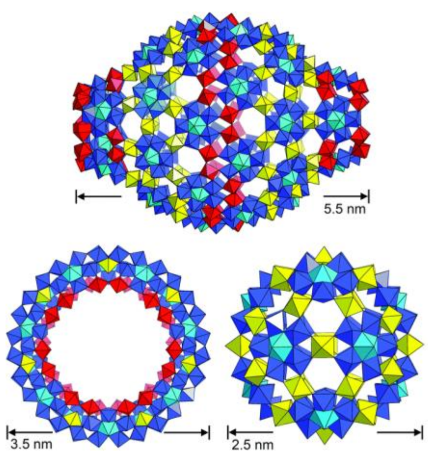
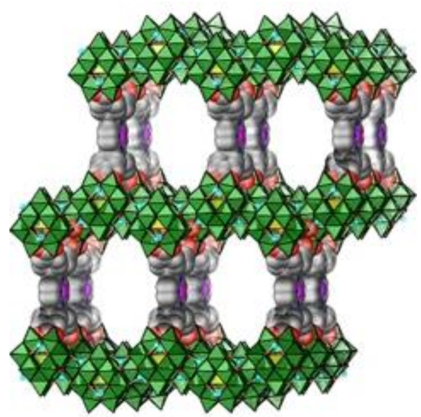
Karlsruhe Institute of Technology

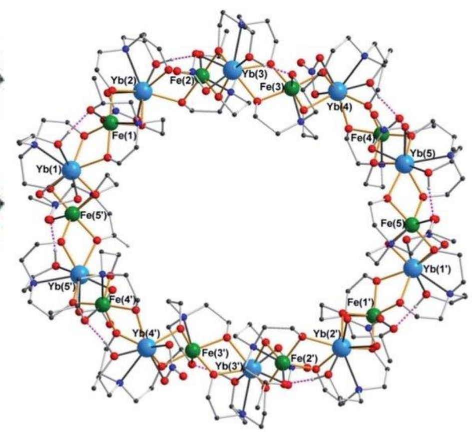
Advanced Functional Inorganic POMs, Coordination Clusters and Framework Materials

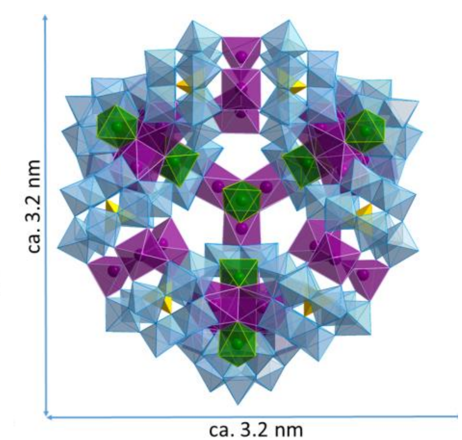
Dr. Masooma Ibrahim

Institute of Nanotechnology (INT)

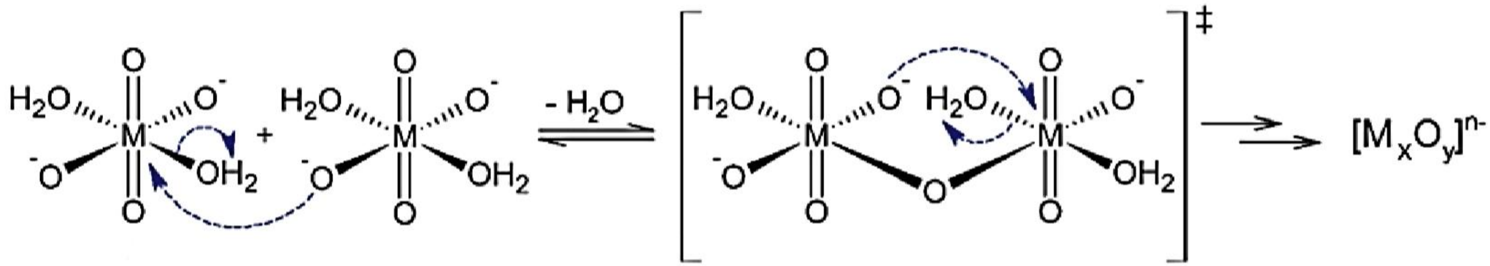


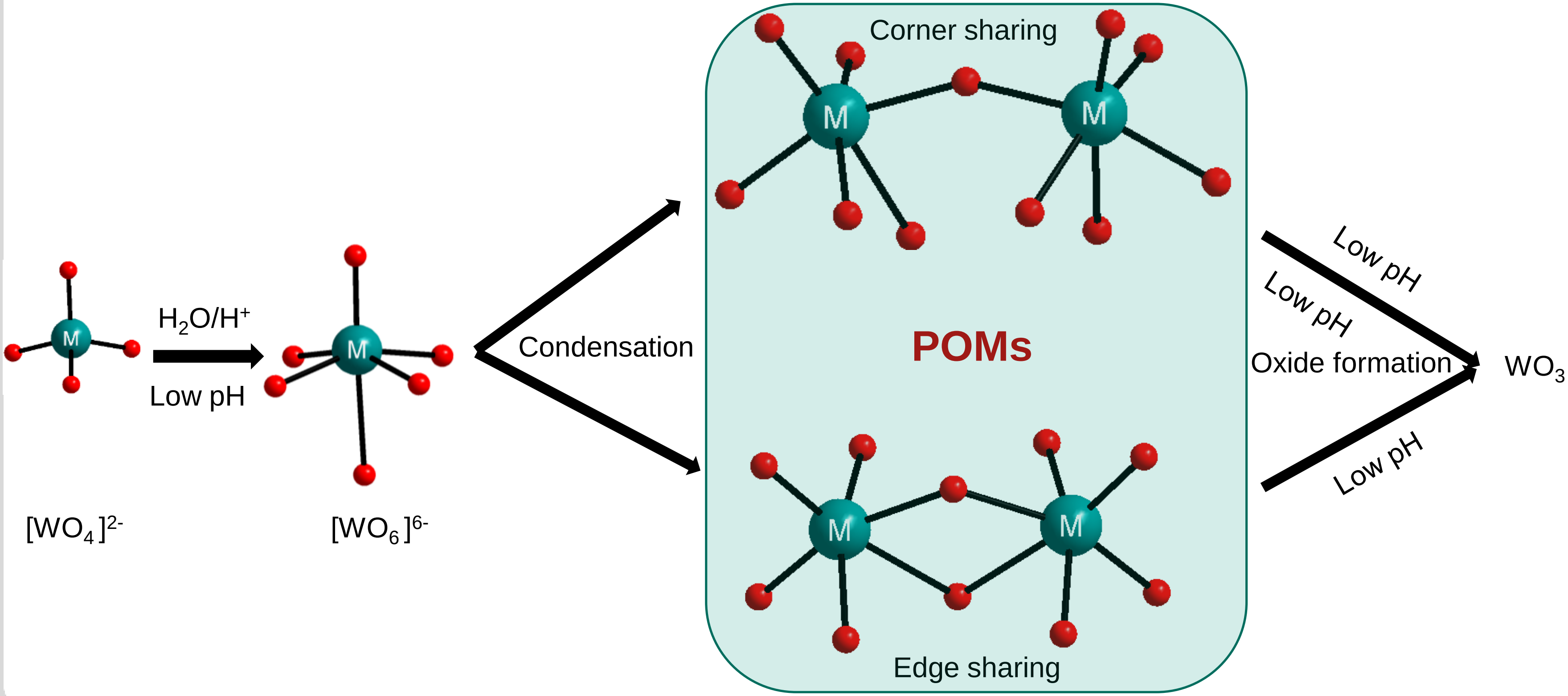






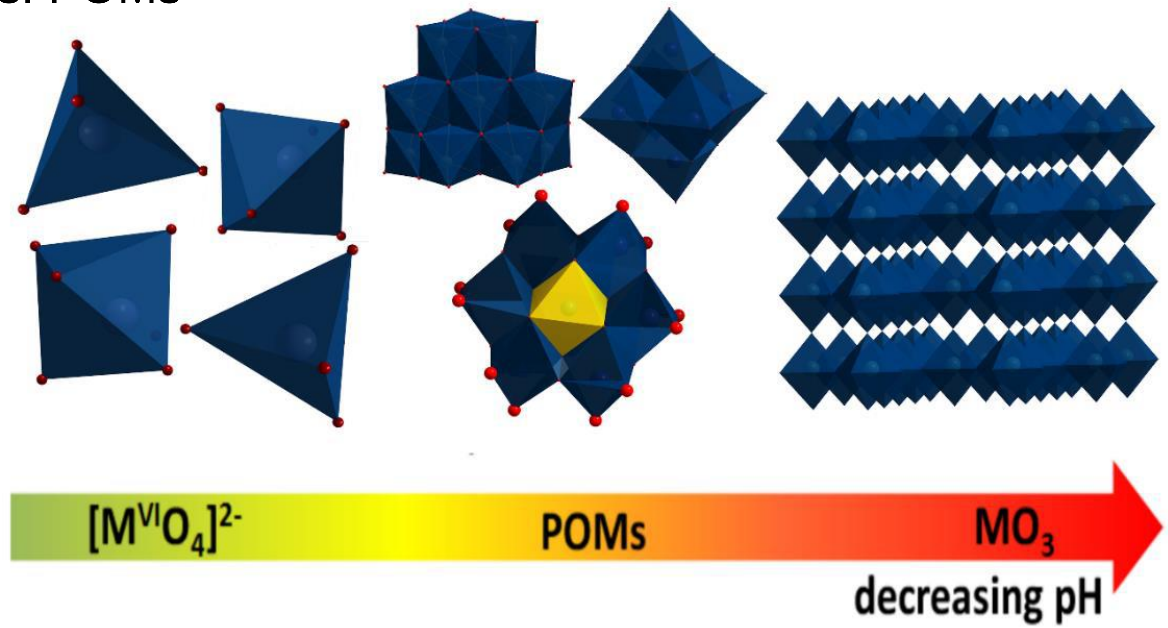
Why POM Species Exist?





Why POM Species Exist?

Potent factors for the formation of molecular metal oxide aggregates: POMs



Control of the pH is required in order to avoid the formation of infinite powder solid oxides (MO_3 lattices). Thus, POM clusters can be “trapped” between mononuclear metal ions and the infinite metal oxides

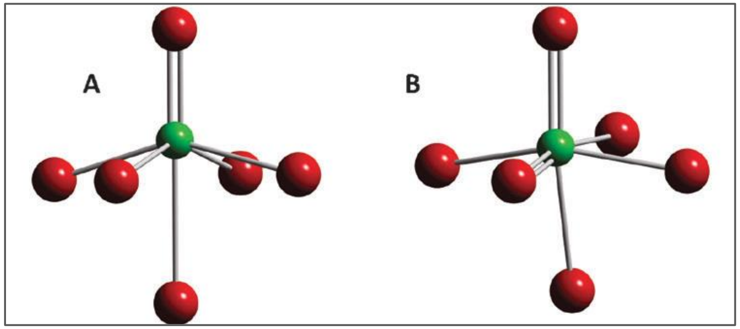
Dark teal polyhedra: $\{MO_4\}$ and $\{MO_6\}$, light yellow polyhedron: $\{XO_4\}$, red spheres: O.

Why POM Species Exist?

- The $V^{IV,V}/Mo^{V,VI}/W^{V,VI}$ metal centers: Highest two oxidation states

Empty d-orbitals: strong **metal oxide π-bonding** in addition to the coordinative bond formed between metal centre and oxygen ligand. Ligand orbital (px, py) and metal d-orbitals of similar symmetry (d_{xy}, d_{xy}, d_{yz}). **Terminal M=O** with decreased basicity (and nucleophilicity)

Limits the growth of the metal-oxide structures and results in the formation of **discrete clusters** rather than in infinite solid-state structures.



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

A. Müller, S. Roy, *Coord. Chem. Rev*. 2003, 245, 153

Why POM Species Exist? Potent Factors

- The ability to accept different numbers of oxygen ligands to form coordination polyhedra ranging from **tetrahedral [MO_4] to pentagonal bipyramidal [MO_7]** units.

↓

Diversity in V-, Mo-and W-based POMs:

Elements (oxidation state)	Coordination number	Ionic radius/Å
Mo(V)	4	0.46
	6	0.61
Mo(VI)	4	0.41
	5	0.50
	6	0.59
	7	0.73
W(V)	6	0.62
W(VI)	4	0.42
	5	0.51
	6	0.60
V(IV)	5	0.53
	6	0.58
V(V)	4	0.35
	5	0.46
	6	0.54
Cr(V)	4	0.34
	6	0.49 (E)
Cr(VI)	4	0.26
	6	0.44 (C)
Ta(V)	6	0.64
Nb(V)	6	0.64
Al(III)	4	0.39
	5	0.48
	6	0.53

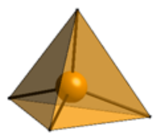
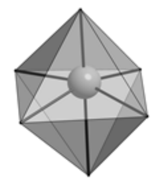
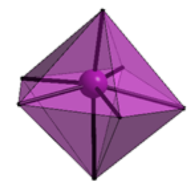
In contrast, elements such as Cr, Ta and Nb do not exhibit this versatile coordination geometry and consequently are limited in the number of polyoxoanions they are able to form.

E = Estimated
C = Calculated

R. D. Shannon, *Acta Cryst*. Section A 1976, 32, 751-767

Why POM Species Exist? Potent Factors

Karlsruhe Institute of Technology

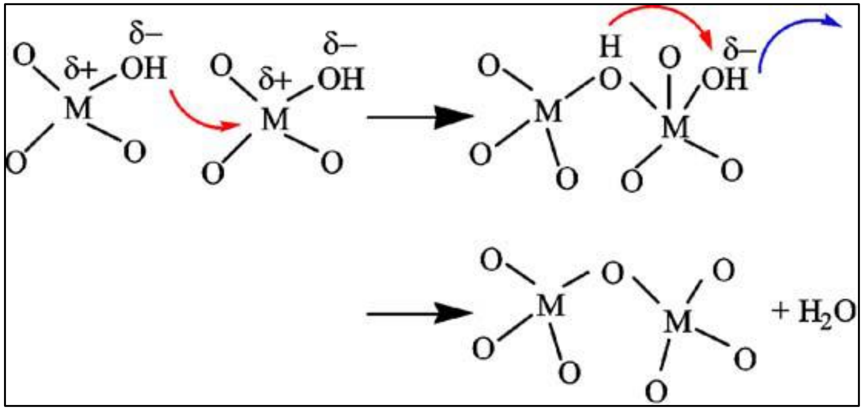
Coordination number (CN)	**4**	**5**	**6**	**7**
Polyhedron	Tetrahedron 	Square pyramid 	Octahedron 	Pentagonal bipyramid 
Found in	Metavanadates	Polyvanadates	Majority of POMs	Mo-blues

Why POM Species Exist? Potent Factors

$$2\,[CrO_4]^{2-} + 2\,H^+ \rightleftharpoons [Cr_2O_7]^{2-} + H_2O$$

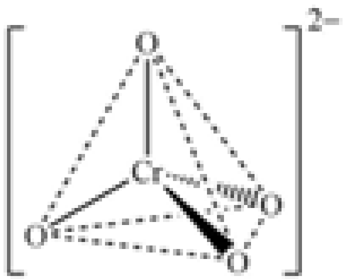
Oxolation mechanism

Oxo-bridge formation via two step

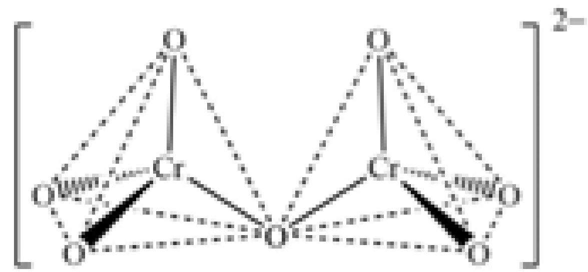


Why POM Species Exist? Potent Factors

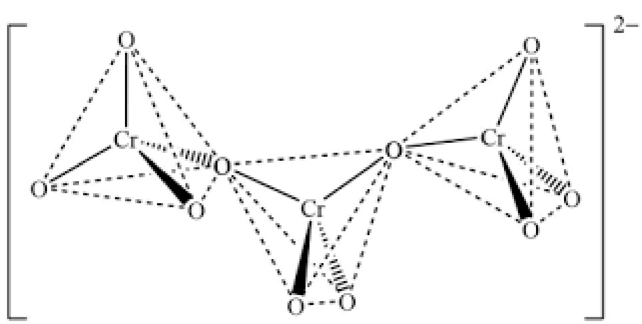
$$2\,[CrO_4]^{2-} + 2\,H^+ \rightleftharpoons [Cr_2O_7]^{2-} + H_2O$$



