I would like to stay in Berkeley as long as work is going on, and then spend a couple of weeks on the coast, then I plan to visit old friends - Connerly, Davis, Debye, etc. - and to meet some people whom I have never seen, such as Huggins.

An optical apparatus could be wanted for me. I should like to see your apparatus and perhaps help in making some improvements possibly I shall have a crystal now which I should like some quantitative data. But most of all I want to talk with you and the rest in your laboratory.

I thank you very much for the manuscript you sent me. Your general description of your method is very interesting, and the work itself very valuable. I was also very much interested in your X-ray crystallography, with the description of all kinds of structures. The quality structure shows me, satisfying the electrostatic model rule is well as it does. HILSHUTE

August 1929

continued investigations. HILSHUTE is working along with HILSHUTE, Pauling, which has a structure already related to the one which is mentioned in the HILSHUTE paper as well as the structure of benzene.

My wife and boy are looking forward to seeing you in Manchester, and join me in sending greetings to you and Mrs. Bragg.

Yours sincerely,
LINUS PAULING

Letter from Linus Pauling to W.L. Bragg. July 15, 1929.

Linus Pauling Attempts

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Professor W.L. Bragg,
Physical Laboratory,
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Dear Professor Bragg:

I have decided definitely to stay in Pasadena now, although I was very much interested in the possibility of going to Harvard. But staying here means that I shall have the opportunity of coming to Manchester for a few months. We can leave Pasadena early in March, 1939. It will still be necessary for me to spend a month in Berkeley then; I have a connection with the University of California requiring that I give lectures in chemistry and physics for a month every year. Hence we can't arrive in Manchester until about the end of April. I suppose you close up sometime in July, or perhaps June. I would like to stay in Manchester as long as work is going on, and then spend a couple of months on the Continent; I plan to visit old friends - Sommerfeld, Ewald, Debye, Mark - and to meet some people whom I have never seen, such as Niggli.

No special apparatus would be needed for me. I should like to see your apparatus and perhaps help in making some measurements; possibly I shall have a crystal from which I should like some quantitative data. But most of all I want to talk with you and the men in your laboratory.

I thank you very much for the manuscript you sent me. Your general description of your method is very interesting, and the work itself very valuable. I was also very much interested in your Faraday Society address, with its description of silicate structures. The cyanite structure pleases me, satisfying the electrostatic valence rule so well as it does. Sillimanite

Bragg-2 7-1 5-29

and andalusite as worked out by Taylor seem alright too. The electrostatic valence rule isn't rigorous, and could perhaps be restated in the following way: In a crystal containing anions in an approximately close-packed arrangement $\sum Si$ should be equal to S for every anion (or very nearly equal to S); if the anions are not close-packed, those having fewer than 12 anion-contacts should have $\sum Si$ less than S , the others having $\sum Si$ greater than S .

I am pleased too with Naray-Szabo's staurolite structure, which also satisfies the rule. You may be interested in a method of distinguishing between $(OH)^\infty$ and $(OHO)^3$ groups in crystals containing O and H. If for every H there is one I in the crystal with $\sum s=1$, the existence of hydroxyl ion is indicated; but if for every H there are two O's with $\sum s=3/2$, we may accept this as showing that the two O's are joined by a hydrogen bond, as are the two F's in the acid fluoride ion, FHF^∞ . Examples of the first class, with OH^∞ , are topaz and the members of the chondrodite series; of the second, with OHO^3 , staurolite and diaspore, $AlHO_2$, göthite, $FeHO_2$, manzanite, $MnHO_2$, whose structure Mr. Ewing and I have just worked out. Now we can see that a necessary condition for the isomorphous replacement of OH^∞ by F^∞ in a crystal is that the crystal belongs to the first class, and as a matter of fact the mineralogists report this replacement in topaz and chondrodite, etc., but not in staurolite and diaspore, etc.

I met Warren in Boston, and enjoyed talking with him. I'm hoping that after his year with you he will come to Pasadena.

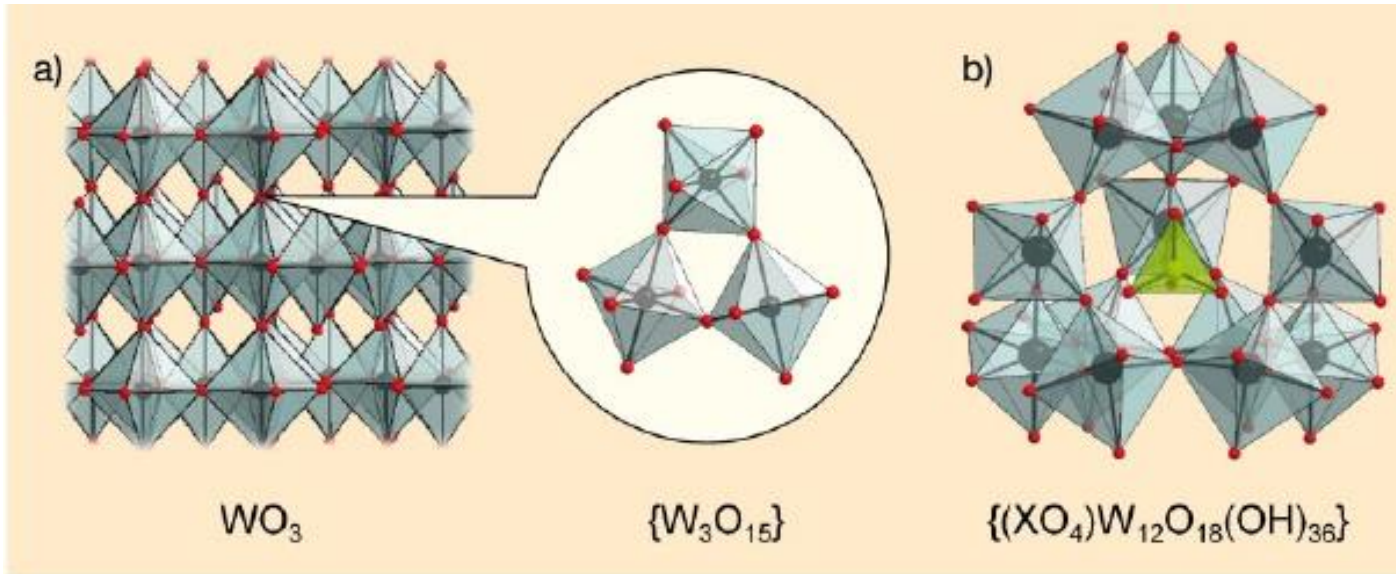
We have been working away at several oxides and hope to have several new structures before long. We are making use of the same method as for brookite - to find a coordinated structure with the correct size of unit and space-group symmetry, to distort the polyhedra in order to predict parameter values as closely as possible, and then consider small changes in the parameters to get the best agreement between structure factors and visually

Bragg-3 7-15-29

estimated intensities. Sturdivant is getting along well with tantalite, Ta_2FeO_6 , which has a structure closely related to one which we mention in the brookite paper as not being the structure of brookite.

My wife and boy are looking forward to coming to Manchester, and join me in sending greetings to you and Mrs. Bragg.

