Definitions

Cluster (Chemistry) - ensemble of atoms or molecules intermediate in size between a molecule and a bulk solid. The can be made up of diverse nuclearities and stoichiometry. (Mingos and Wales 1990, Introduction to Cluster Chemistry)

Examples: Fullerene, Diborane, Water

Metal Cluster: (1) Compounds that contain metal-metal bonds. (2) A compound that contains a group of two or more atoms where direct and substantial metal bonding is present. (Huheey Inorganic Chemistry Huheey, JE,Harper and Row, New York)

Examples: Co₂(CO)₈, Rh₂(OAc)₄, Stryker’s reagent.

Etymology of “Cluster”

Derived from the Middle English “cluster” and Old English “clyster” meaning “bunch.” Also from Proto-Germanic klas meaning “to clump, lump together.” Related to icelandic “cluster; bunch of grapes.”

Metal Cluster History [Clustory?]

12th century - Historically Metal cluster was calomel (Hg₂Cl₂). Later used to treat syphilis and Laxative for George III.

1826 - First polyoxometallate discovered as PMo₁₂O₄₀⁴⁻ anion by Berzelius.

1908 - Miolett-Rosenheim Hypothesis postulated about the structure of 12-molybdophosphoric acid as a polyoxometallate cluster.

1928 - Linus Pauling proposes structure that accurately accounts for structure of polyoxytungstate anion

1934 - J. F. Keggin obtains first crystal structure of polyoxo-metalate. Now referred to as Keggin structure.

1953 - X-Ray Evidence for Metal-to-Metal Bonds in Cupric and Chromous Acetate (Schoening)

1964 - F. A. Cotton (Wilkinson Student) discovers Re₂Cl₈²⁻ which contained metal-metal bond.

Early 1960s - Cotton coins terms cluster when referring to chemical entities that contain one or more metal-metal bond.

Focus of This Presentation

– Homo and Heterometallic Dinuclear metal clusters
– Polyoxometallate complexes
– Biologically relevant metal clusters and their related congeners.
– Higher order Metal clusters
– Future of Metal Clusters in Synthetic Chemistry and Catalysis

Further Resources not fully in the scope of this GM

Bimetallic Lewis Acids (Qin GM 2015) Transition Metal Photochemistry (Farmer GM 2015)
Metal Pairs (Cornella 2016) Organometallic Oddities (O’Malley 2003)

Preparation of Metal Clusters

Hydrothermal Synthesis

– Crystallization of substances from high temperature conditions. Usually, the reactions are run in aqueous media.
– Most reactions are run in steel pressure vessels in an autoclave, on the order of days.
– The first documented growth of a crystal was by Karl Emil von Schafhäutl with the synthesis of quartz crystal. Robert Bunsen also what a major developer of the technique.
– The production of quartz was done by this method after a whortage occured during WWII.

Solution Synthesis

– Reactions are usually carried out in flasks, filtered, and product is crystallized.
– Sometimes crystallization times are on the order of weeks.
– Examples of clusters generated by this method are polyoxometalates, iron-oxo clusters, etc.

Metal Cluster: (1) Compounds that contain metal-metal bonds. (2) A compound that contains a group of two or more atoms where direct and substantial metal bonding is present.

Examples:

Co₂(CO)₈, $7.6/g (Aldrich) (exists as bridged an non-bridged isomers)

Honey Nut Clusters (crispy wheat & rice flakes with delicious honey nut flavored clusters)

( CURRENTLY UNAVAILABLE FROM AMAZON)

Fullerene - C₆₀ $134/g (Aldrich)

Various metal salts + ligands (if needed) + solvent temperature time

Metal cluster crystals

Metal Cluster History [Clustory?]
Preparation of Metal Clusters (continued)

Solid-state synthesis
- Reactions are usually carried out in alumina or silver boats at very high temperatures.
- Usually reaction times are on the order of days to weeks.
- This method of synthesis is typically used in the preparation of unligated metal salts.
- Products are typically characterized by powder x-ray diffraction analysis.

\[
\begin{align*}
\text{various metal salts} & \quad \text{high temperature (500 – 1200 °C)} \\
& \quad \text{time} \\
\rightarrow & \quad \text{metal cluster powder}
\end{align*}
\]

Reductive methods under CO atmosphere
- Reactions usually start with an air stable oxidized form with stoichiometric metallic reductant.
- Some methods employ 1 atm of CO, while others require harsher pressures.
- Most methods for preparation require inert atmosphere or "filtering under CO."
- Products are typically characterized by elemental analysis and x-ray diffraction.

Example 1:
\[
\text{RhCl}_3 + 2\text{Cu} + 4\text{CO} + \text{NaCl} \longrightarrow \text{Na}[\text{Rh(CO)}_2\text{Cl}]_2 + 2\text{Cu(CO)Cl}
\]
\[
4\text{Na}[\text{Rh(CO)}_2\text{Cl}]_2 + 6\text{CO} + 2\text{H}_2\text{O} \longrightarrow \text{Rh}_4(\text{CO})_{12} + 2\text{CO}_2 + 4\text{NaC} + 4\text{HCl}
\]
- After the transformation, CO atmosphere must be present during all filtration. This
  is not only to prevent the complex from decomposition, but also to prevent
  the precipitation of the insoluble CuCl by decomposition of Cu(CO)Cl.