$[CrO_4]^{2-}$

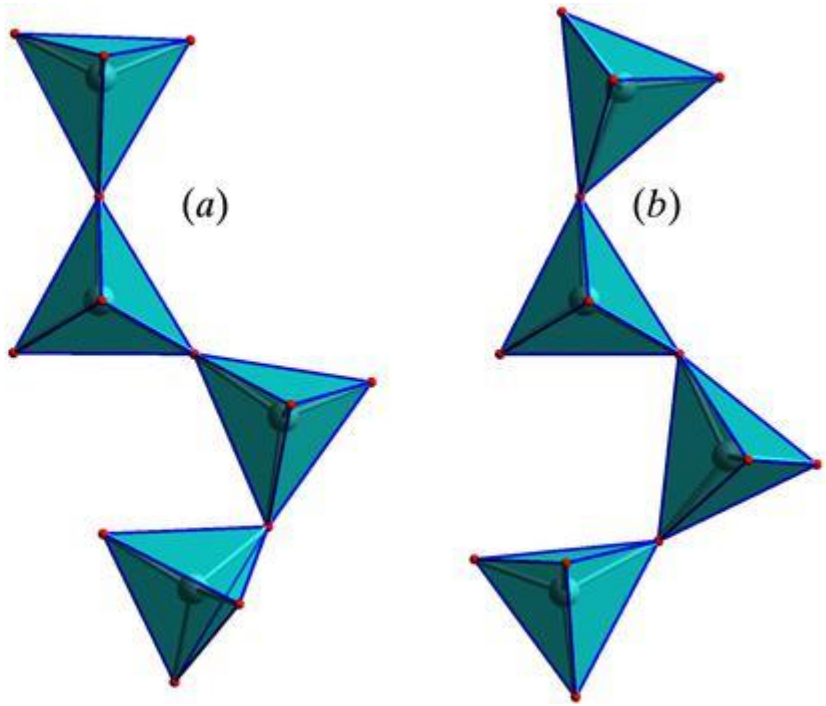


$[Cr_2O_7]^{2-}$



$[Cr_3O_{10}]^{2-}$

Why POM Species Exist? Potent Factors



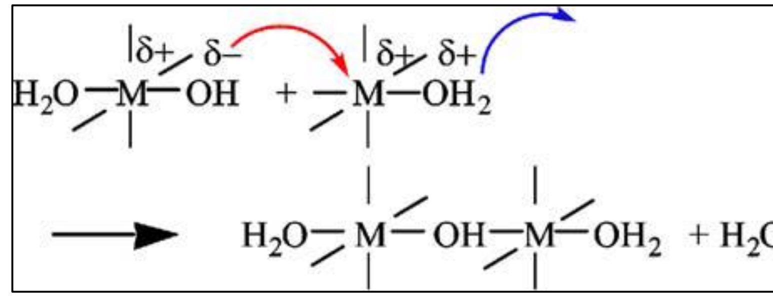
The configuration of $[Cr_4O_{13}]^{2-}$ chains in (*a*) $K_2Cr_4O_{13}$, (*b*) $Cs_2Cr_4O_{13}$

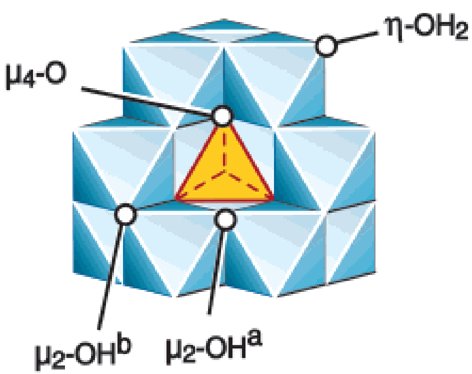
B.M. Casari, V. Langer, *Acta Crystallogr C*. 2005, 61,117-119.

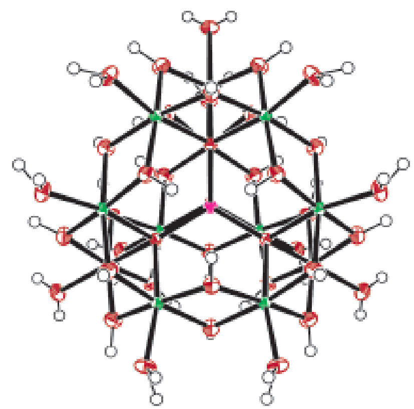
Why POM Species Exist? Potent Factors

Keggin-type aluminum polyoxocation

Olation mechanism
Hydroxo-bridge formation via a single step





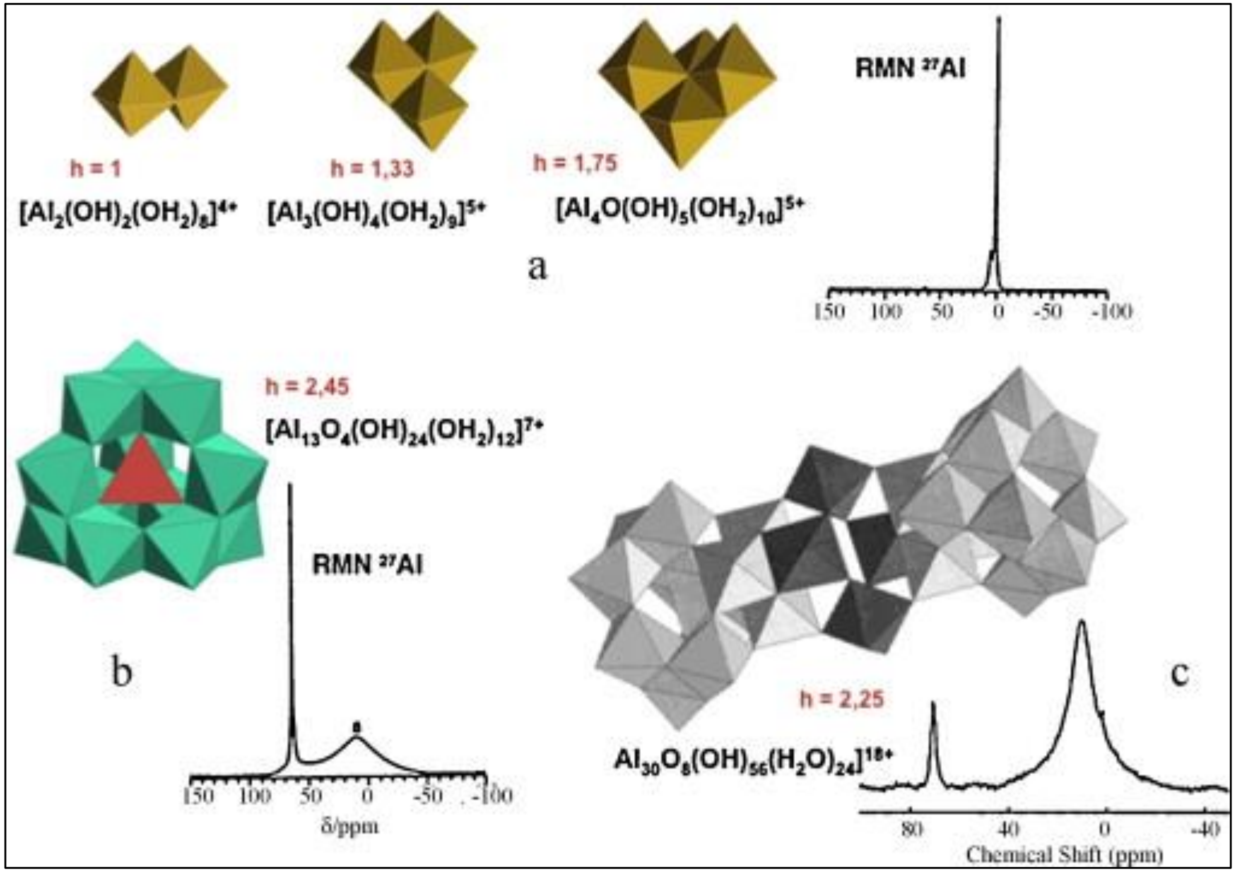


$[MO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$

J.P. Jolivet, C. Chaneac, D. Chiche, S. Cassaignon, O. Durupthy, J. Hernandez, *Comptes Rendus Geosciences*, 2011, 343, 113-122

Why POM Species Exist? Potent Factors

Keggin-type aluminum polyoxocation



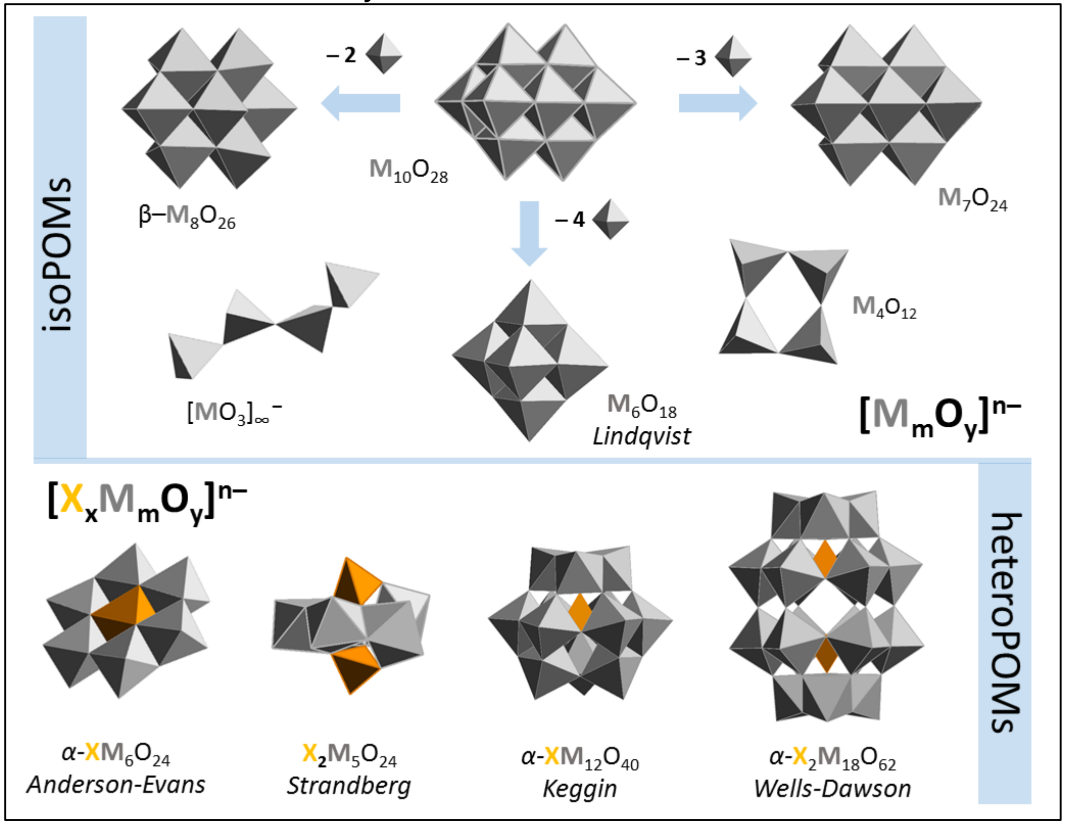
J.P. Jolivet, C. Chaneac, D. Chiche, S. Cassaignon, O. Durupthy, J. Hernandez, *Comptes Rendus Geosciences*, 2011, 343, 113-122

Classification of Polyoxometalates

1. **Isopolyoxometalates (isoPOMs)**
2. **Heteropolyoxometalates (heteroPOMs)**

General formula: $[M_mO_y]^{q-}$

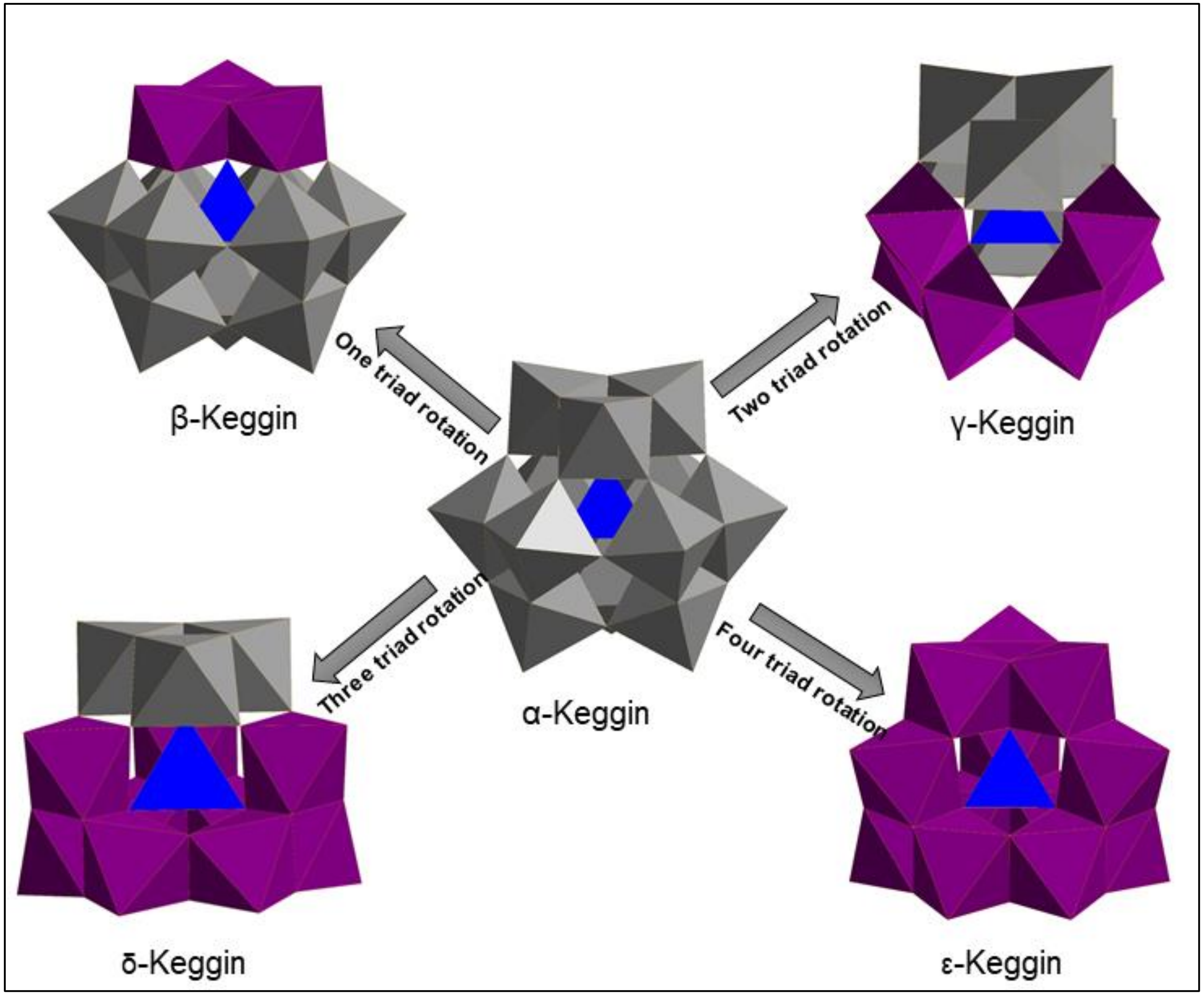
General formula: $[X_xM_mO_y]^{q-}$



(M = W, Mo ; X = Si^{IV}, Ge^{IV}, P^{V})

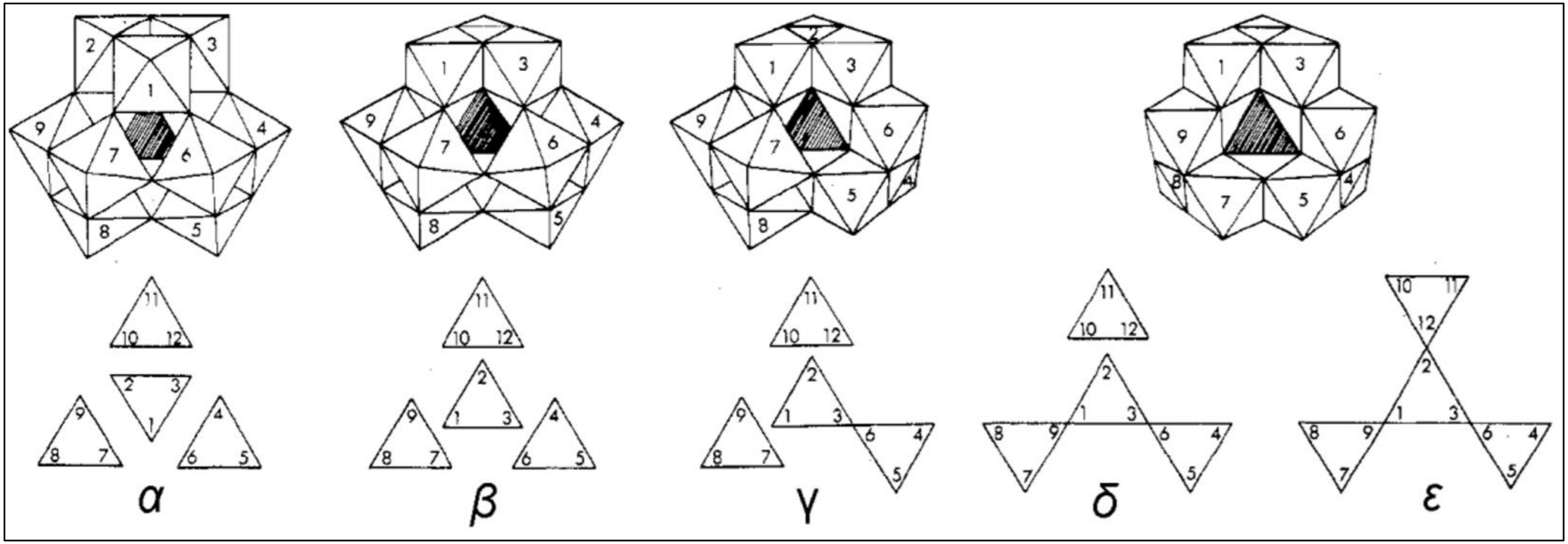
Caballero, Jagoba Martín. “Hybrid polyoxometalates: synthesis, crystal structures, thermostructural behavior and anchoring to tailored polymeric surfaces.” (2017)