Structural Model by Pauling (1929)



Linus Pauling

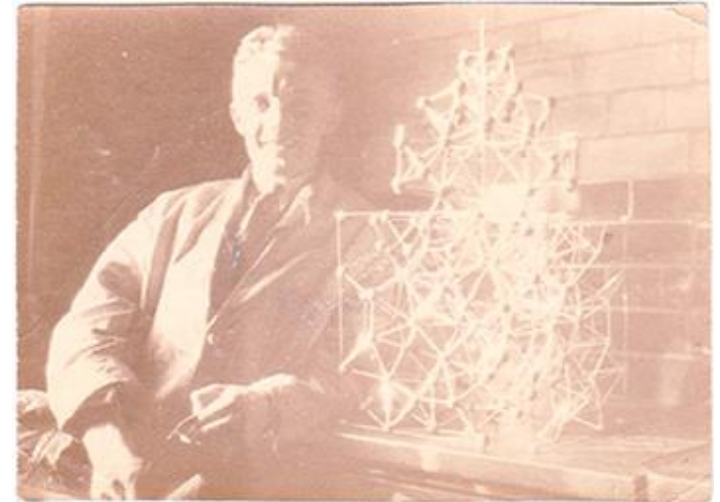
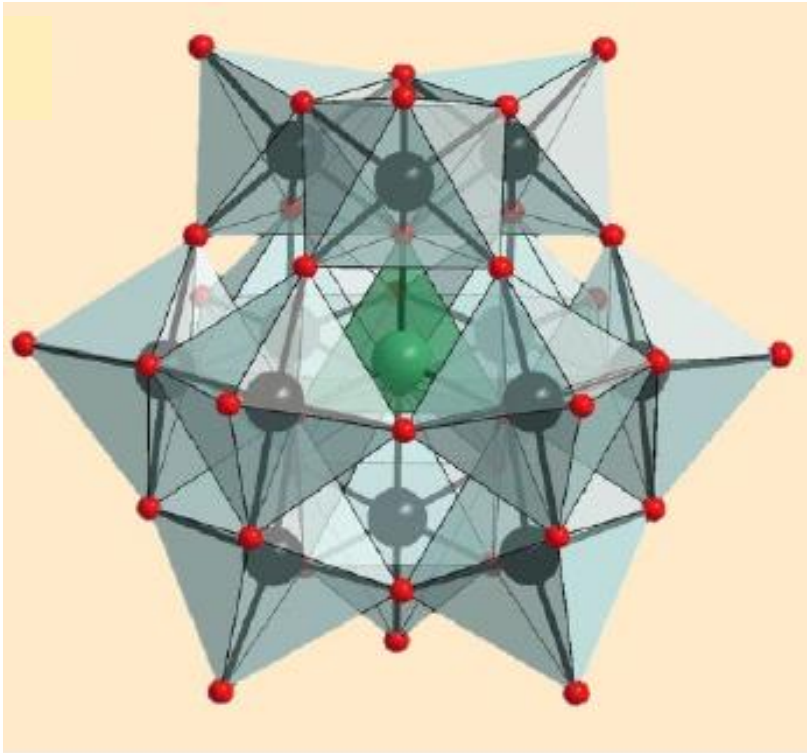
a) Tungsten(VI) oxide WO_3 and $\{W_3O_{15}\}$ -Unit.

b) 12-phosphotungstic acid Color code: W = black, O = red, XO_4 = green

L. Pauling, *J. Am. Chem. Soc.* 51, 2868–2880.

A. Kondinski and T. N. Parac-Vogt, *Front. Chem.*, 2018, 6, 34

Structural Model by Keggin (1933)



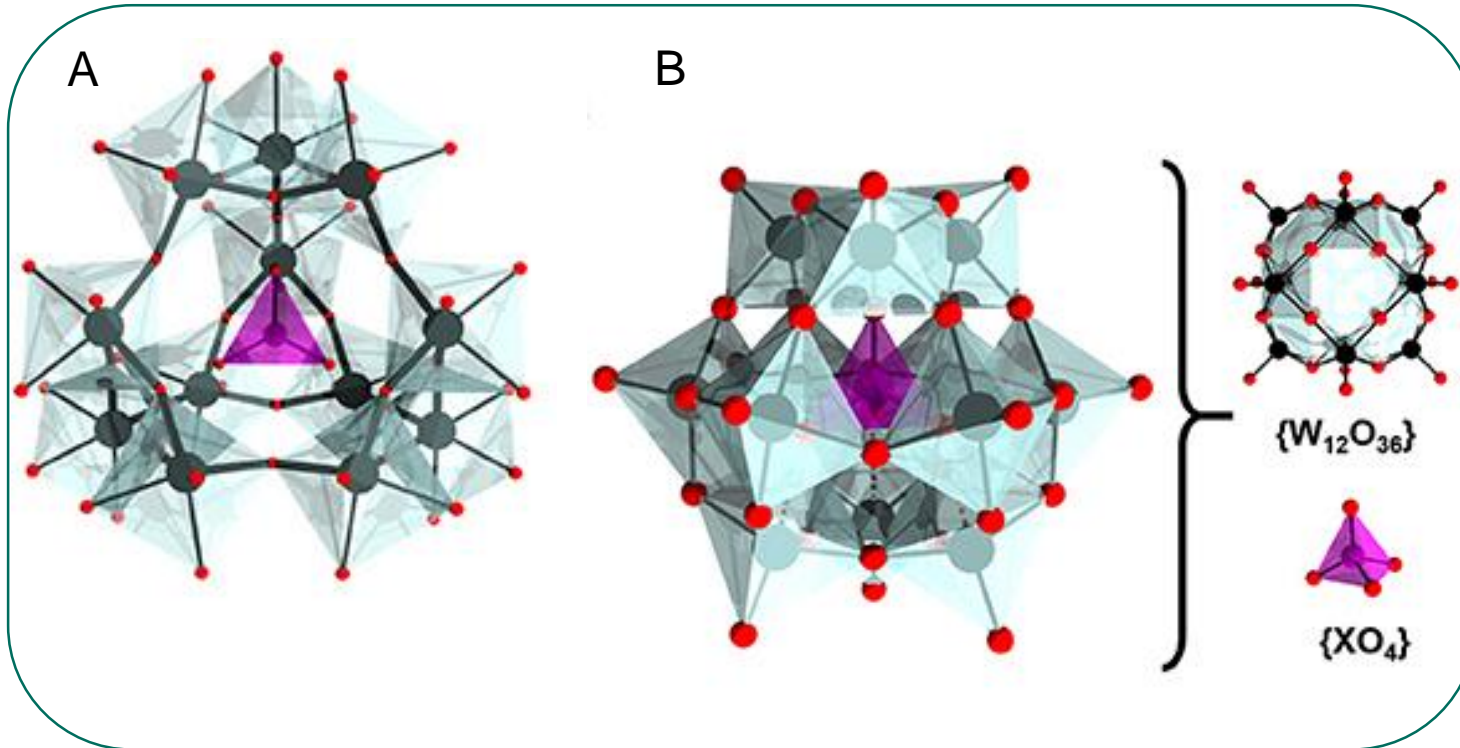
James Fargher Keggin

12-phosphotungstic acid $[PW_{12}O_{40}]^{3-}$
Color code: W = black, O = red, PO_4 = green