Example 2:
\[
\text{MnCl}_2 + 2\text{Na} + 2\text{benzophenone} \quad \text{CO (200 atm)} \quad \longrightarrow \quad \text{Mn}_2(\text{CO})_{10}
\]

The Chemistry of Metal-Carbonyl Clusters

Examples of metal carbonyl clusters and their geometry:

- \(\text{Mn}_2(\text{CO})_{10}\)
- \(\text{Fe}_3(\text{CO})_{12}\)
- \(\text{Co}_4(\text{CO})_{12}\)
- \(\text{Tc}_2(\text{CO})_{10}\)
- \(\text{Ru}_3(\text{CO})_{12}\)
- \(\text{Rh}_4(\text{CO})_{12}\)

Most metal carbonyl clusters can form higher order clusters (e.g. \(\text{Co}_4(\text{CO})_{12}\)) that
are useful in catalytic processes (\textit{vide infra}). They are generally soluble in
organic solvent.

- Many heterometallic metal clusters can catalyze reactions such as hydroformylation,
  hydrogenation, desulfurization olefin isomerization and related reactions.
- For an extensive survey of these reactions, see \textit{Chem. Rev. 2015, 115, 28.}
- For a few examples, see below:

\[
\begin{align*}
\text{isomerization of 1,4-COD to 1,3-COD} & \quad \text{isomerization of 1-octene to other isomers} \\
\text{M = Mo, conversion of butane to ethane} & \quad \text{hydrogenation of naphthalene to cis-decalin}
\end{align*}
\]
Reactions promoted/catalyzed by metal carbonyl clusters

**Mn$_2$(CO)$_{10}$**


\[ 4 \overset{\text{Mn$_2$(CO)$_{10}$}}{\rightarrow} \text{THF, 150 °C} \]

product can be hydrogenated or oxidized with Mn still ligated.

**Atom transfer reactions:** *TL*, 2002, 43, 2535.

**Hydrogenation Reaction with (µ-H$_2$)Os$_3$(CO)$_{10}$**


**EtO$_2$CCH=CCO$_2$Et**

isolable by chromatography

**Dalton Trans.**, 2011, 40, 9358.

**CCl$_4$ + **

61% yield

77% yield

59% yield

**RCl$_4$ + **

cat. (3 mol %)

Cl$_2$RC=CHBr

R = CO$_2$Et, 69%; COSPr, 32%

D, 25%

– This study further validated a study done in the past by Kochi (see GM).

– This complex has been shown to be stable in solution, but the addition of ligands like TMEDA (known to enhance cross-coupling) disturbs the stability producing mononuclear species.
Polyoxometalates: Some of the First-discovered Metal Clusters

Lindquist Hexamolybdate structure

Decavanadatedate structure

Dawson Structure \((\text{P}_2\text{M}_{18}\text{O}_{62})^\text{6}\) -6

Keggin Structure \((\text{PW}_{12}\text{O}_{40})^{-3}\)

Top View

Preyssler Structure \((\text{EuP}_5\text{W}_{30}\text{O}_{110})^{-12}\)

Side View

Recent Reactions of Polyoxometalate Clusters


\[
\begin{align*}
\text{R}_1\text{R}_3\text{R}_2 & \quad \text{TBA}_4(\text{W}_{10}\text{O}_{32}) \\
\text{MeO} & \quad \text{MeO} \\
97\% \text{ yield} & \quad 90\% \text{ yield} \\
90\% \text{ yield} & \quad 85\% \text{ yield} \\
\end{align*}
\]


\[
\begin{align*}
\text{Bu}_4\text{N (}\gamma\text{-HPV}_2\text{PW}_{10}\text{O}_{46}) & \quad \text{H}_2\text{O}_2 (1 \text{ equiv}) \\
\text{CH}_3\text{CN-tBuOH, 1 --, 1--4 h} & \quad \text{R}_1\text{R}_3\text{R}_2 \\
92\% \text{ yield} & \quad 75\% \text{ yield} \\
37\% \text{ yield} & \quad 93\% \text{ yield} \\
50\% \text{ yield} & \quad 51\% \text{ yield} \\
\end{align*}
\]

- Reactivity of this Vanadium POM cluster reminiscent of DMDO/TFDO
- Selectivity Governed by catalyst size and not a radical mech!