Structural Isomers of Keggin Ion



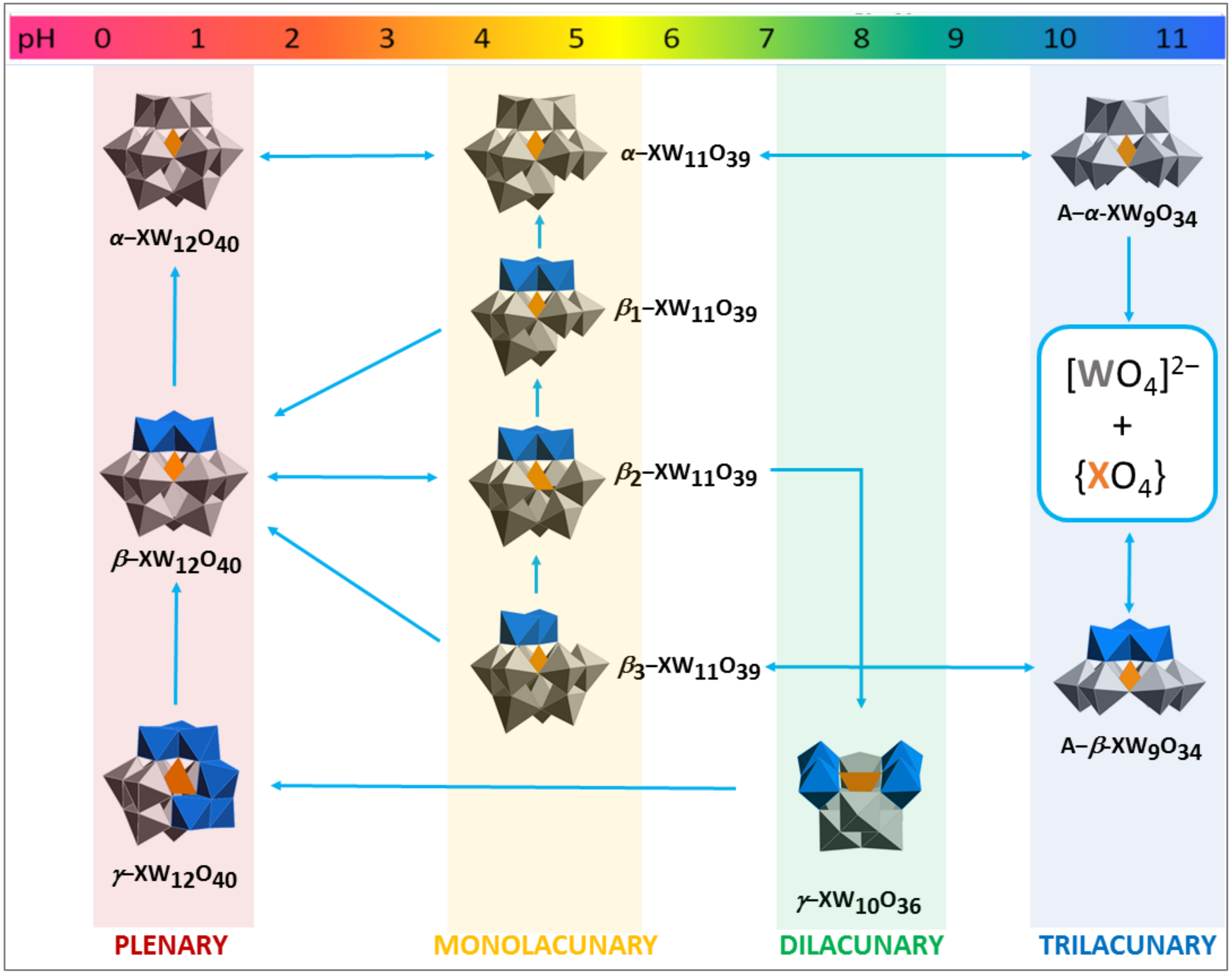
L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc*., 1970, 92, 3794-3797

Isomerization: Structural Isomers of Keggin ion



L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, 1970, 92, 3794-3797

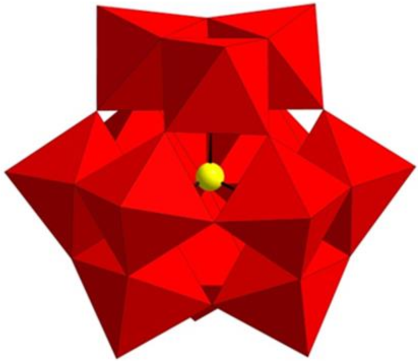
Formation of Ligands: Lacunary POMs



Caballero, Jagoba Martín. “Hybrid polyoxometalates: synthesis, crystal structures, thermostructural behavior and anchoring to tailored polymeric surfaces.” (2017)

Formation of Ligands: Lacunary POMs

A-Type and *B*-Type Keggin

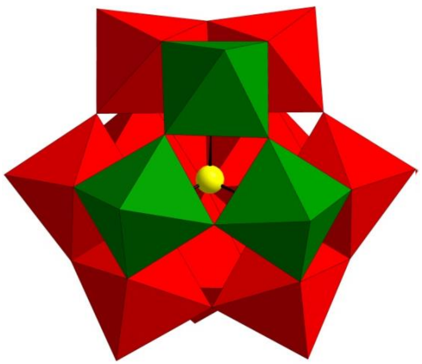


$[(XO_4)M_{12}O_{36}]^{n-}$

A. Tézé, A.G. Hervé, *Inorganic Syntheses* ***1990, Vol. 27.***

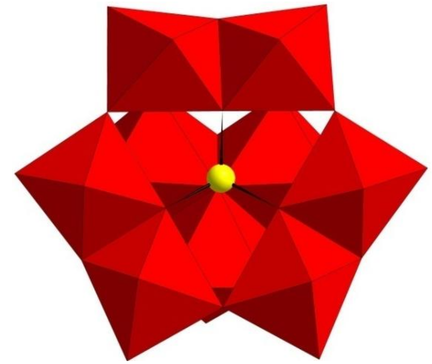
Formation of Ligands: Lacunary POMs

A-Type and *B*-Type Keggin



$[(XO_4)M_{12}O_{36}]^{n-}$

Loss of corner shared octahedra

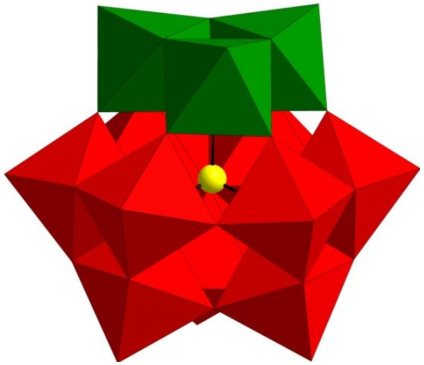


***A*-type trilacunary polyanion**
(6 oxo ligand)

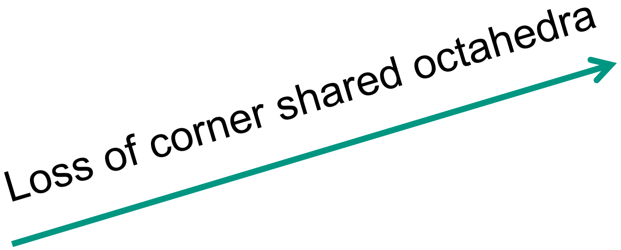
A. Tézé, A.G. Hervé, *Inorganic Syntheses* ***1990, Vol. 27.***

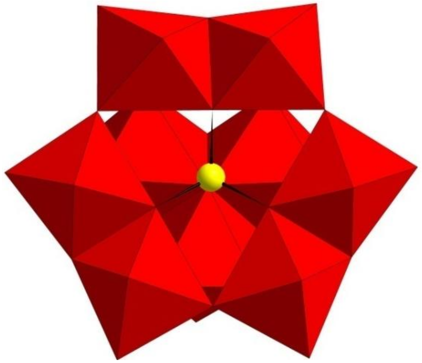
Formation of Ligands: Lacunary POMs

A-Type and *B*-Type Keggin



$[(XO_4)M_{12}O_{36}]^{n-}$



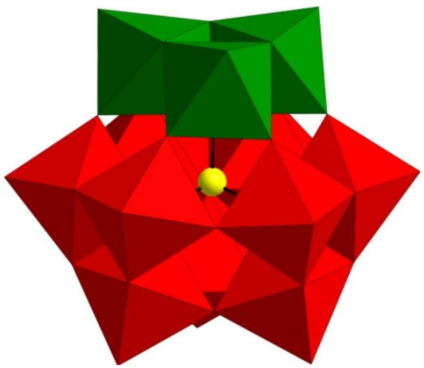


***A*-type trilacunary polyanion**
(6 oxo ligand)

A. Tézé, A.G. Hervé, *Inorganic Syntheses* ***1990, Vol. 27.***

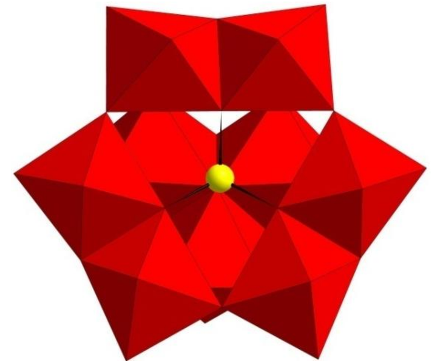
Formation of Ligands: Lacunary POMs

A-Type and *B*-Type Keggin



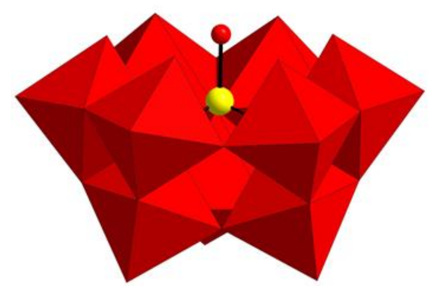
$[(XO_4)M_{12}O_{36}]^{n-}$

Loss of corner shared octahedra



***A*-type trilacunary polyanion**
(6 oxo ligand)

Loss of edge shared octahedra

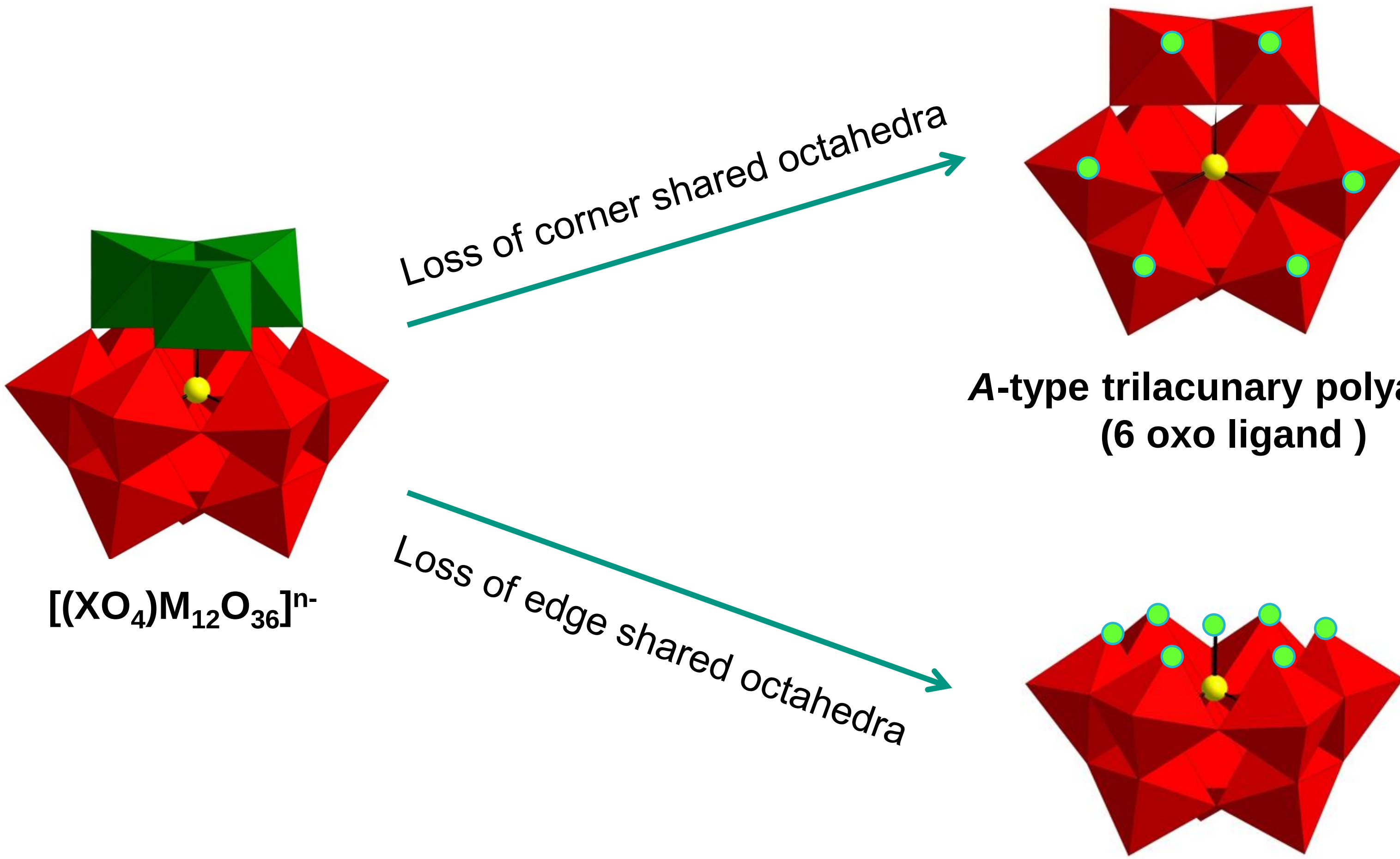


***B*-type trilacunary polyanion**
(7 oxo ligand)

A. Tézé, A.G. Hervé, *Inorganic Syntheses* ***1990, Vol. 27.***

Formation of Ligands: Lacunary POMs

A-Type and *B*-Type Keggin



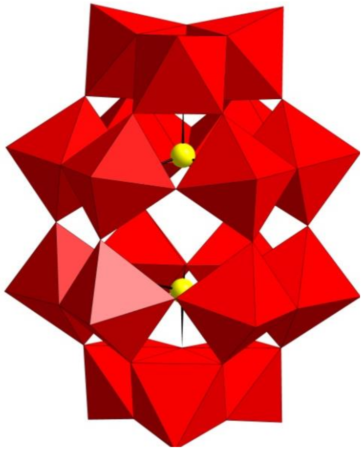
$[(XO_4)M_{12}O_{36}]^{n-}$

***A*-type trilacunary polyanion**
(6 oxo ligand)

***B*-type trilacunary polyanion**
(7 oxo ligand)

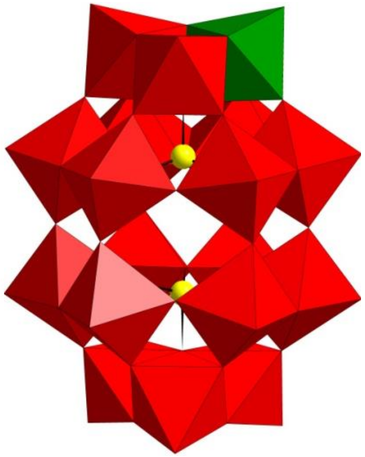
A. Tézé, A.G. Hervé, *Inorganic Syntheses* ***1990, Vol. 27.***