J. F. Keggin, *Nature* 1933, 131, 908–909.

A. Kondinski and T. N. Parac-Vogt, *Front. Chem.*, 2018, 6, 34

Comparison of Structural Models



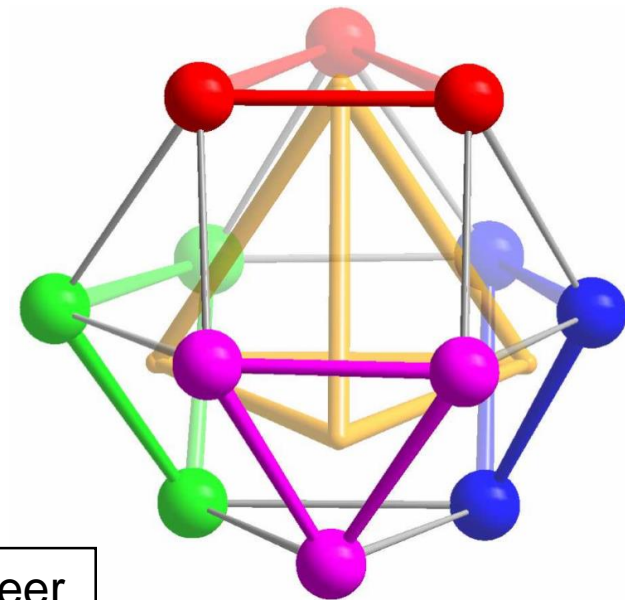
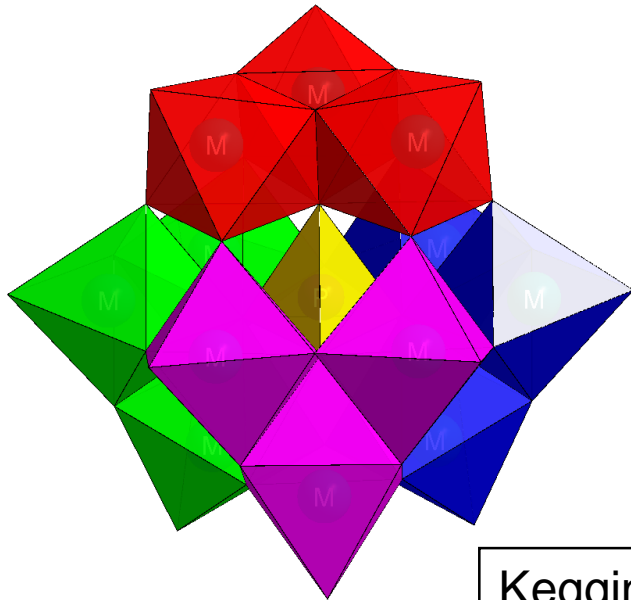
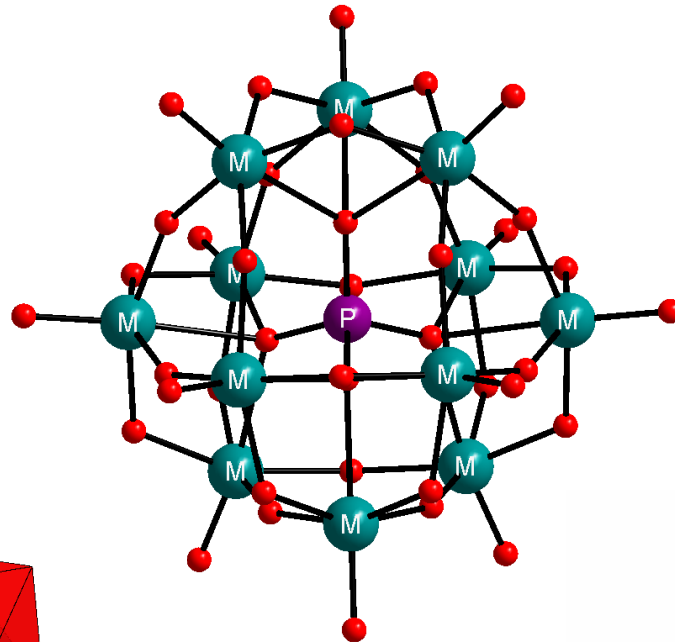
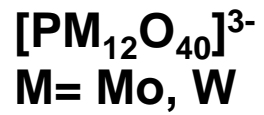
(Left) Linus Pauling
(Right) James Fargher Keggin

(A) Pauling's structural model $[(XO_4)W_{12}O_{18}(OH)_{36}]^{q-}$

(B) Keggin structure $\{(XO_4)@W_{12}O_{36}\}$

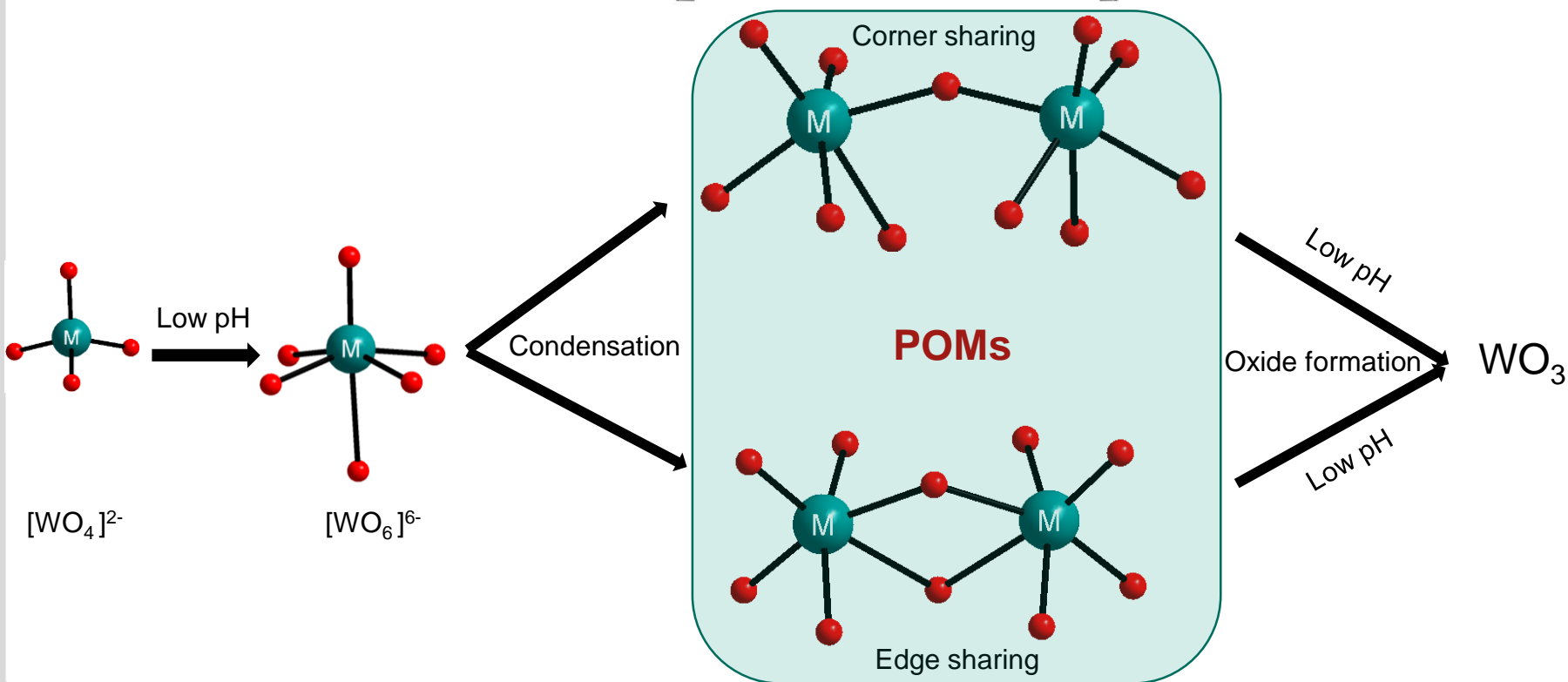
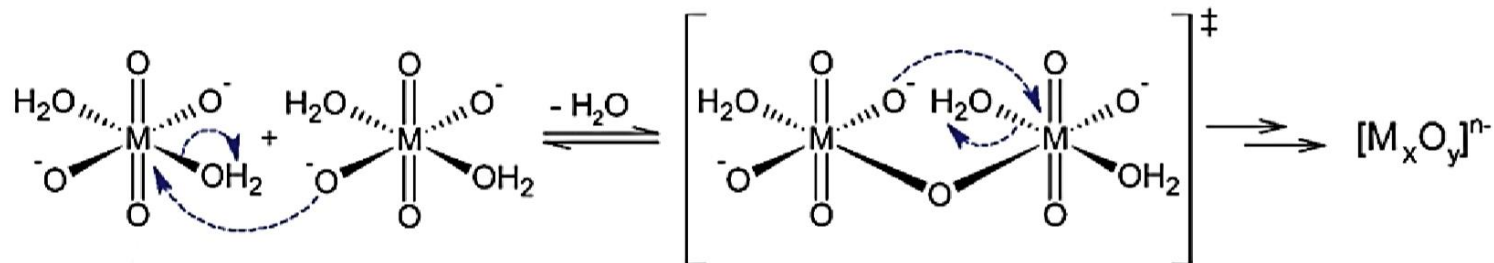
Color code: W = black, O = red, XO_4 = purple