- Most POMs are synthesized from their parent oxides and structure is controlled by altering pH.
- POMs are non-toxic but have interesting anti-HIV and anti-cancer properties.
**Metal Clusters**

**Arone C-H Oxidation:** Angew. Chem., Int. Ed. 2012, 51, 7275.

Bu₄N (γ-HPV₂PW₁₀O₄₀) (0.05 mol %) H₂O₂ (1 equiv) → R<sub>1</sub>CHO

CH₃CN-tBuOH, 1 →, 1–4 h

<table>
<thead>
<tr>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>OH</td>
<td>63% yield</td>
</tr>
<tr>
<td>MeO</td>
<td>MeO</td>
<td>93% yield</td>
</tr>
<tr>
<td>OH</td>
<td>OH</td>
<td>63% yield</td>
</tr>
<tr>
<td>OMe</td>
<td>MeO</td>
<td>93% yield</td>
</tr>
<tr>
<td>OMe</td>
<td>OH</td>
<td>46% yield</td>
</tr>
<tr>
<td>OH</td>
<td>H</td>
<td>82% yield</td>
</tr>
</tbody>
</table>

**Electrochemical Benzylic Oxidation:** J. Am. Chem. Soc. 2015, 137, 5916.

H₂PV₂PMo₁₀O₄₀ (2 equiv) H₂SO₄ rt → 50 °C

<table>
<thead>
<tr>
<th>CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>97% (96)</td>
</tr>
<tr>
<td>45% (98)</td>
</tr>
<tr>
<td>99% (94)</td>
</tr>
<tr>
<td>99% (98)</td>
</tr>
</tbody>
</table>

- Protonated POM accepts electron from arene producing radical cation.
- Radical cation undergoes proton transfer to form benzylic radical.
- Benzylic radical is further oxidized and captured by water.
- Benzylic alcohol is further oxidized by POM to aldehyde.
- Overoxidation (<1%) is not observed.

**Reactions of Polyoxometalates**

**Carbonylation reactions with POMs:** J. Am. Chem. Soc. 1995, 117, 4704.

TBA₄(W₁₀O₃₂) 550 W Hg lamp (Pyrex filter) CO (~ 9mM)

CH₃CN, 25 °C, 16 h

<table>
<thead>
<tr>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>54 turn. (68 % sel.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18 turn. (69 % sel.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 turn. (85 % sel.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 turn.</td>
<td></td>
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</tr>
</tbody>
</table>

**C-H alkylation/alkenylation:** J. Am. Chem. Soc. 1993, 115, 12212.

TBA₄(W₁₀O₃₂), hv, C₂H₄ or C₂H₂

CH₃CN, rt

<table>
<thead>
<tr>
<th>CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 – 5% conversion</td>
</tr>
</tbody>
</table>

**Dehydrogenation:** J. Am. Chem. Soc. 1990, 112, 6585

TBA₄(W₁₀O₃₂), hv

CH₃CN, rt

<table>
<thead>
<tr>
<th>CO₂Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>58% yield</td>
</tr>
<tr>
<td>61% yield</td>
</tr>
<tr>
<td>52% yield</td>
</tr>
<tr>
<td>90% yield</td>
</tr>
</tbody>
</table>

- Protonated POM accepts electron from arene producing radical cation.
- Radical cation undergoes proton transfer to form benzylic radical.
- Benzylic radical is further oxidized and captured by water.
- Benzylic alcohol is further oxidized by POM to aldehyde.
- Overoxidation (<1%) is not observed.
Iron Sulfur Clusters

- Iron-sulfur clusters are important co-factors in metalloenzymes that participate in substrate binding, electron transfer, and regulation of gene expression.
- Clusters do not form spontaneously in nature but rather require complex biosynthesis to form.
- 120 distinct types of enzymes that contain Fe-S clusters.
- Postulated to have an important role in the origin of life.

Mechanism of Aconitase utilizes an Iron-Sulfur Cluster

- Citric acid is converted to isocitrate through cis-aconitate.
- The dehydration is facilitated by the iron-sulfur cluster acting as a Lewis acid.
- This is one of the few mechanism where the iron cluster does not change oxidation state. Most react in electron transfer processes like the one below.

Iron-sulfur clusters play a role in mitochondria function through electron transport.
Metal Clusters with underdeveloped reactivity

**Inorg. Chem. 2016, 55, 540.**

\[
\text{Cu(OAc)}_2 + \text{K}_2\text{Sb}_2(\text{tartrate})_2 \xrightarrow{1. \text{NaOAc/AcOH}} \xrightarrow{2. \text{K}_2\text{CO}_3} \text{K}_2\text{Sb}_2(\text{tartrate})_2
\]

*Dalton Trans. 1985, 737.*

\[
\begin{align*}
\text{NiCl}_2 + & \xrightarrow{\text{KOH}} \xrightarrow{\text{EtOH}} \text{KOH} \\
\text{CoCl}_2 + & \xrightarrow{\text{KOH}} \xrightarrow{\text{EtOH}} \text{KOH}
\end{align*}
\]


\[
\text{[W}_{18}\text{O}_{54}(\text{SeO}_3)_2]^{-4}
\]


- Several reduction events for the tungsten cage (gray area)
- Orange area is the oxidation of the Se dopant.