Formation of Ligands: Wells-Dawson Lacunary POMs



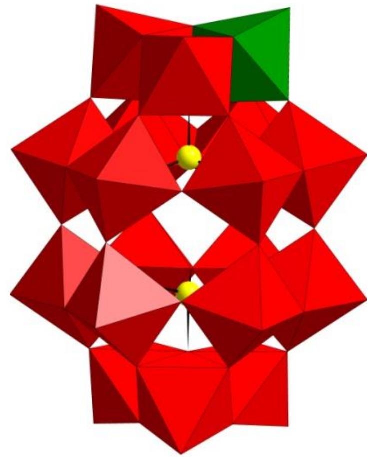
$[(XO_4)_2W_{18}O_{54}]^{n-}$

Formation of Ligands: Wells-Dawson Lacunary POMs



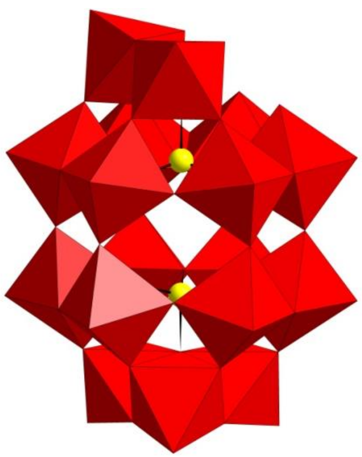
$[(XO_4)_2W_{18}O_{54}]^{n-}$

Formation of Ligands: Wells-Dawson Lacunary POMs



$[(XO_4)_2W_{18}O_{54}]^{n-}$

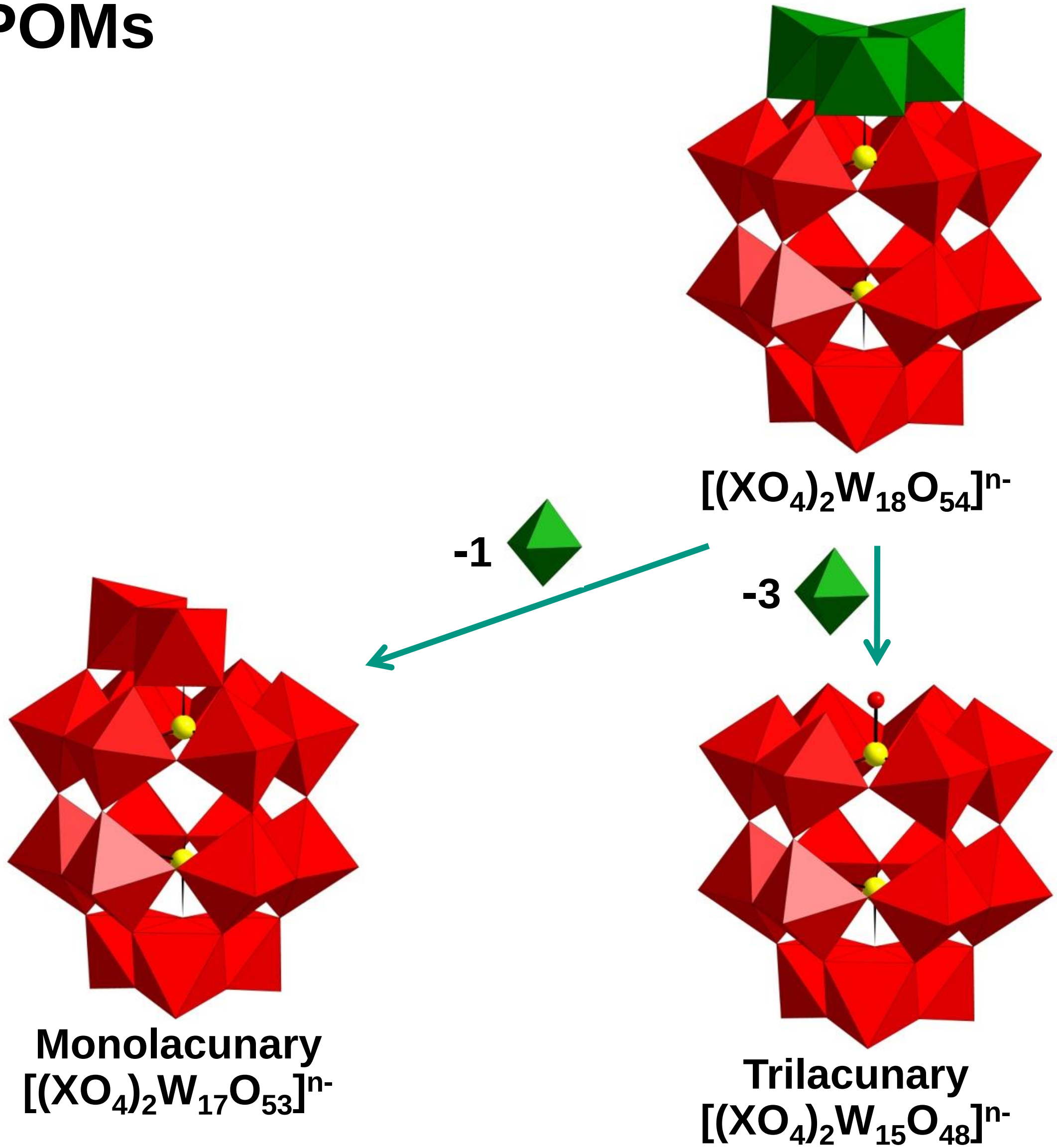
-1



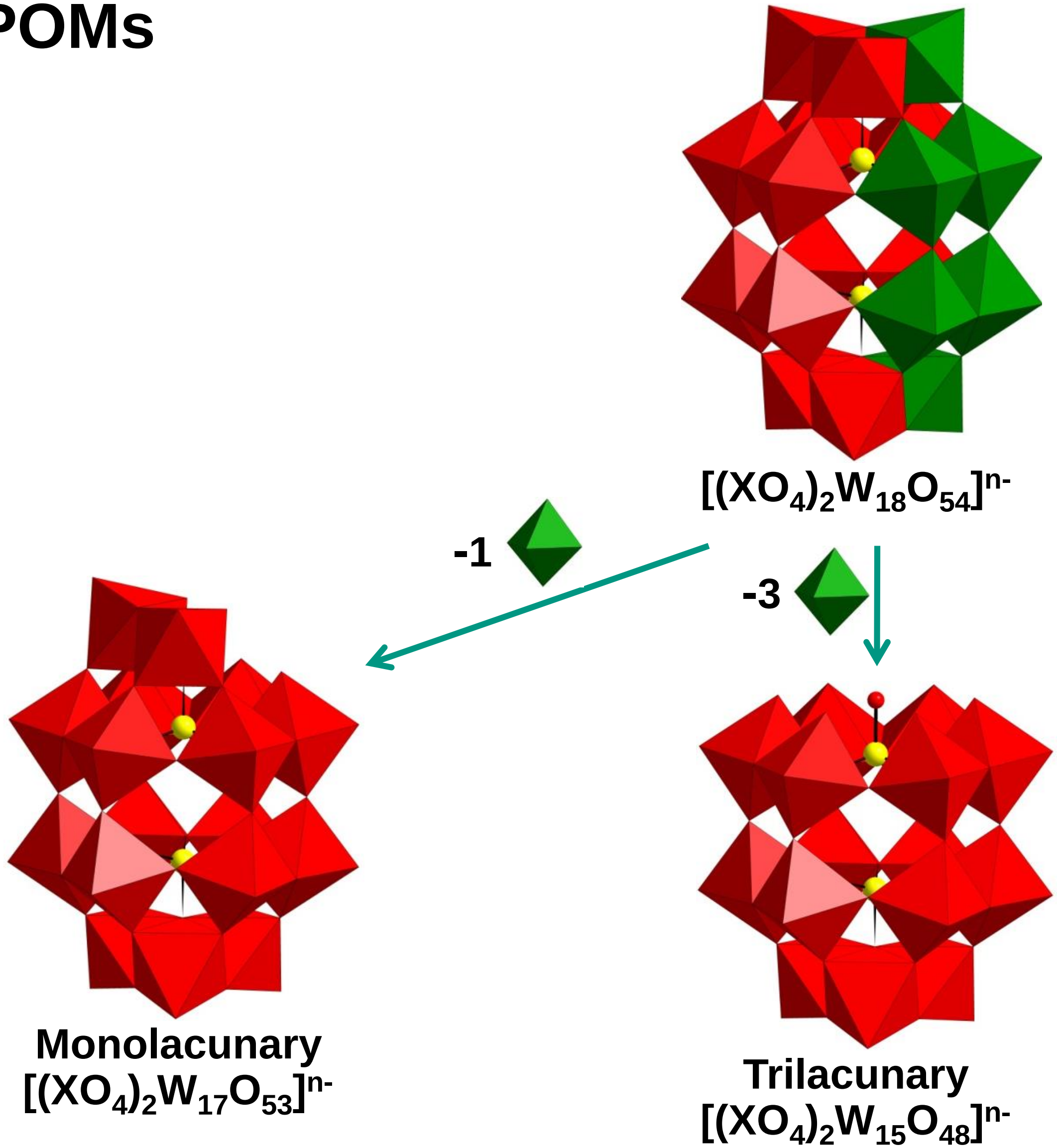
Monolacunary
$[(XO_4)_2W_{17}O_{53}]^{n-}$

Formation of Ligands: Wells-Dawson Lacunary POMs

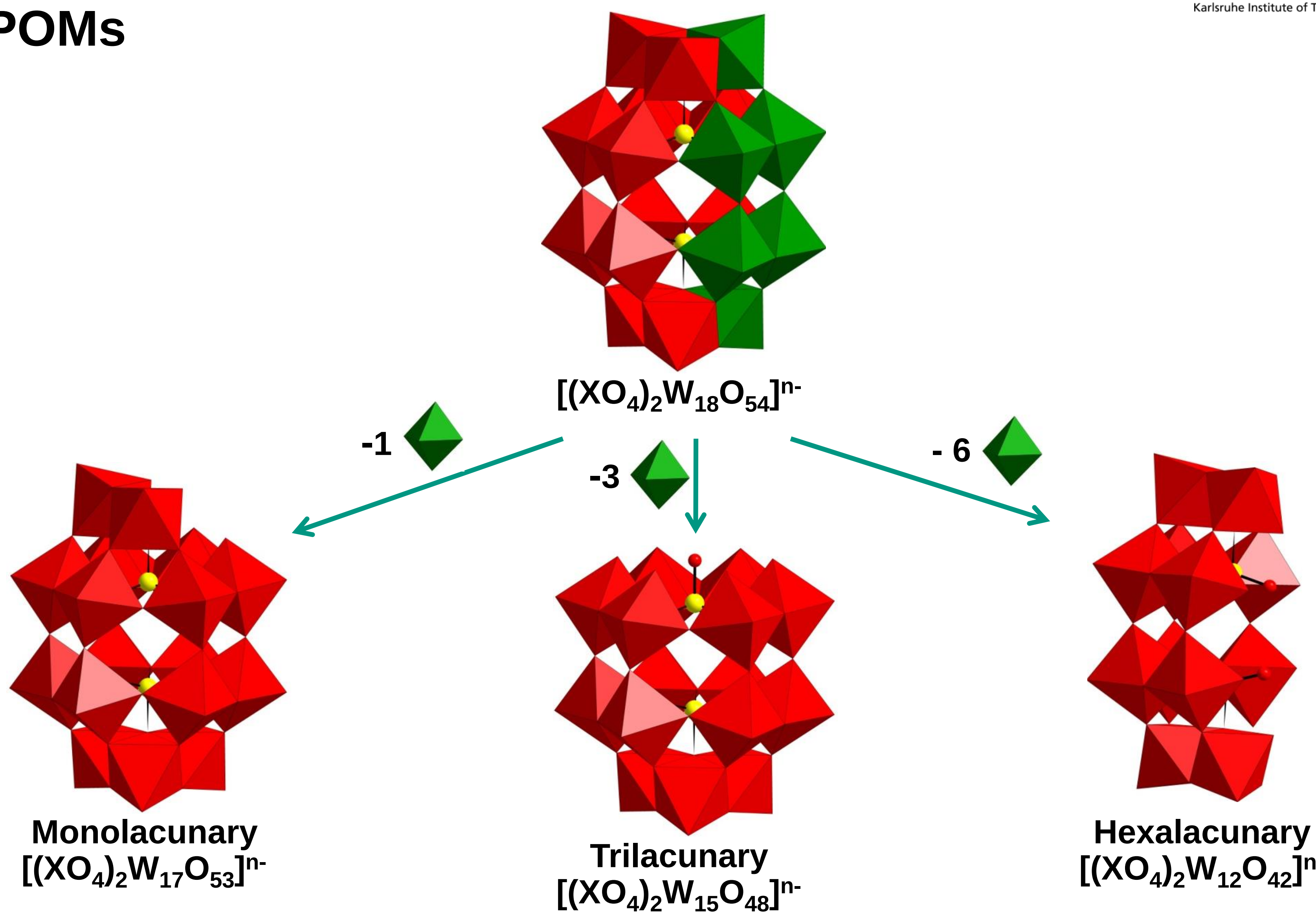
Karlsruhe Institute of Technology



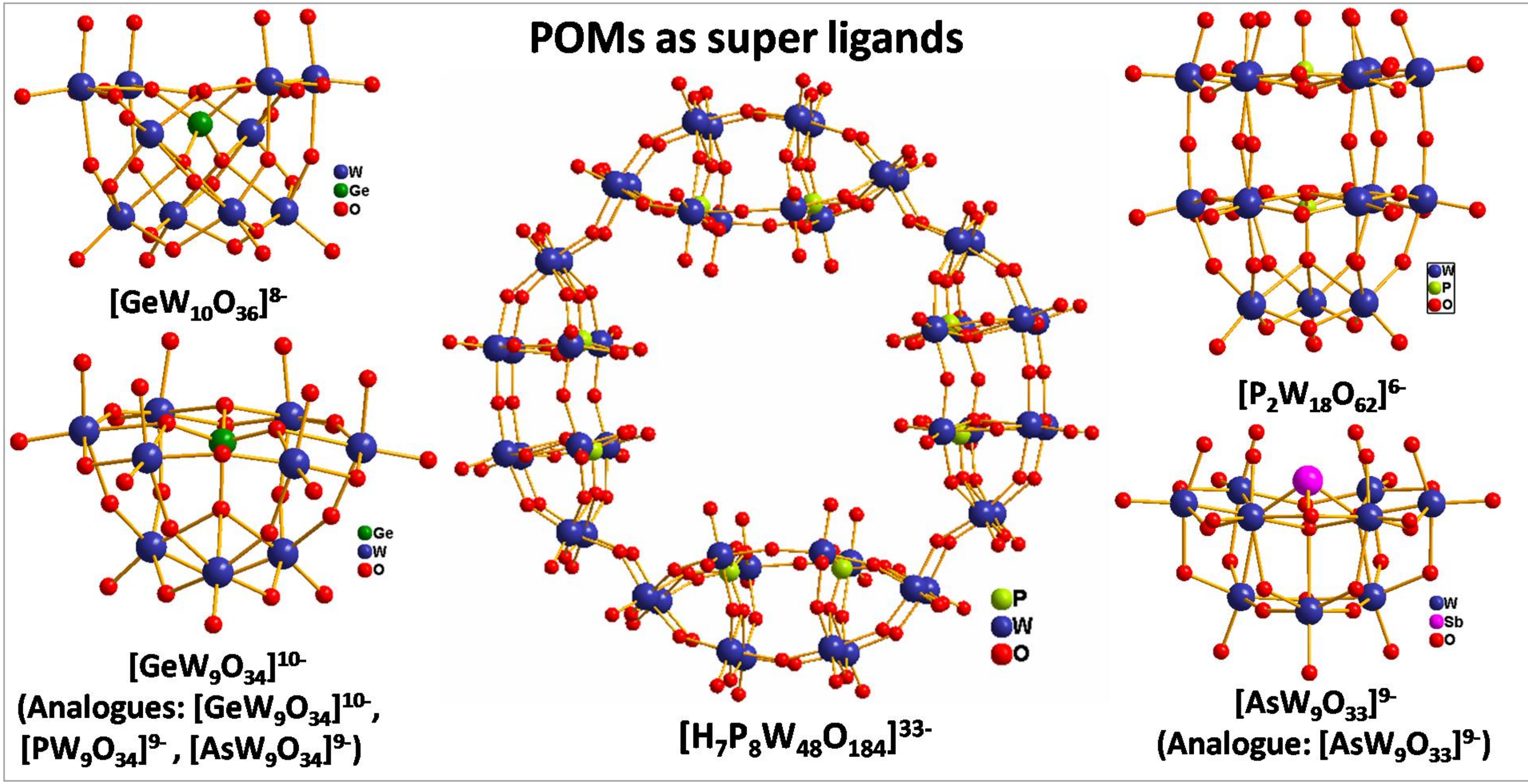
Formation of Ligands: Wells-Dawson Lacunary POMs