Keggin Structure



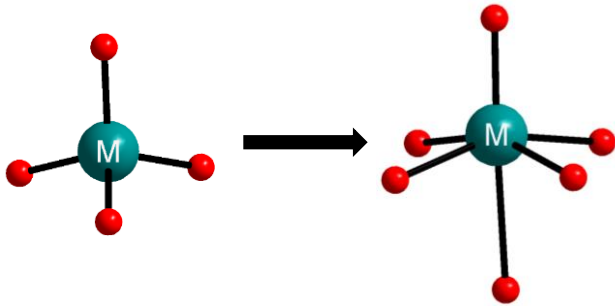
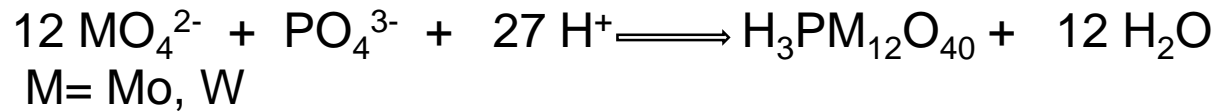
Keggin is the POM pioneer

Formation of POM Building Blocks and Self-Assembly

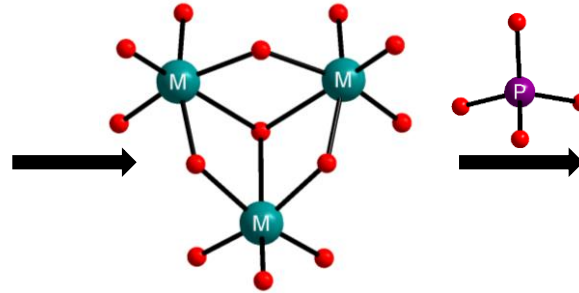


Formation of Keggin Cluster and Self-Assembly

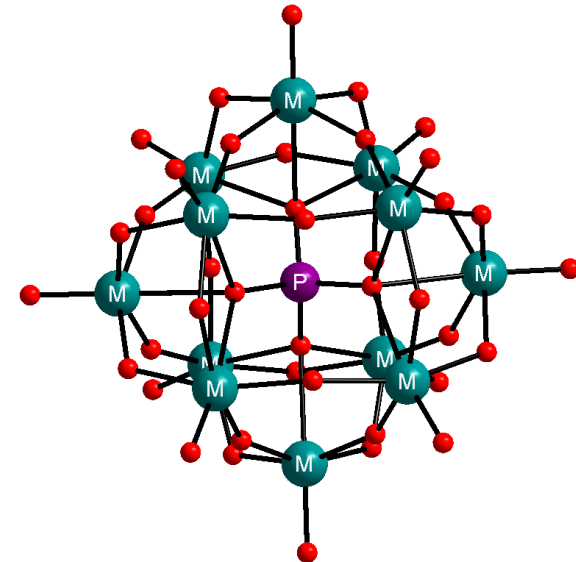
Keggin Structure: Foundation of modern supramolecular chemistry