Formation of Ligands: Wells-Dawson Lacunary POMs



All-Inorganic Lacunary POM Ligands



Functionalization of Polyoxometalates

Lacunary POMs

+

3*d*/4f/3d-4f-Metal Ions

↓

Polynuclear 3*d*/4f/3d-4f-Containing POMs

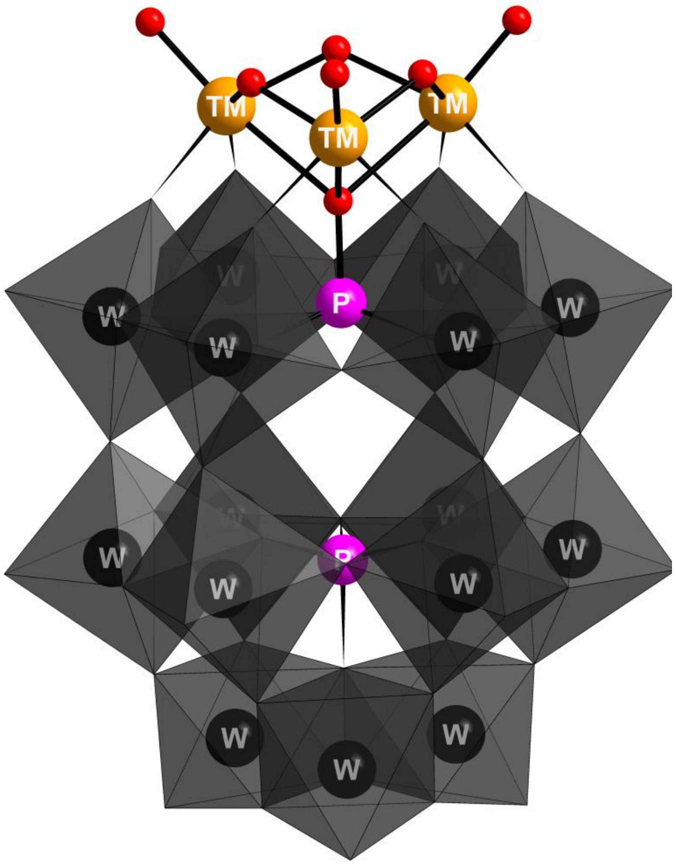
↓

POM-based multifunctional systems

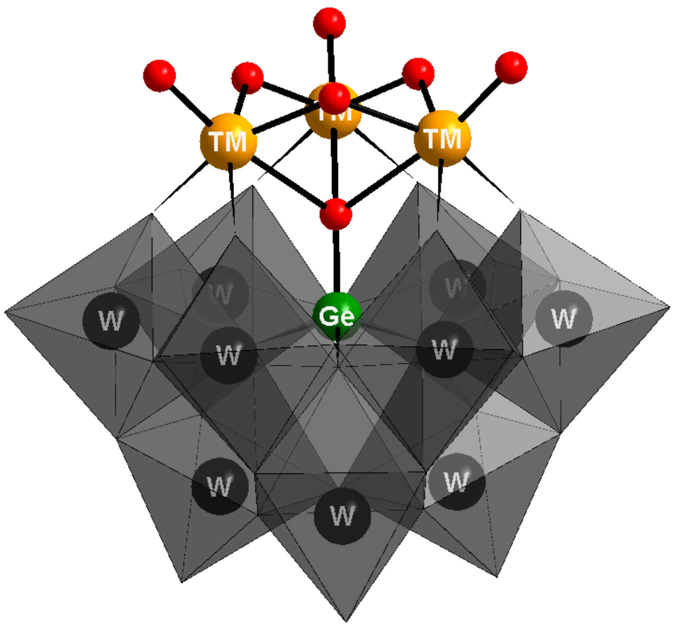
Functionalization of Polyoxometalates

Karlsruhe Institute of Technology

Trilacunary Wells-Dawson ion $[P_2W_{15}O_{56}]^{12-}$



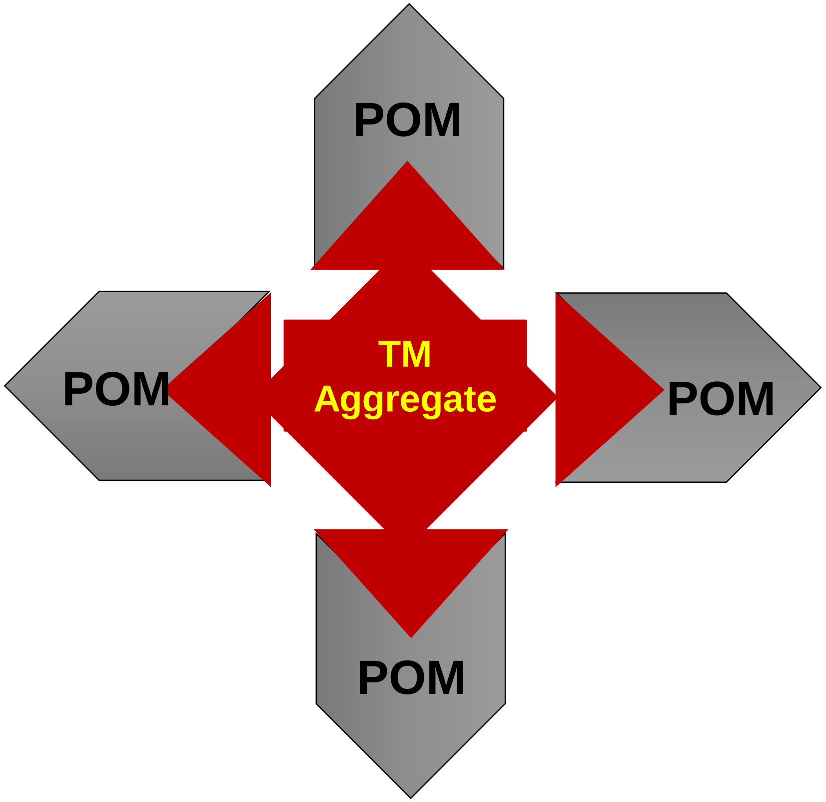
Trilacunary Keggin ion $[GeW_9O_{34}]^{10-}$



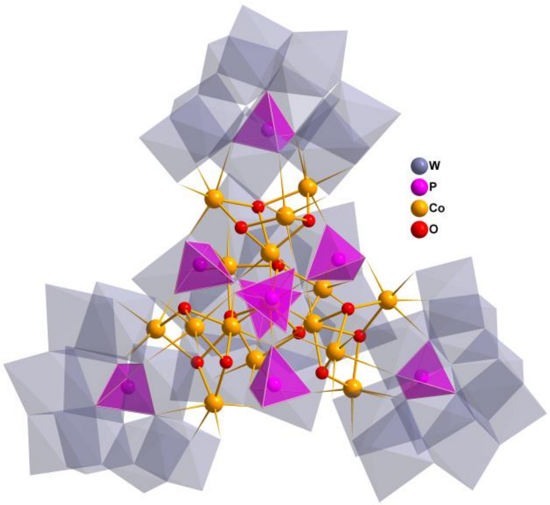
The exposed surface oxygen atoms, formed by removal of a W_3O_6 trimer from a saturated or plenary POMs with TM.

Functionalization of Polyoxometalates

Lacunary POMs ✚ 3*d*/4f/3d-4f-Metal Ions

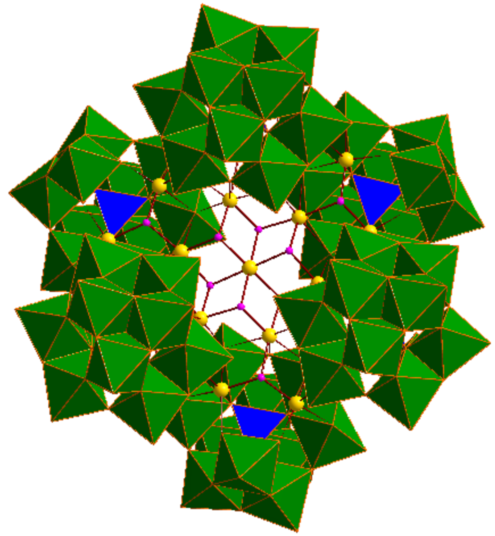


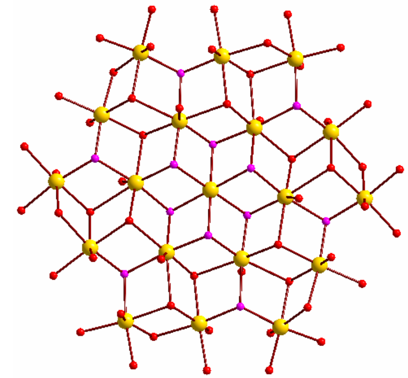
Angew. Chem. Int. Ed. **2011**, 50, 4708.



$[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]^{28-}$

Angew. Chem. Int. Ed. **2011**, *50*, 5961.

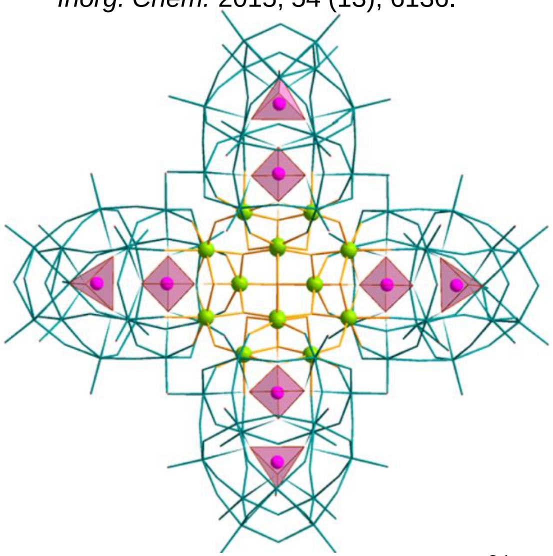




$[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-}$

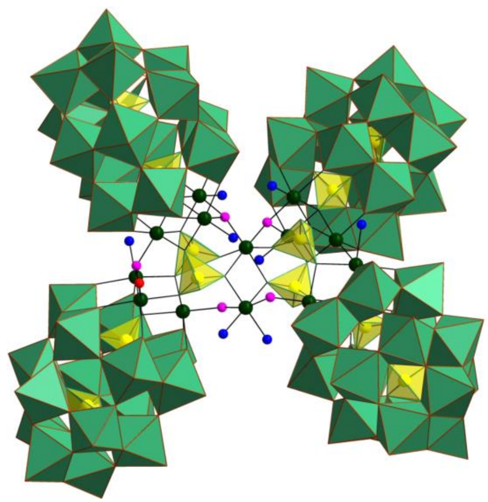
Angew. Chem. Int. Ed. **2015**, 54, 15574.

Inorg. Chem. 2015, 54 (13), 6136.

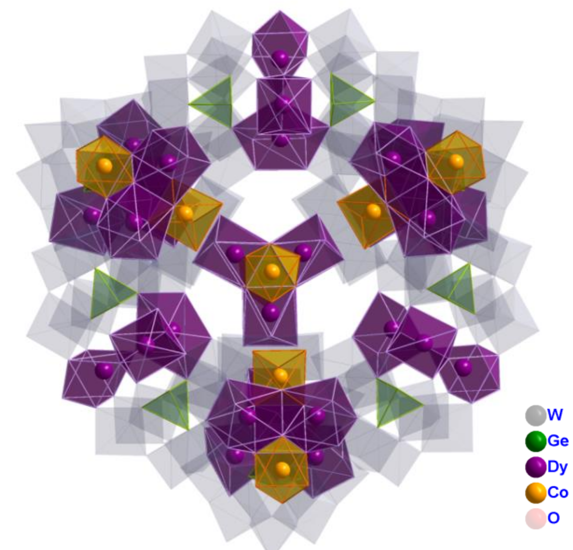


$[Fe_{14}(OH)_{13}O_6\{\alpha\text{-}P_2W_{15}O_{56}\}_4]^{31-}$

Inorg. Chem. **2013**, *52*, 8399.



$[Ni_{14}(OH)_6(H_2O)_{10}(HPO_4)_4(P_2W_{15}O_{56})4]^{34-}$



$[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$

Functionalization of Polyoxometalates

Example

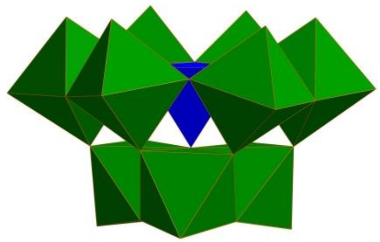
Mn_{19}

Optimized reaction conditions

$MnCl_2 \cdot 4H_2O$

(0.63 mmol)

NaOH pH 8 (RT, 30 min.)
3.0 mmol Na_3PO_4 (70 ºC 1 hr.)

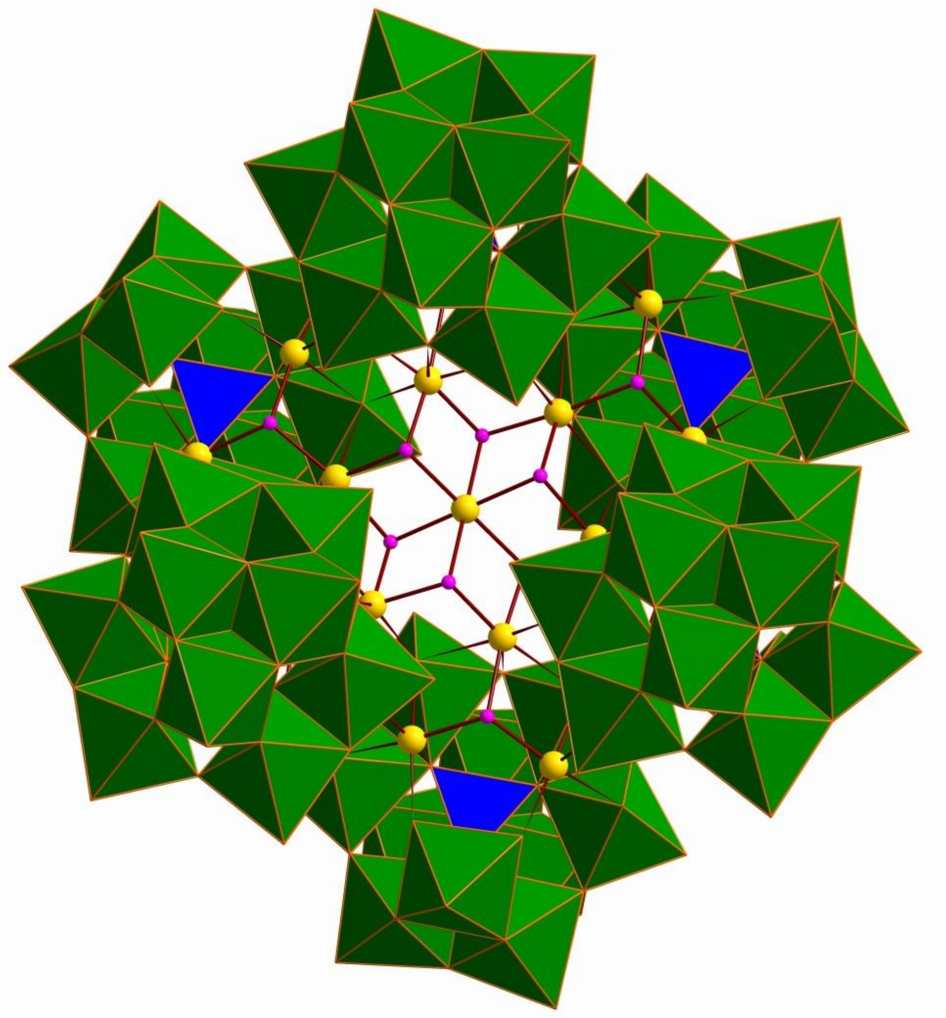


[*A*-*α*-$SiW_9O_{34}]^{10-}$
(0.20 mmol)

$Na_{34}[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6] \cdot 115H_2O$

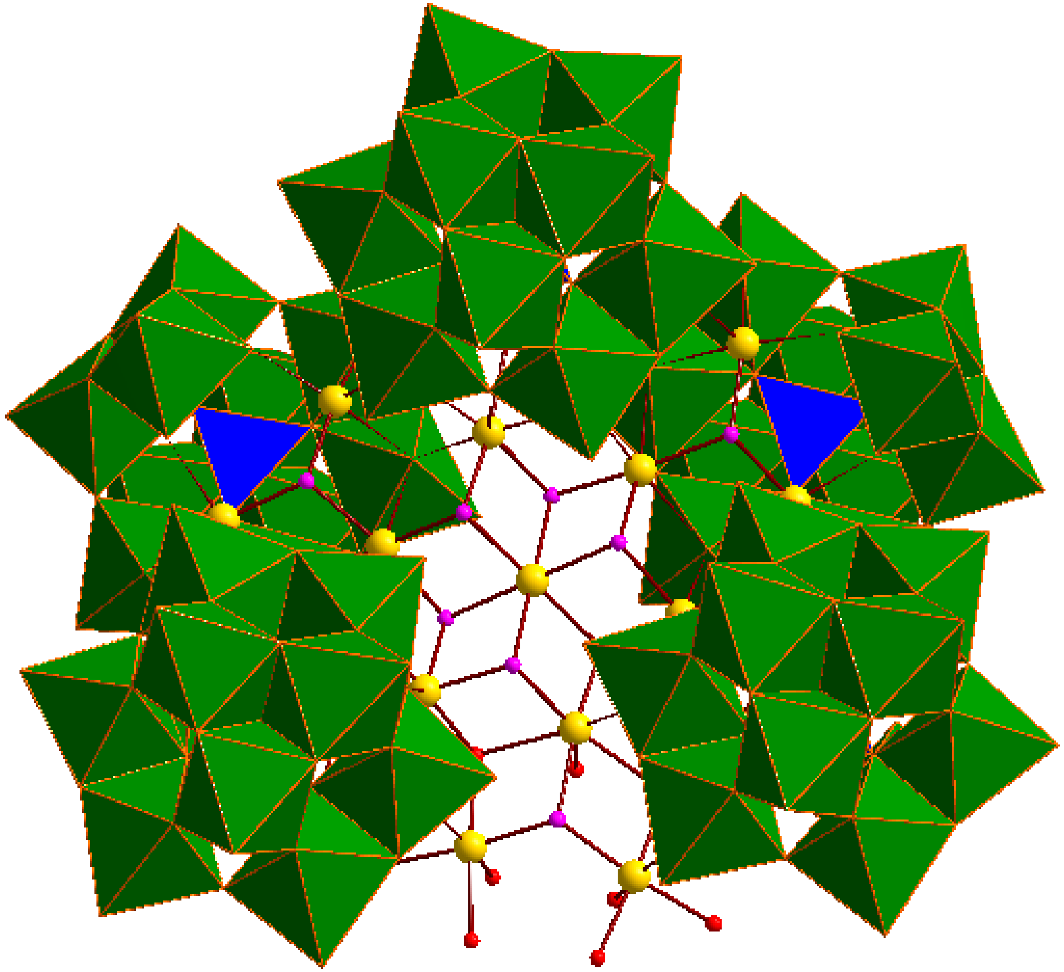
B. S. Bassil, M. Ibrahim, R. Al-Oweini, M. Asano, Z. Wang, J. van Tol, N. S. Dalal, K.-Yong Choi, U. Kortz, *Angew. Chem. Int. Ed.* **2011**, *50*, 5961-5964.

Functionalization of Polyoxometalates

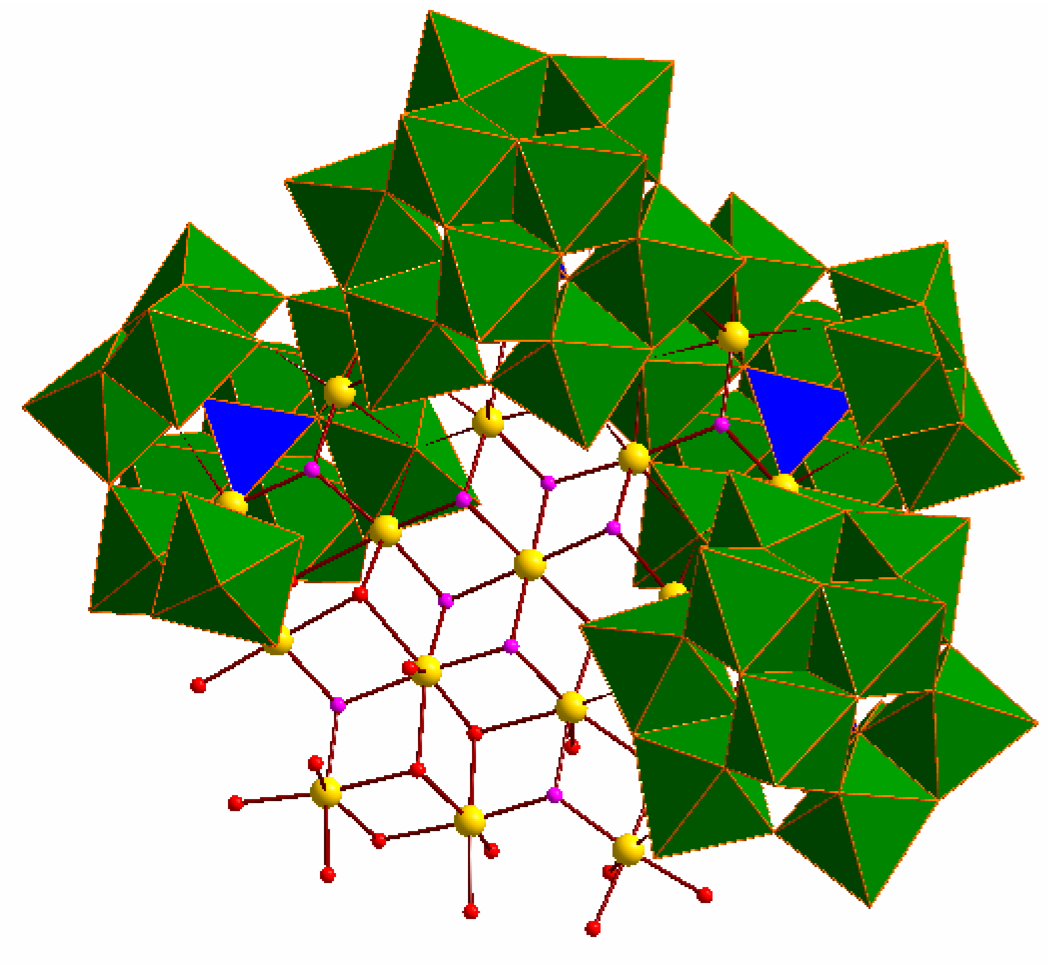


Mn_{19}

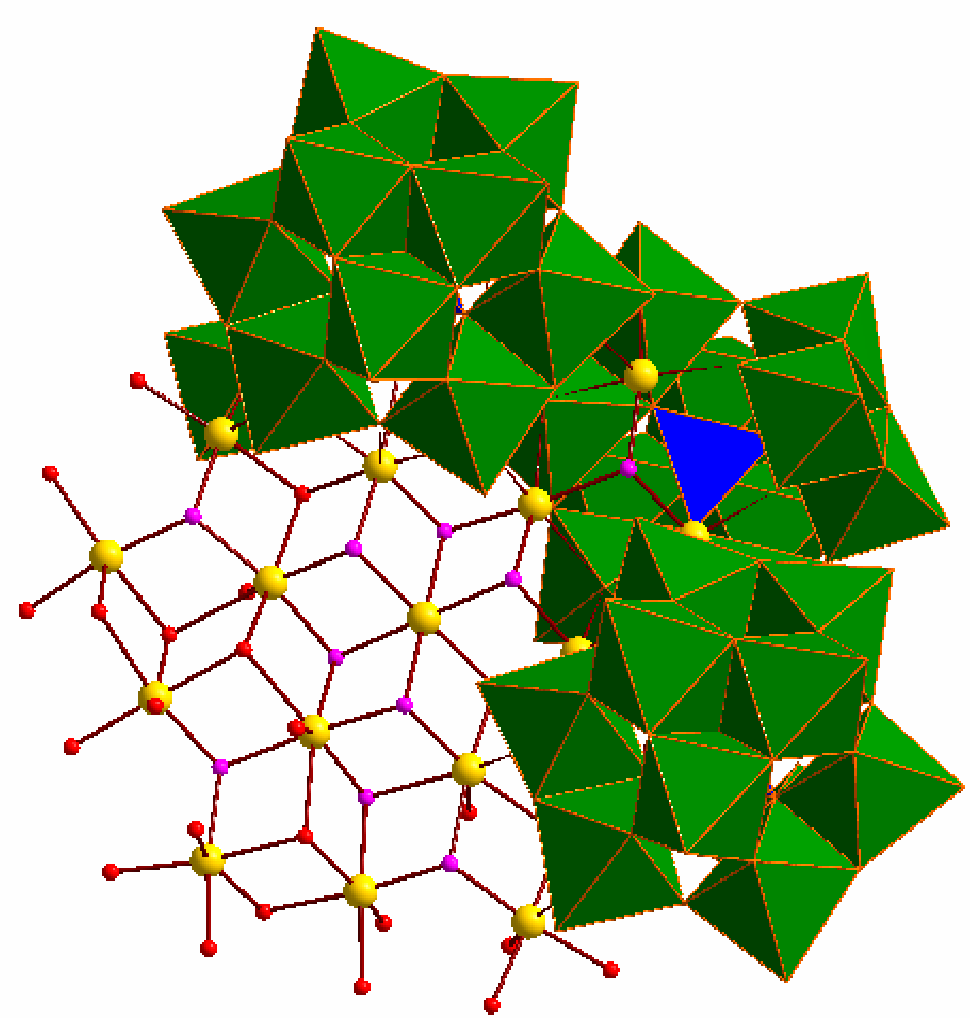
Functionalization of Polyoxometalates



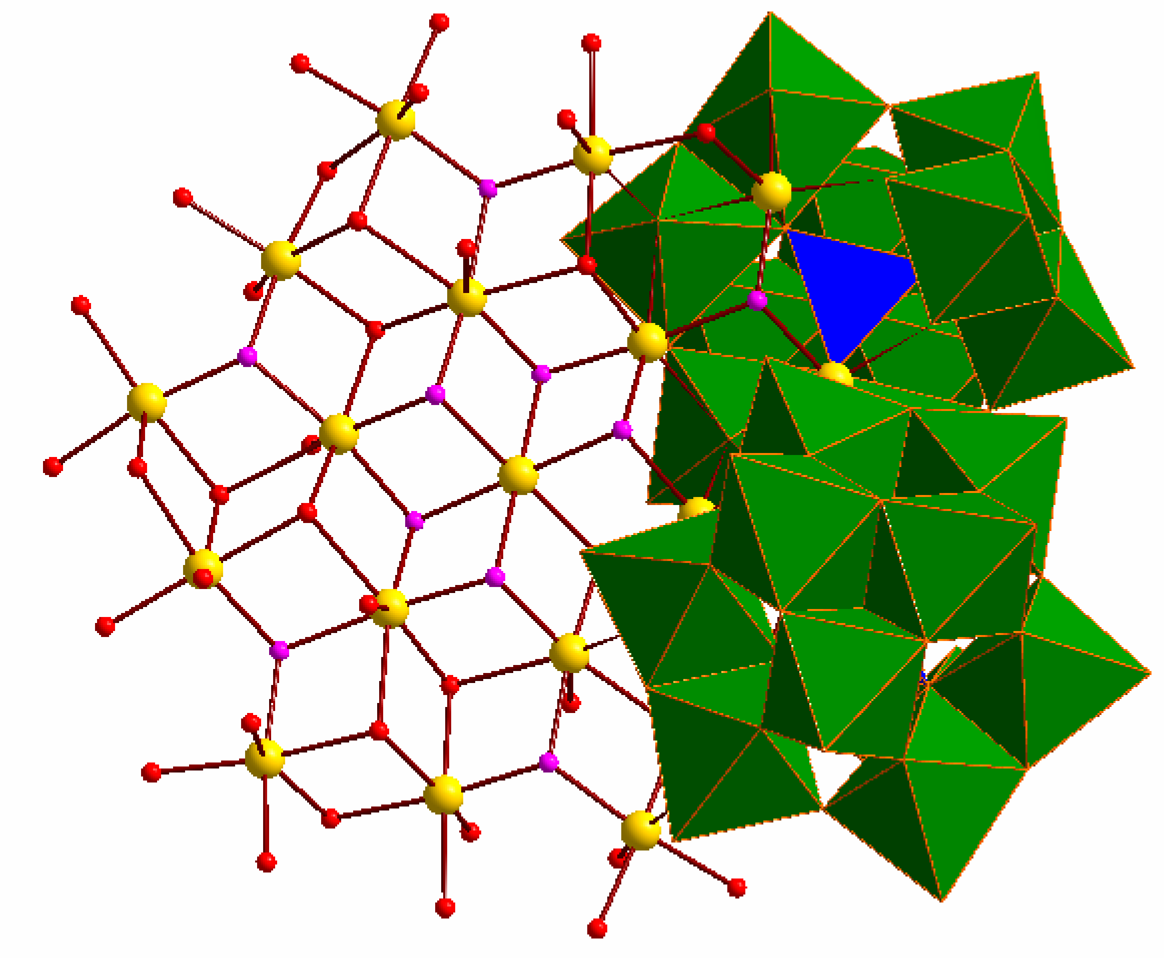
Functionalization of Polyoxometalates



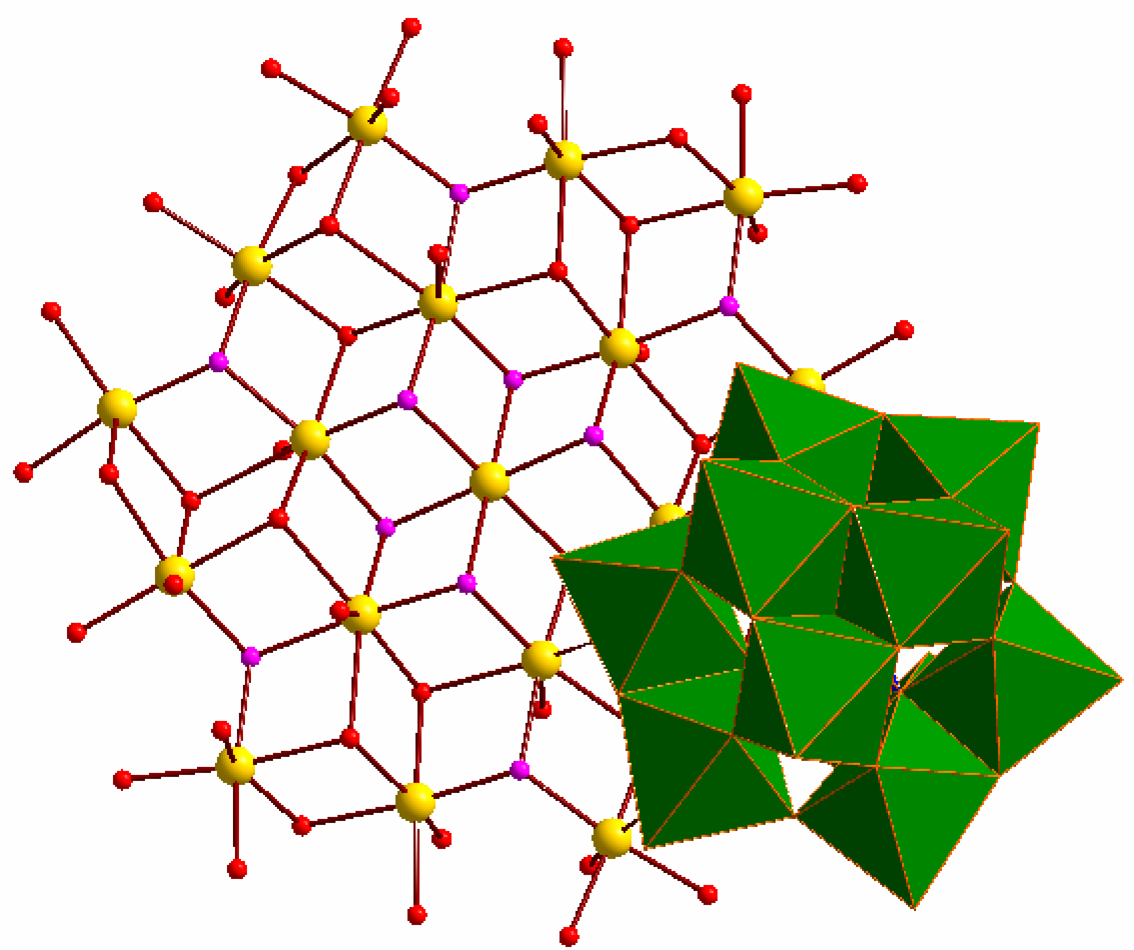
Functionalization of Polyoxometalates



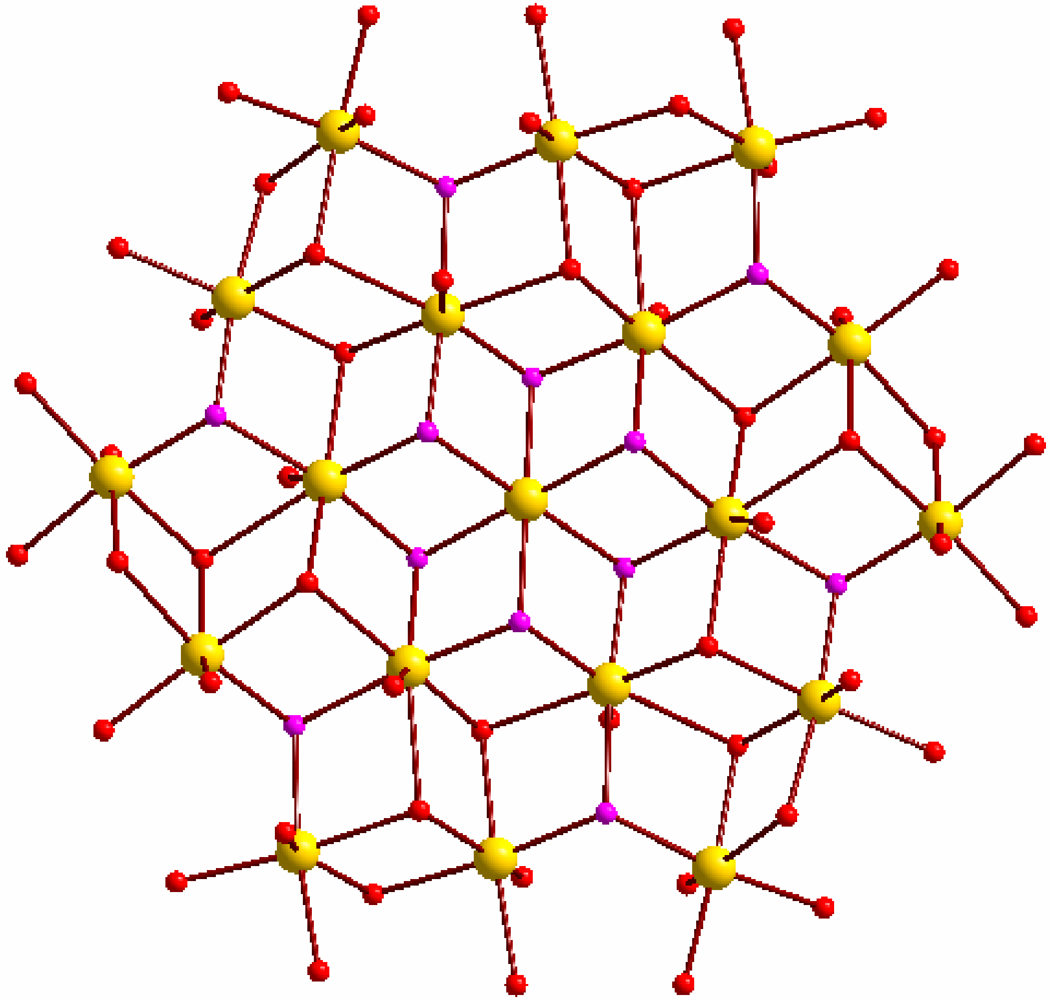
Functionalization of Polyoxometalates



Functionalization of Polyoxometalates

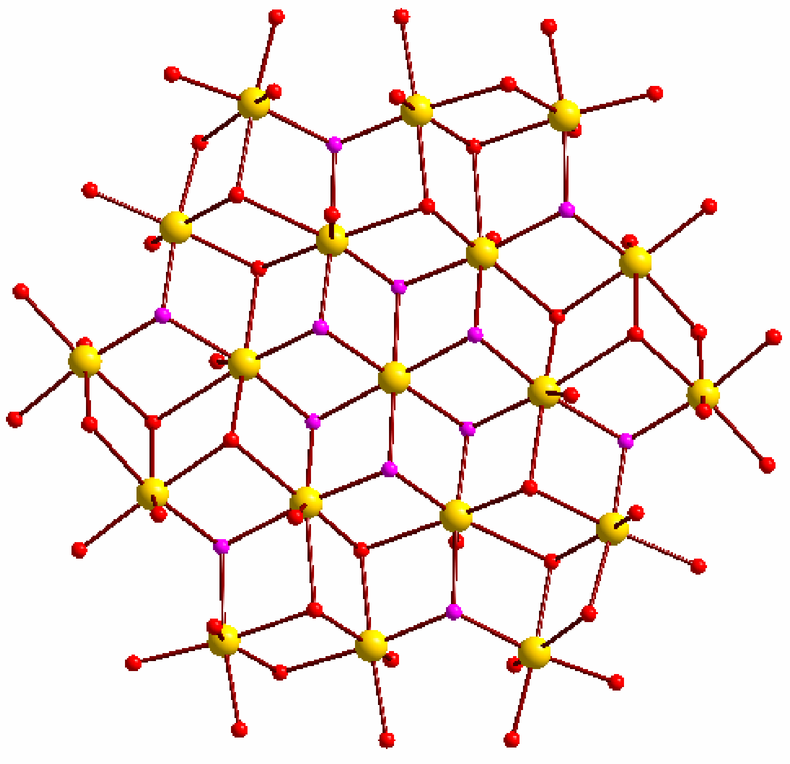


Functionalization of Polyoxometalates

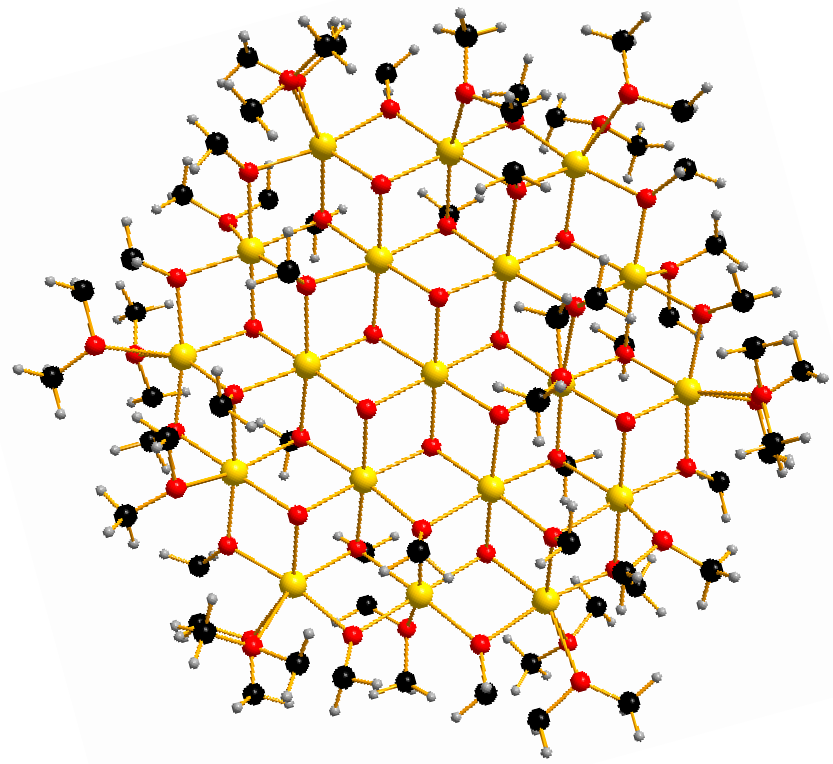


Protonated oxygens pink balls, Mn yellow balls, O red balls.

Mn_{19} Core: Comparison



Kortz's {Mn_{19}-POM}

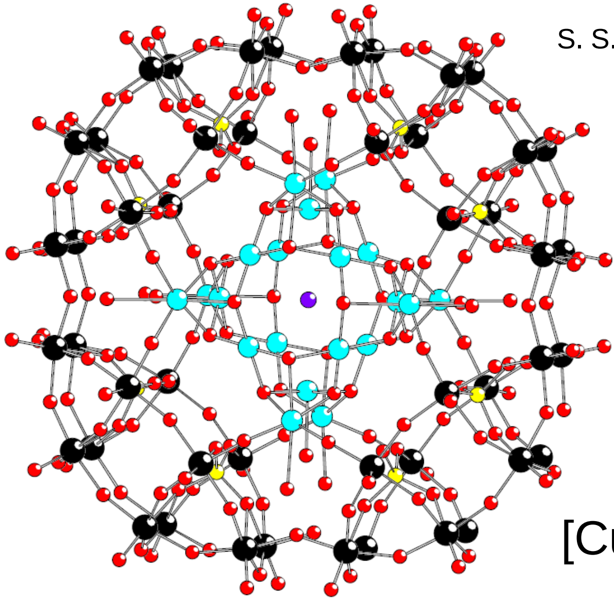


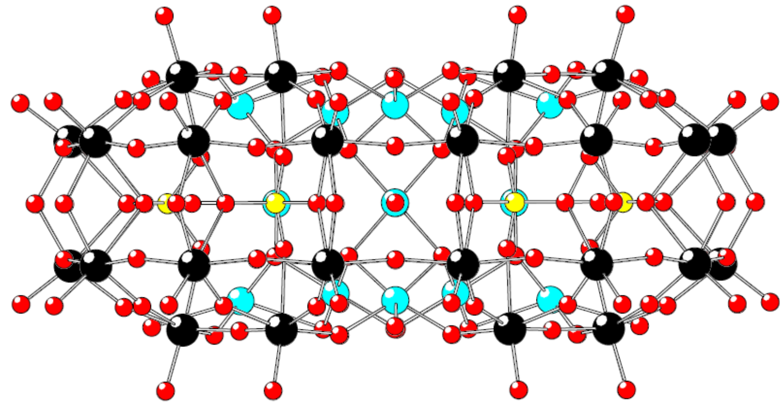
Westin's {Mn_{19}-org}

I. A. M. Pohl, L. G. Westin, M. Kritikos, *Chem. Eur. J.* **2001**, *7*, 3439.