Expansion of coordination shell

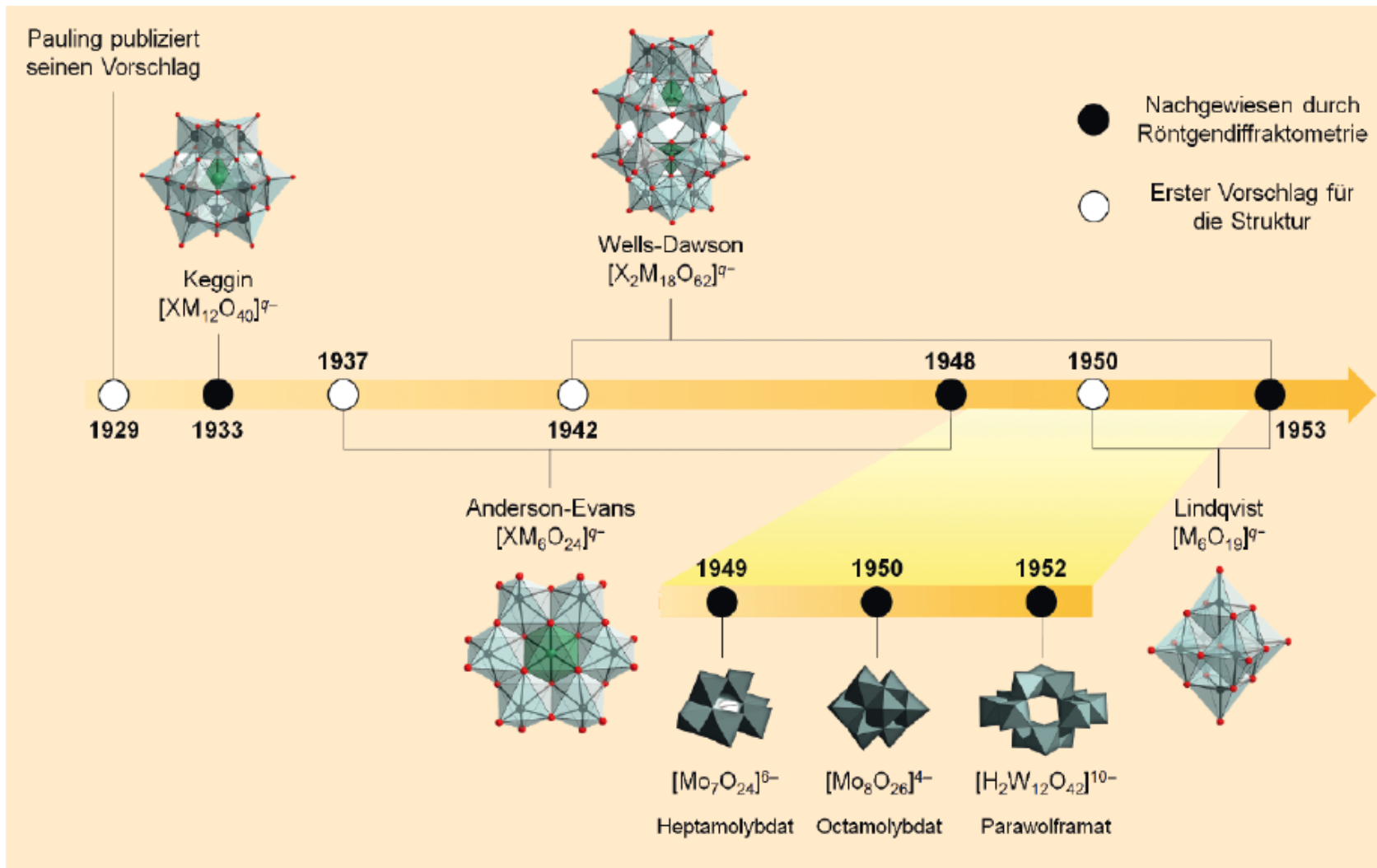


Triad assembly



Templated self-assembly

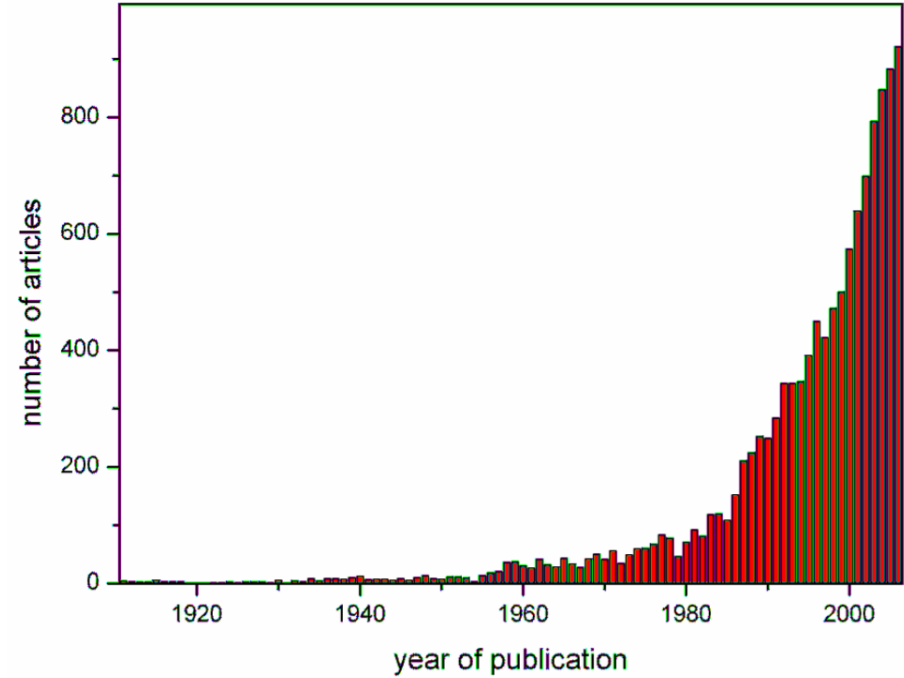
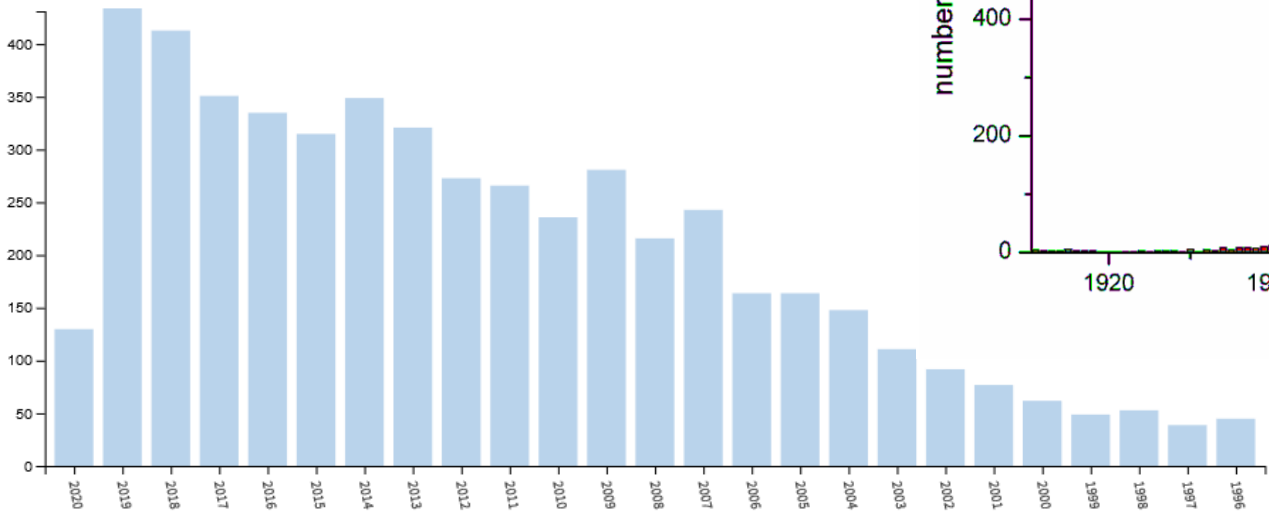
Development POM Chemistry



Number of Publications

Illustration of the exponential increase in the number of publications containing “polyoxometalate” as a keyword over the last century.

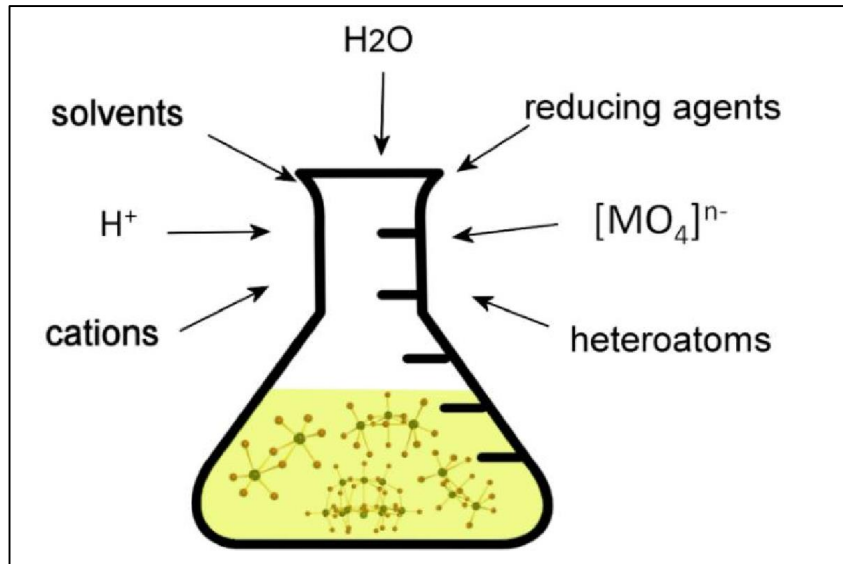
Data taken from SciFinder Scholar.



Number of publications containing “polyoxometalate” as a keyword over the last 25 years. Data taken from Web of Science.

Classic Synthetic Approaches

'One-pot' Synthesis



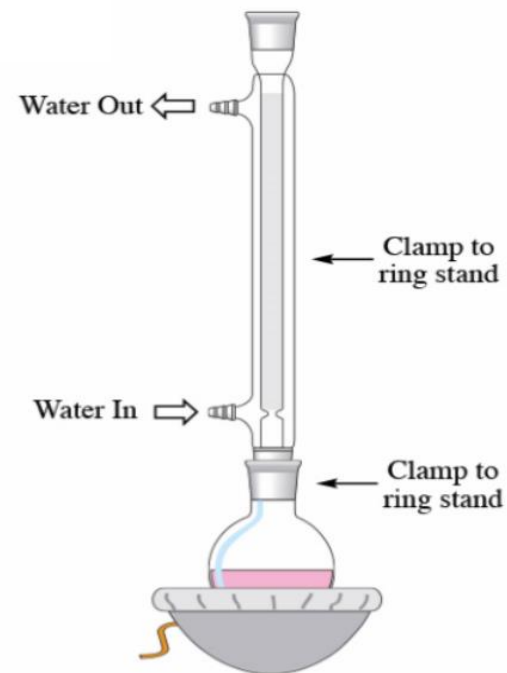
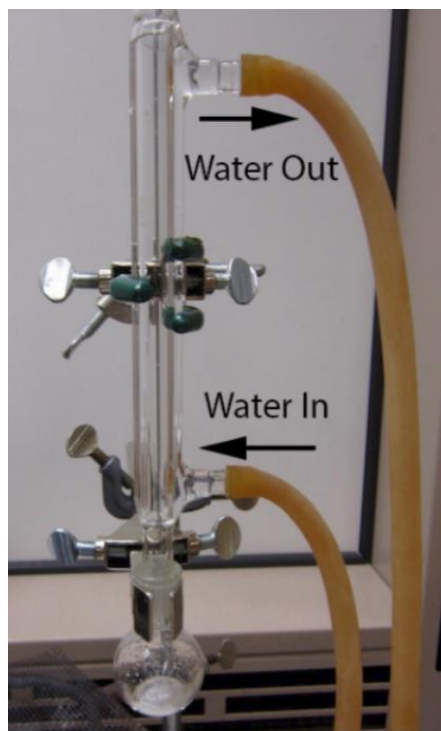
Factors that affect the synthesis/isolation of POMs