Karlsruhe Institute of Technology

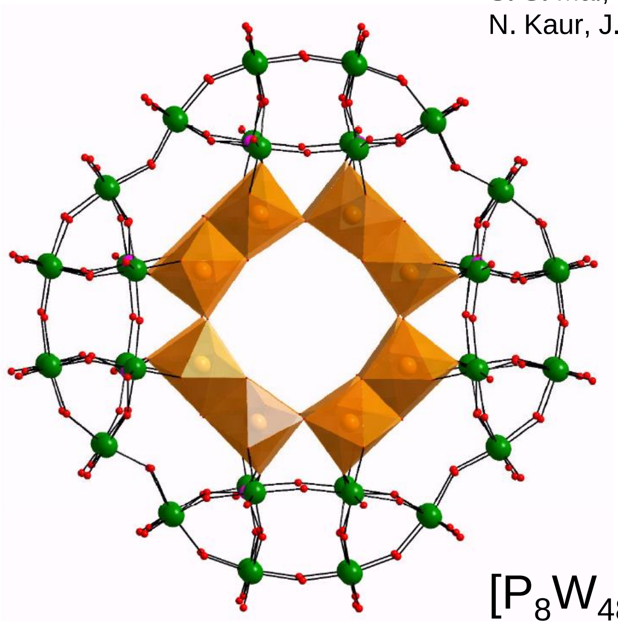
S. S. Mal and U. Kortz, Angew. *Chem., Int. Ed.*, **2005***, 3*, 3777.

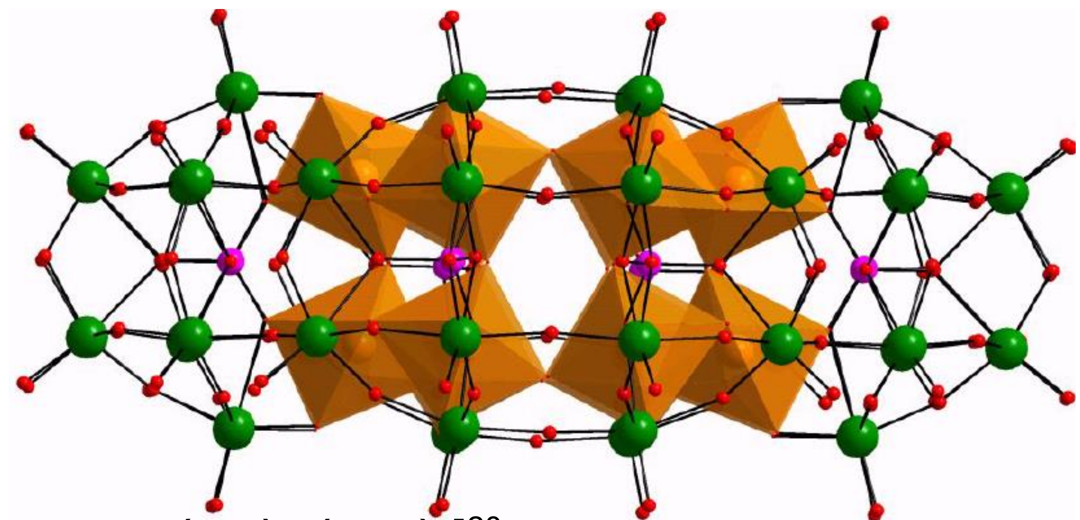




$[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184}]^{25-}$

S. S. Mal, M. H. Dickman, U. Kortz, A. M. Todea, A. Merca, H. Bögge, T. Glaser, A. Müller, S. Nellutla, N. Kaur, J. Van Tol, N. S. Dalal, B. Keita and L. Nadjo, *Chem. – Eur. J.*, **2008**, *14*, 1186.

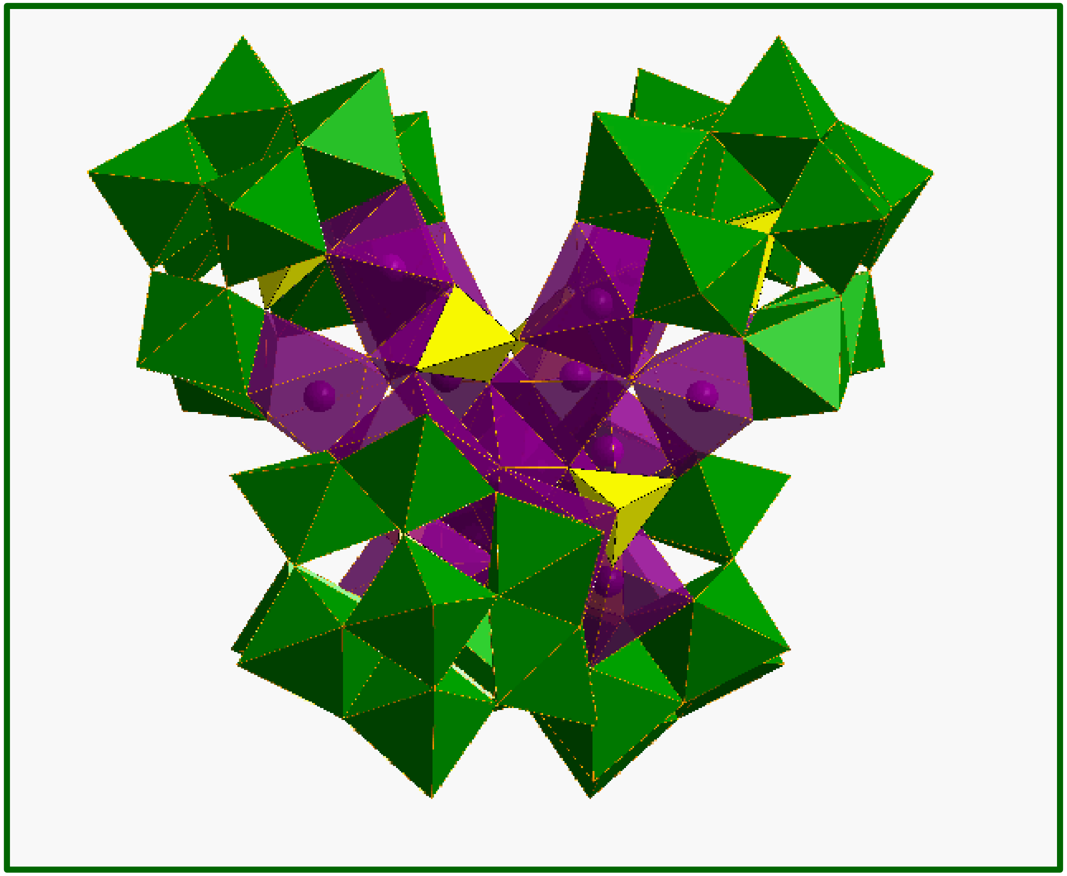




$[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$

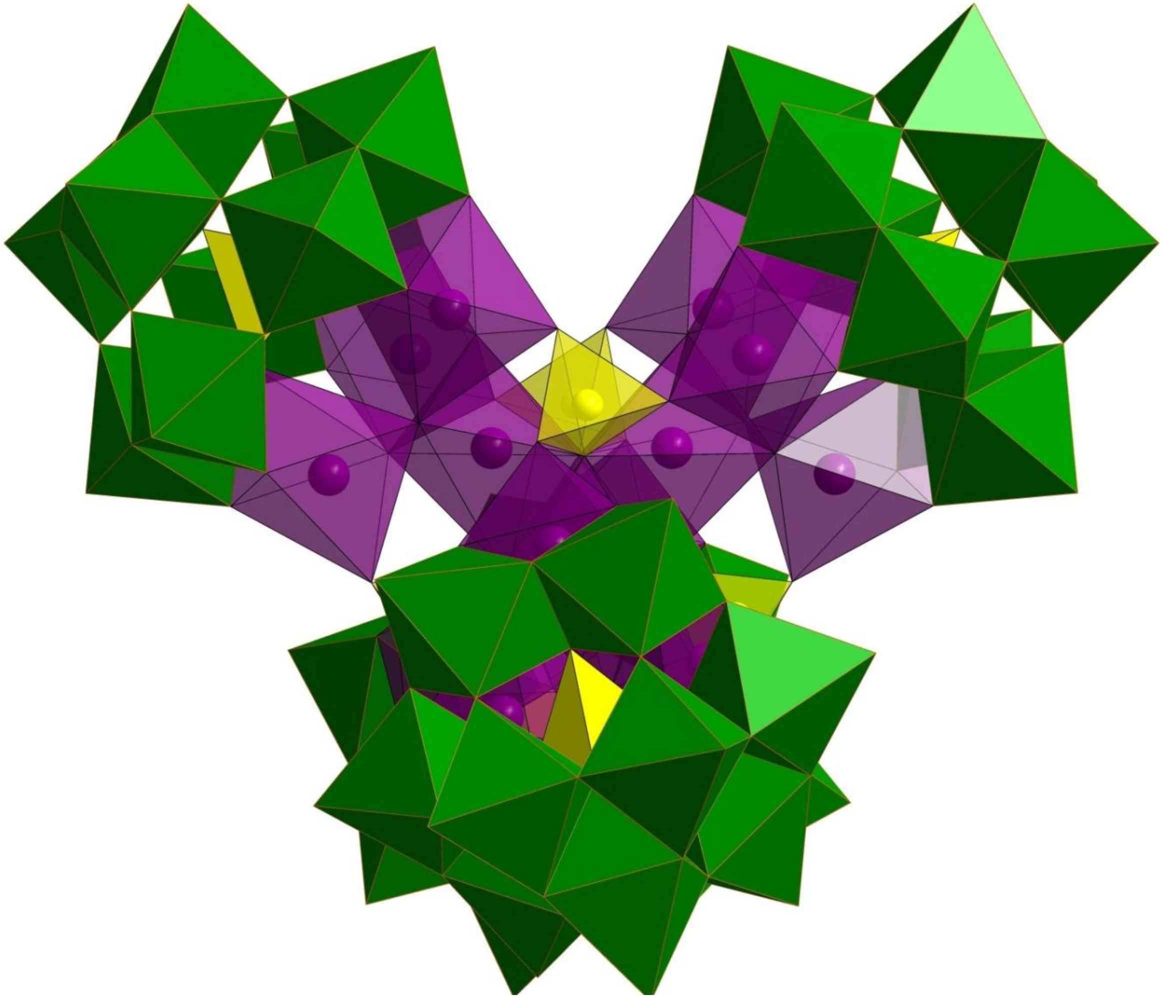
Functionalization of Polyoxometalates

$[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]^{28-}$ (Co_{16})

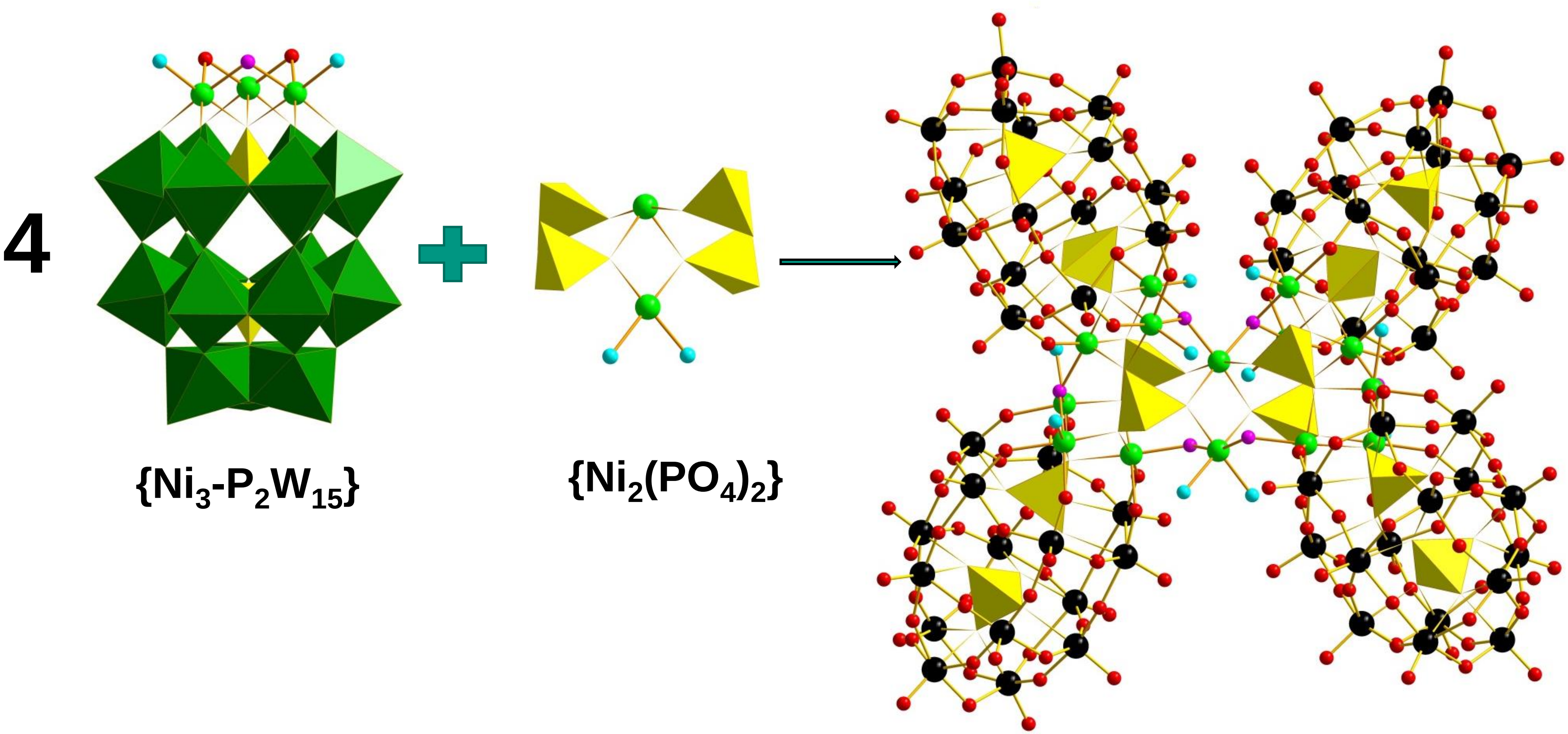


M. Ibrahim, Y. Lan, B. S. Bassil, Y. Xiang, A. Suchopar, A. K. Powell, U. Kortz, *Angew. Chem. Int. Ed.* **2011**, *50*, 4708.

Functionalization of Polyoxometalates



Functionalization of Polyoxometalates



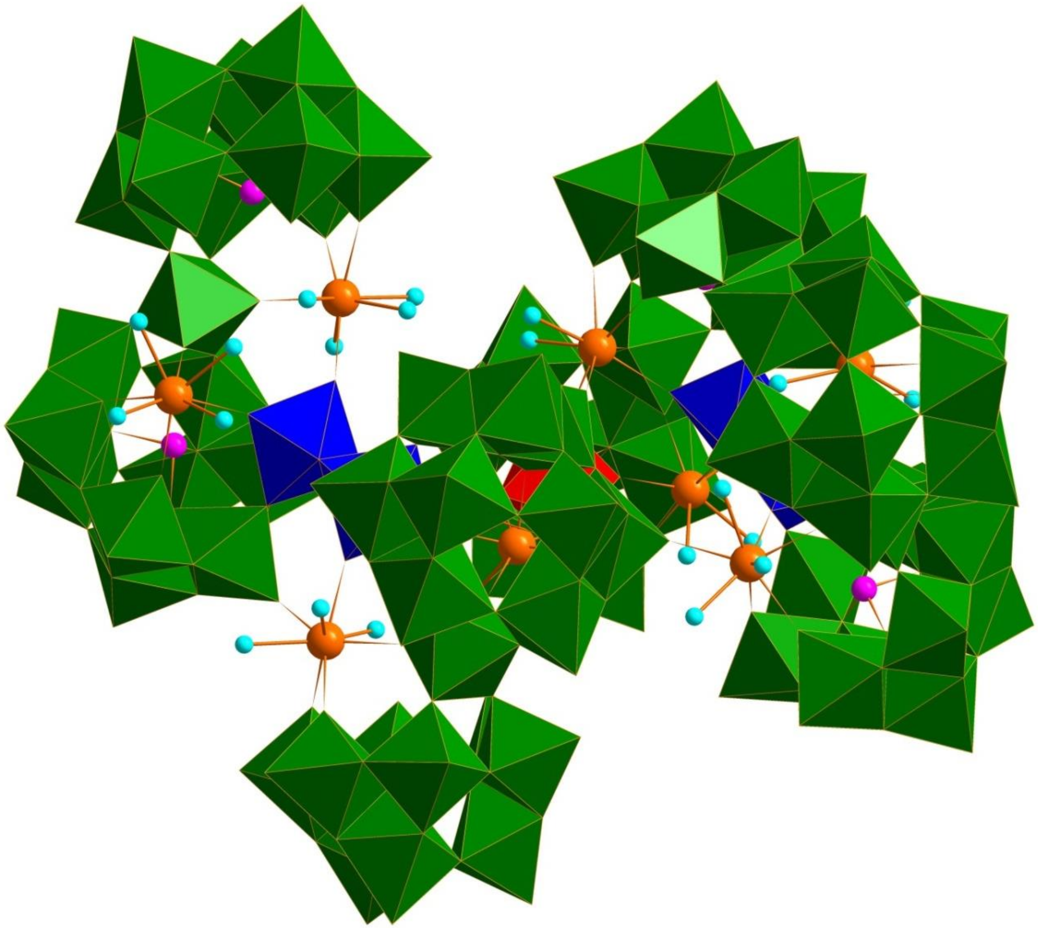
$[(Ni_{14}(H_2O)_{10}(OH)_6(PO_3(OH))_4(\alpha\text{-}P_2W_{15}O_{56})_4]^{34-}$ (Ni_{14})

M. Ibrahim, Y. Xiang, B. S. Bassil, Y. Lan, A. K. Powell, P. de Oliveira, B. Keita, U. Kortz. *Inorg. Chem*. 2013, *52*, 8399-8408.

Functionalization of Polyoxometalates

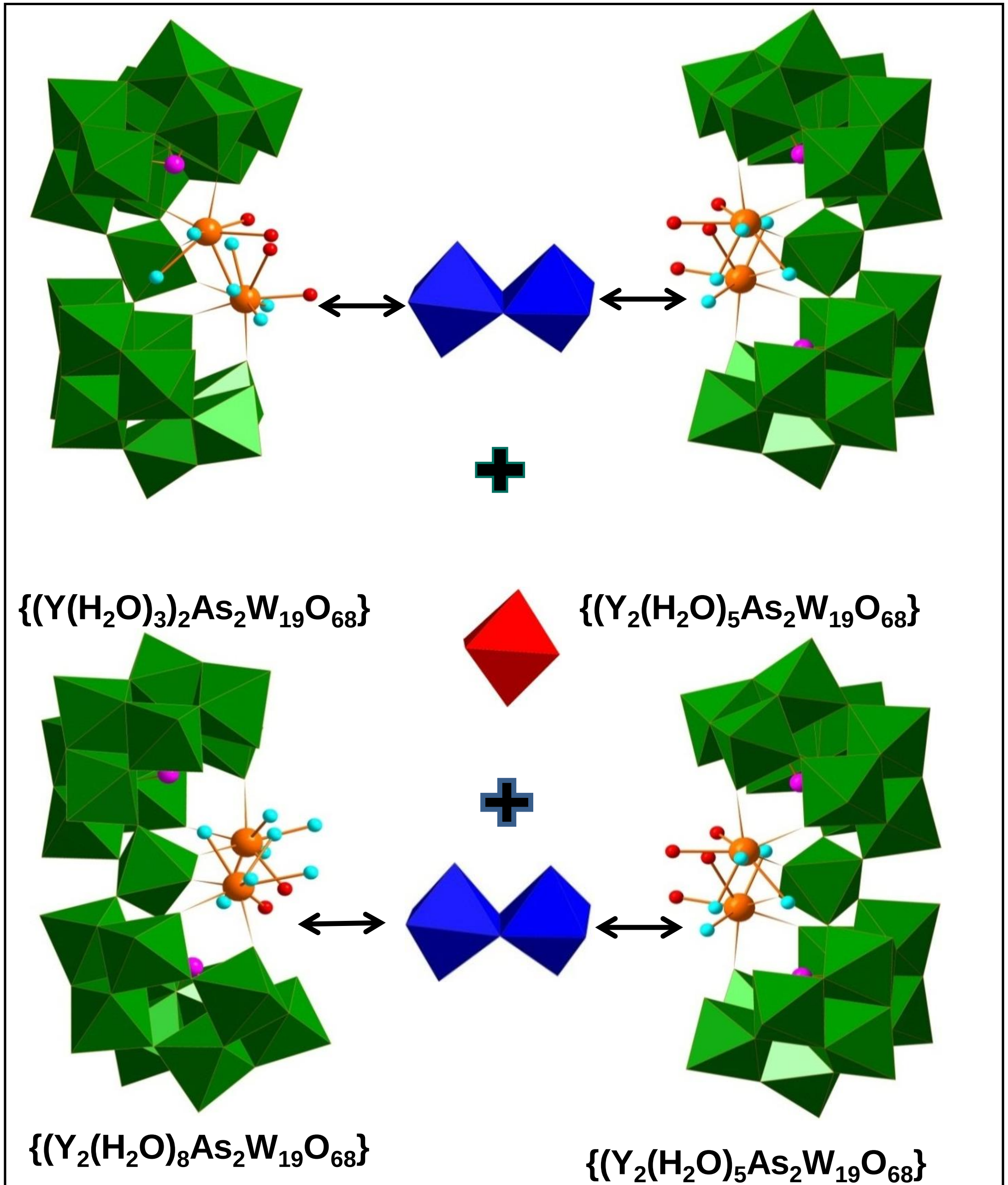
$[\{Y(H_2O)_3\}_8(As_2W_{19}O_{68})_3(As_2W_{19}O_{66})(W_2O_6)_2(WO_6)]^{42-}$

(Y_8)

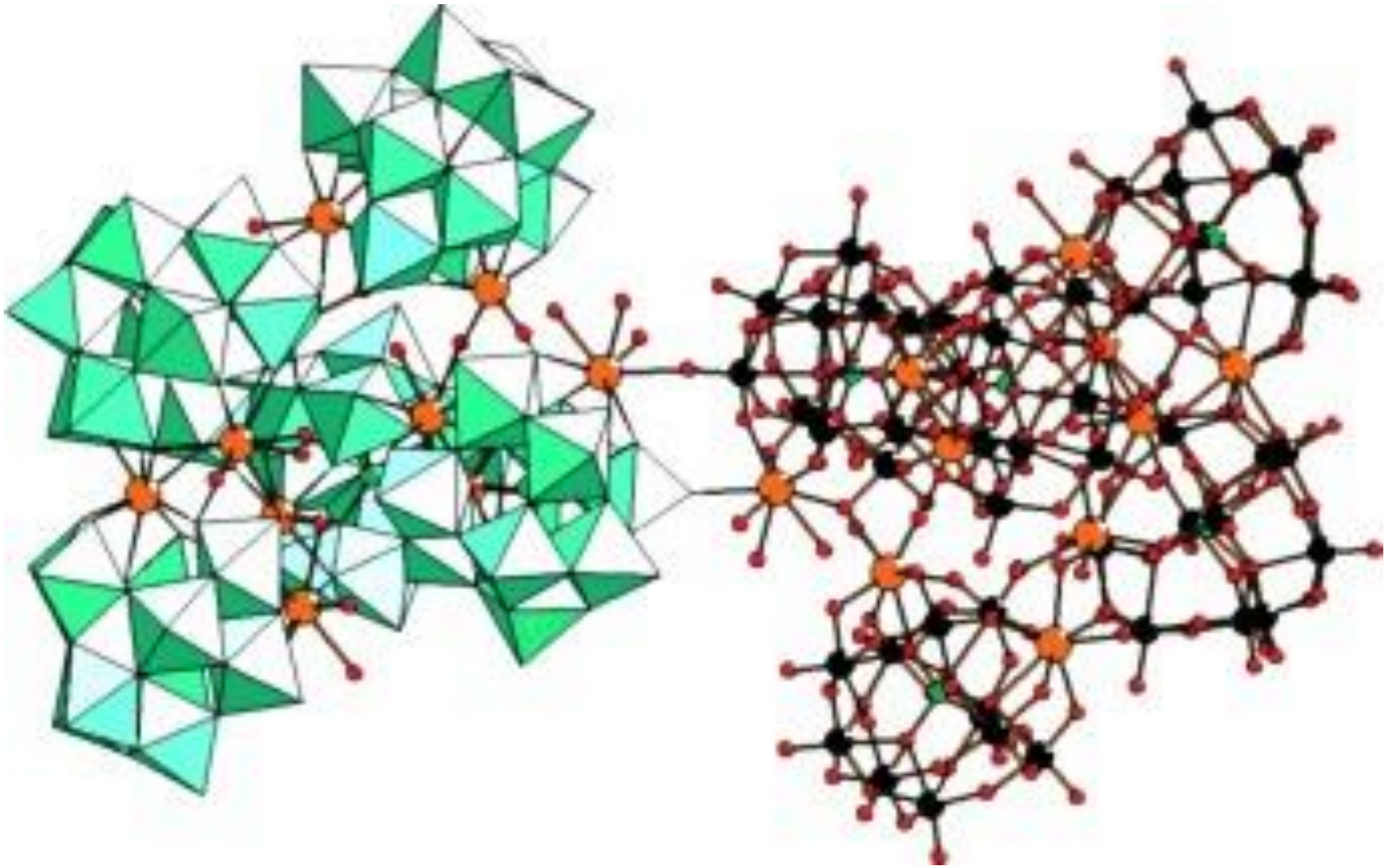


Masooam Ibrahim, Bassem S. Bassil, Ulrich Kortz, *Inorganics*, 2015, *3*, 2, 267-278.

Karlsruhe Institute of Technology



$[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$

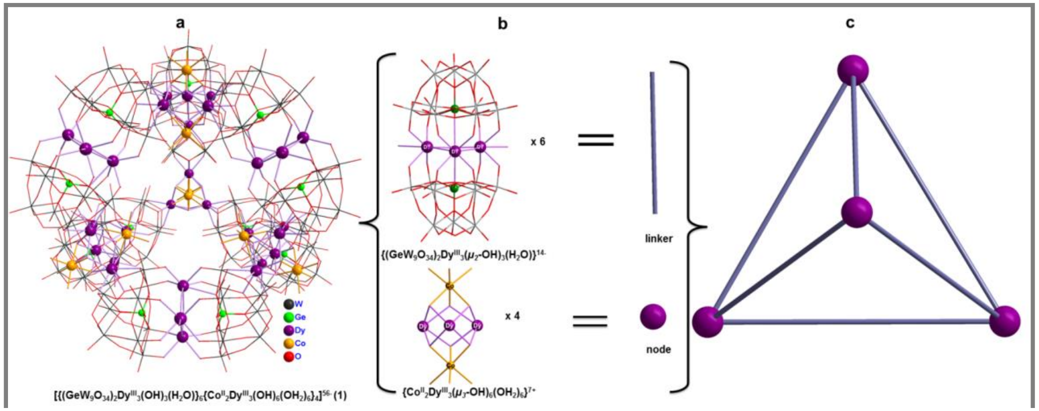


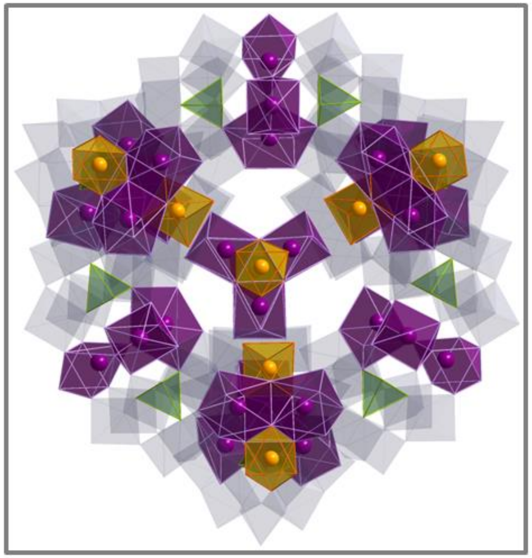
Color code: W black, Ce orange, Ge green, O red, WO_6 octahedra light blue

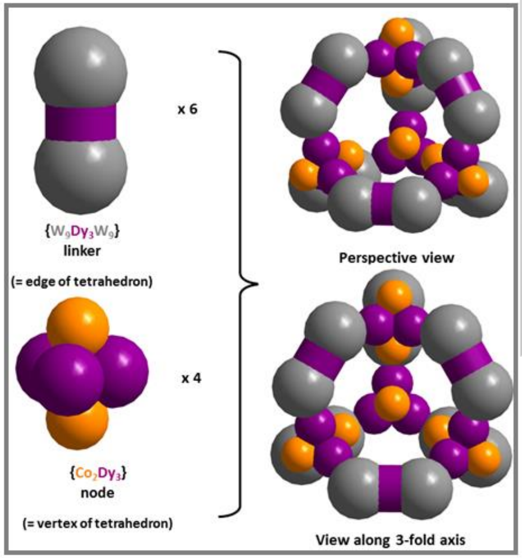
B. S. Bassil, M. H. Dickman, I. Römer, B. von der Kammer, U. Kortz, *Angew. Chem. Int. Ed.* 2007, 46, 6192– 6195.

Functionalized 3d-4f Heterometallic POMs: A new Type

$[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$ **$\{Dy_{30}Co_8\}$**







- The largest discrete heterometallic POM with largest number of dysprosium centers.

- A new structural topology in POM chemistry and is the first to incorporate two different 3d–4f and 4f coordination cluster assemblies within same POM framework.

M. Ibrahim, V. Mereacre, N. Leblanc, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem. Int. Ed,* ***2015****,* 54, 15574.