- pH
- ionic strength
- reaction time
- temperature
- counter cations
- concentration of starting materials

The one-pot may be carried out by various reaction operations such as, **microwave, hydrothermal/solvothermal or refluxing conditions.**

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'One-pot' Synthesis



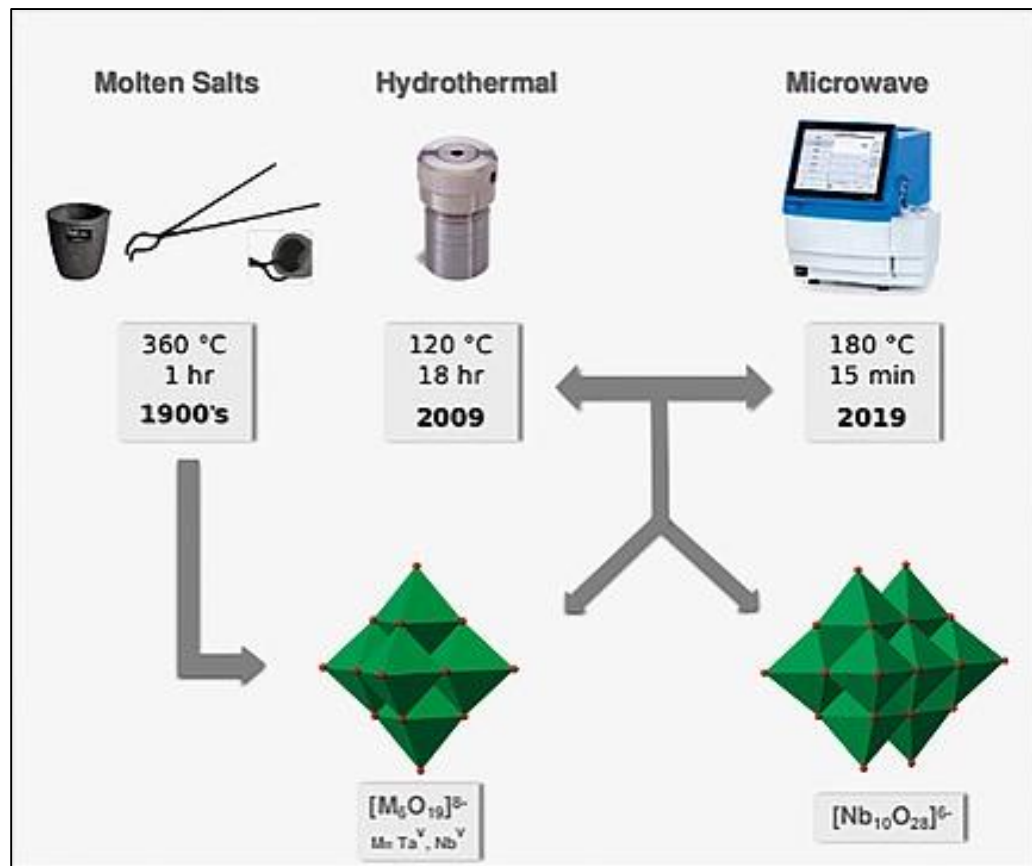
Hydrothermal/solvothermal synthesis

A general-purpose hydrothermal autoclave. The hydrothermal reactions occur inside the Teflon container.

The one-pot may be carried out by various reaction operations such as, **microwave, hydrothermal/solvothermal or refluxing conditions.**

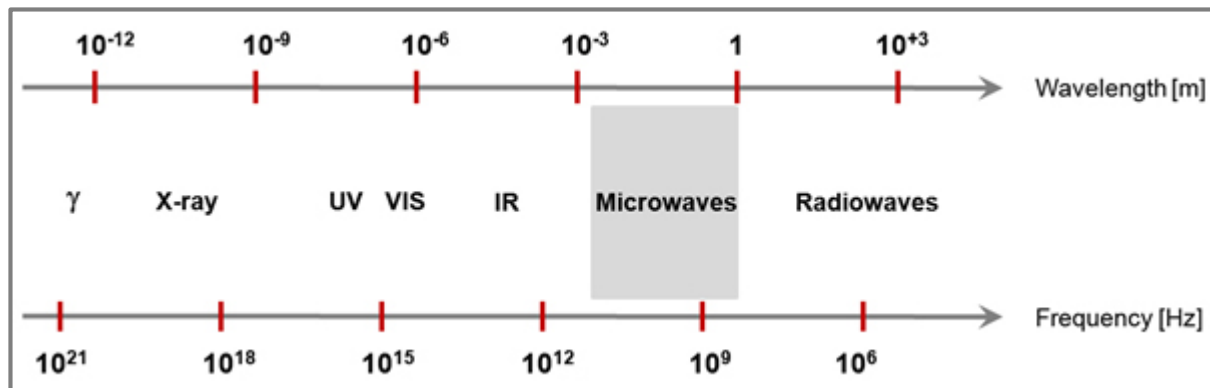
New Synthetic Approach: Microwave-Assisted Synthesis

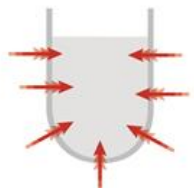

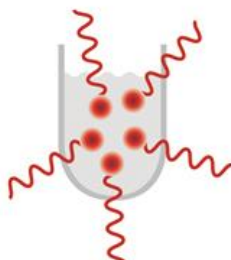

Discovery of new polyoxoniobates and -tantalates.



“Microwaves have the potential to become the bunsen burners of the 21st century”- Prof. C. Oliver Kappe, University of Graz, Austria.

New Synthetic Approach: Microwave-Assisted Synthesis



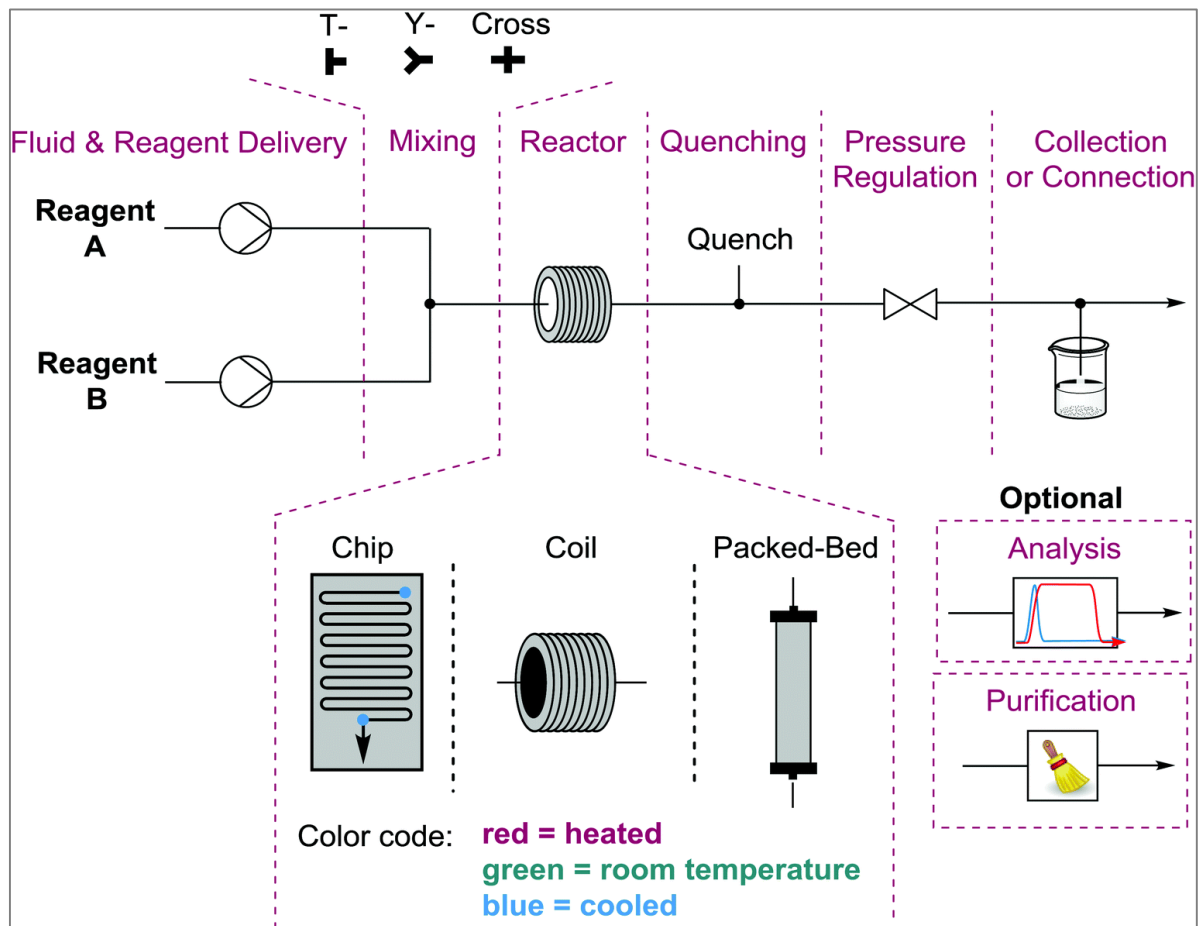
	Heat Source	Heat Introduction	Temperature Distribution
a	Conventional heating:		
b	Microwave heating:		

Frequency range 0.3 to 300 GHz, corresponding to wavelengths between 1 mm to 1 m.

All domestic “kitchen” microwave ovens/commercially available microwave reactors: **2.45 GHz/ wavelength of 12.25 cm**

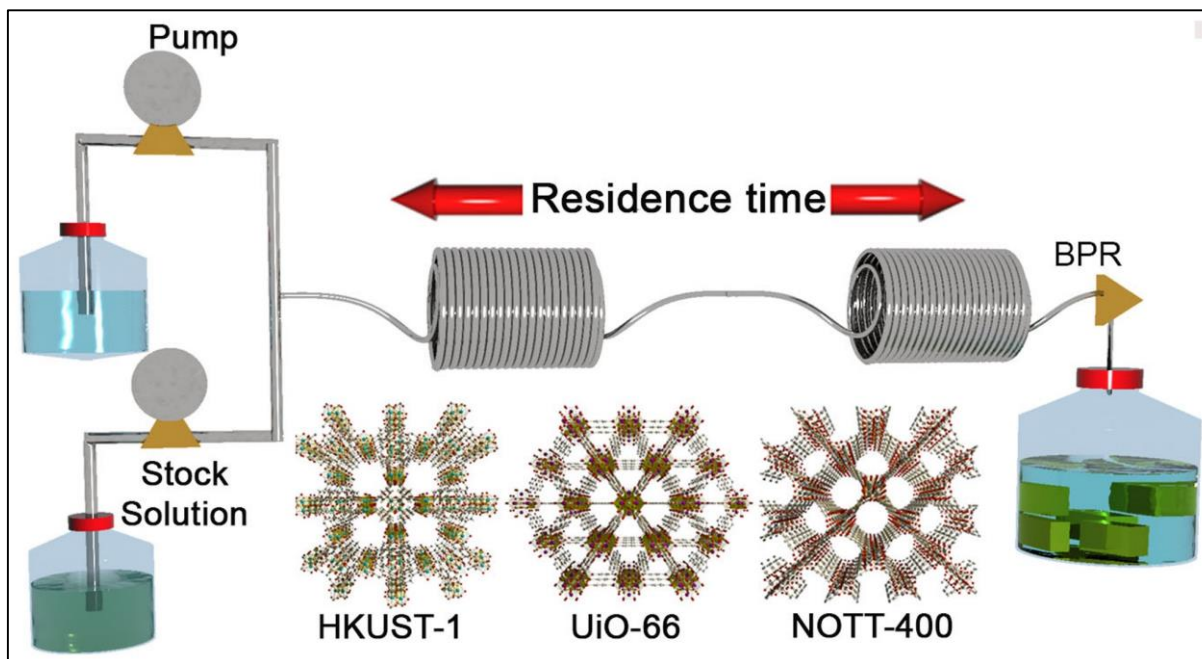
New Synthetic Approach: Flow Reactor System

Chem. Soc. Rev. 2020, 49, 8910-8932



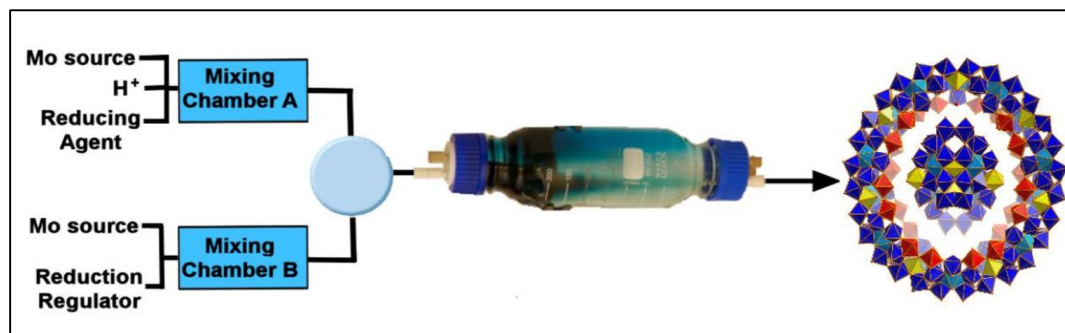
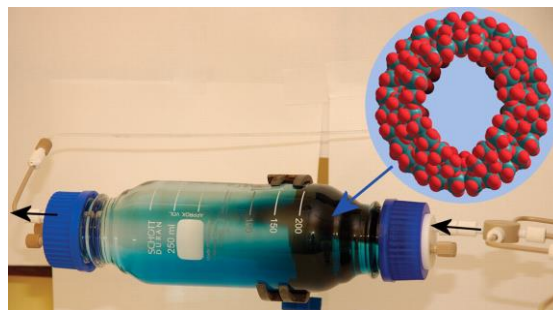
Breakdown of the basic components of a continuous flow system.

New Synthetic Approach: Flow Reactor System



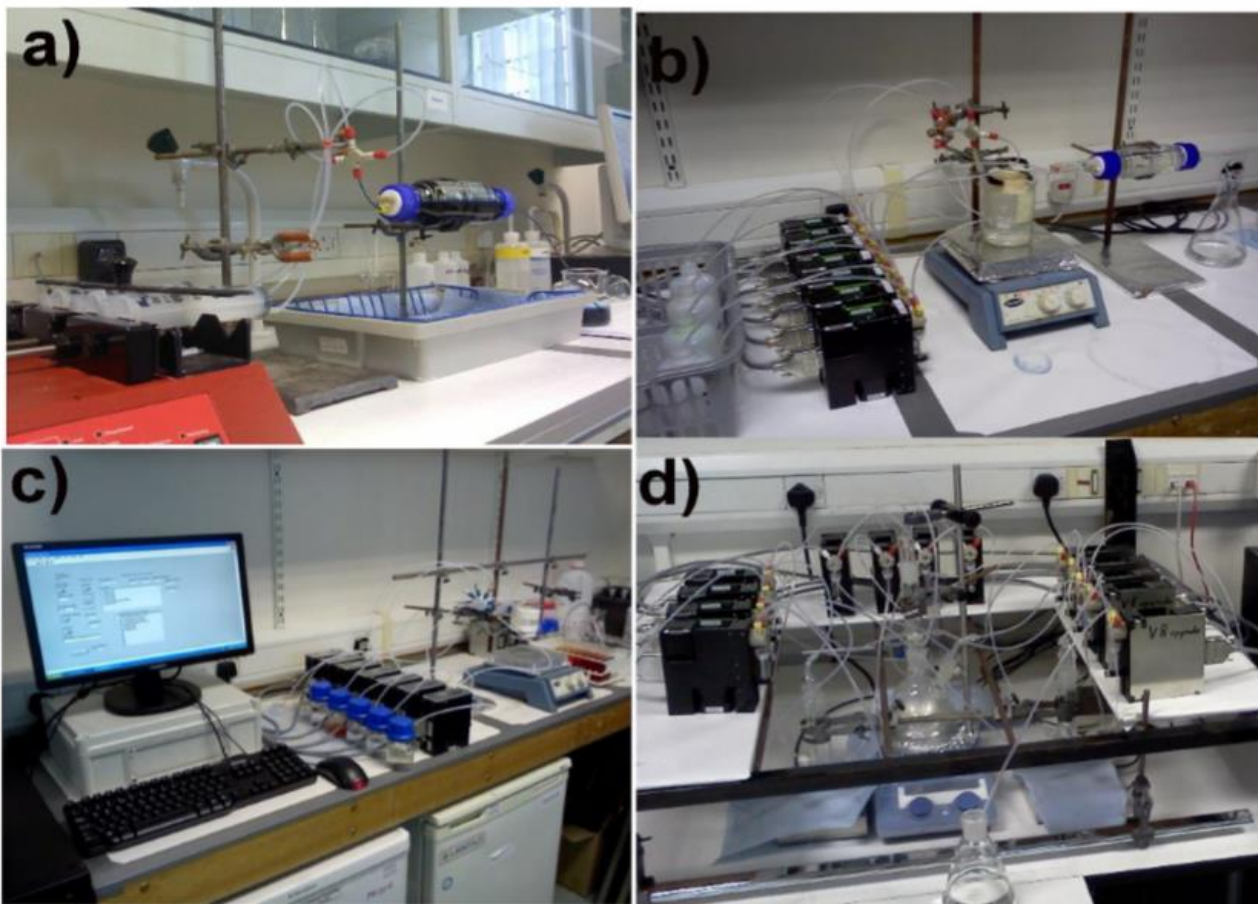
The precursor solutions are pumped continuously, mixed via a static-mixer (T-piece) and enter the coiled reactor tubes at temperature (T). A backpressure regulator (BPR) situated after the reactor coil is used to maintain a constant liquid pressure. The residence time can be varied by changing the length of the reactor or pumping rates.

New Synthetic Approach: Flow Reactor System



Representation of the flow system from which the blue reduction gradient formed within the vessel during the assembly of $\{\text{Mo}_{186}\}$.

New Synthetic Approach: Flow Reactor System



(a) One simple pump controls the flow rate of the whole system (b) Multiple electronic pumps control the individual flow rates of each starting materials (c) Computer control (d) Multi-batched networked flow system

H. N. Miras, G. J. T. Cooper, D.-L. Long, H. Bögge, A. Müller, C. Streb, L. Cronin, *Science*, 2010, 327, 72-74.

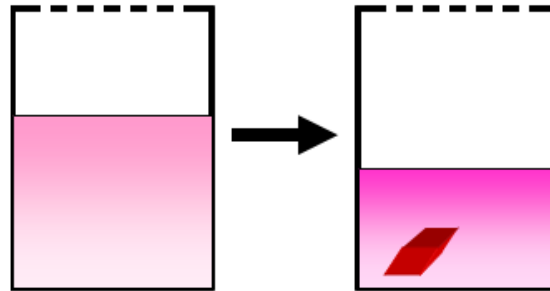
Growing Quality Crystals

Crystallization techniques

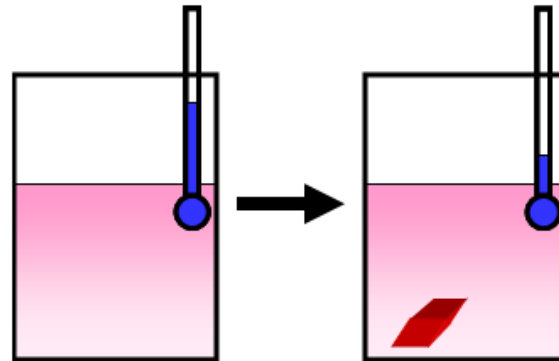
Diffraction quality crystals: 0.1 to 0.3 mm



- Slow Evaporation



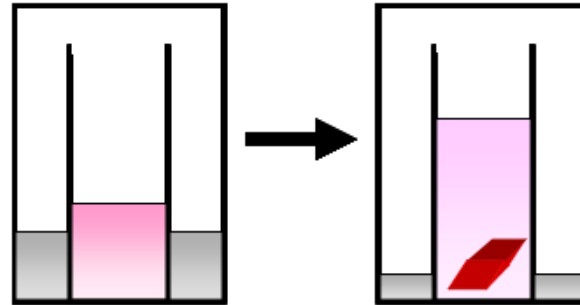
- Slow Cooling



<https://web.mit.edu/x-ray/crystallize.html>

Growing Quality Crystals

- Vapor Diffusion



- Liquid-Liquid Diffusion

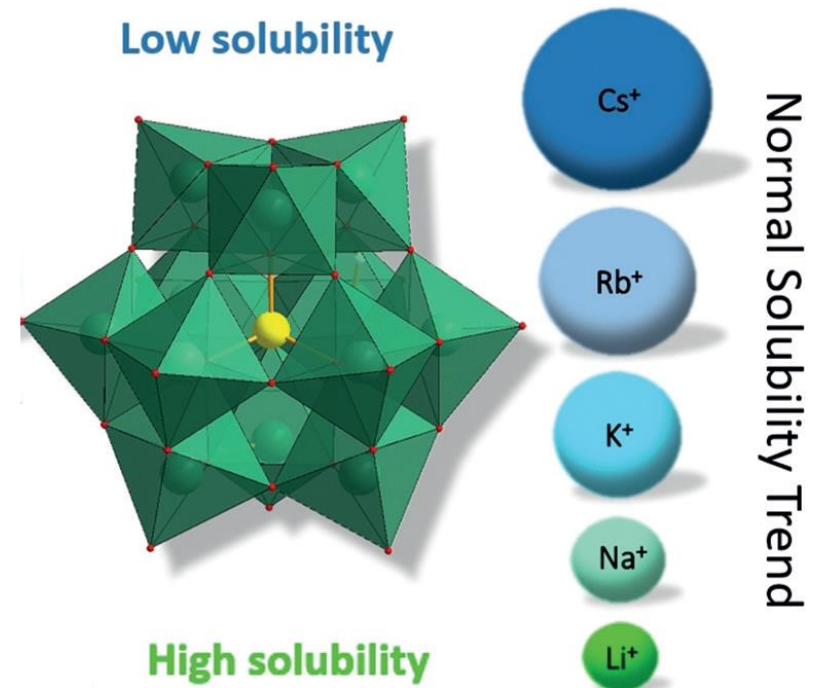


Growing Quality Crystals

- Use of Alkali Metal Cations (Aqueous System)

- Use of Organic Cations

Tetra butylammonium cation (TBA⁺)
 Dimethylammonium Cation (DMA⁺)



A. Misra, K. Kozma, C. Streb, M. Nyman, *Angew. Chem. Int. Ed.* 2020, 59, 596-612.