Supramolecular Chemistry

Outline

Lecture 8: Assembly of Materials using Hydrogen Bonding

Lecture 9: Assembly of Materials using Metal Ion Complexation

Lecture 10: Applications of New Materials

Handouts:
www.chem.usyd.edu.au/~kepert_c/notes/3c1j/3c1j.htm

Any questions or requests:
c.kepert@chem.usyd.edu.au
Rm 456 (next to 3rd year inorganic lab)
Overview of Last Week
Clathrates: Crystalline Host-Guest Systems
Limitations of the VDW/Hydrogen Bonding Approach to Clathrate Formation

• Only moderate control over the directionality of host-host interactions
  ⇒ limited “design” capabilities, with multiple structure types possible and only limited predictability of structure-property relationships

• Relative weakness of host-host interactions
  ⇒ moderate thermal and chemical stability, slight solubility
  ⇒ flexibility of lattice can limit size/shape selectivity
  ⇒ presence of strong host-guest interactions may have a dramatic influence on which structure-type will form

For many applications, more robust host lattices with better defined structures are required
  ⇒ need stronger, more directional bonds
## Metal Ion Complexation in 2D Supramolecular Assembly

<table>
<thead>
<tr>
<th>Ditopic Subunit</th>
<th>60°</th>
<th>90°</th>
<th>109.5°</th>
<th>120°</th>
<th>180°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ditopic Subunit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>60°</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>90°</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
<tr>
<td>109.5°</td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
</tr>
<tr>
<td>120°</td>
<td><img src="image21.png" alt="Image" /></td>
<td><img src="image22.png" alt="Image" /></td>
<td><img src="image23.png" alt="Image" /></td>
<td><img src="image24.png" alt="Image" /></td>
<td><img src="image25.png" alt="Image" /></td>
</tr>
<tr>
<td>180°</td>
<td><img src="image26.png" alt="Image" /></td>
<td><img src="image27.png" alt="Image" /></td>
<td><img src="image28.png" alt="Image" /></td>
<td><img src="image29.png" alt="Image" /></td>
<td><img src="image30.png" alt="Image" /></td>
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</tbody>
</table>
Metal Ion Complexation in 3D Supramolecular Assembly

<table>
<thead>
<tr>
<th>Ditopic Subunit</th>
<th>Tritopic Subunit</th>
<th>Angle</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>80-90°</td>
<td>trigonal bipyramid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>109°</td>
<td>tetrahedron</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180°</td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>trigonal bipyramid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>109.5°</td>
<td>&quot;double square&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>adamantanoid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°</td>
<td>truncated tetrahedron</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cuboctahedron</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Metal Ion Complexation in 3D Supramolecular Assembly
Metal Ion Complexation in Materials Assembly

The same idea can be used to create extended frameworks.
Molecular Frameworks

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

+ 

(Metal)\textsuperscript{n+} 

\[
\begin{array}{c}
\downarrow \\
\text{Molecular Framework Complexes}
\end{array}
\]
Design and Construction (“Crystal Engineering”)

Diamond structure built from tetrahedral centres

Robson (1990) - generated the first family of compounds where it was possible to reliably predict the structures before the crystals were actually made.

\[
\text{Cu}^{\text{i}} + [\text{Zn}^{\text{ii}}(\text{CN})_4]^{2-} + \text{N}(\text{CH}_3)_4^{+} \rightarrow
\]
Design and Construction ("Crystal Engineering")

Robson (1990) - expanded diamond-type frameworks using larger tetrahedral building units

Void regions within the lattice are filled with anions and solvent of crystallisation ⇒ opportunity for host-guest chemistry
The Hofmann Clathrates

**Building Molecular Squares (1997)**

Cyano-linkage through two *cis*-positions at 90°.
Capping of other sites.

**Building Square Molecular Layers (1897) - the Hofmann Clathrates**

Cyano-linkage through equatorial sites at 90°.
No capping required.

benzene clathrate  biphenyl clathrate
The Hofmann Clathrates: Structures

Strong interactions in 2D (to form rigid layers) but only weak interactions in the 3rd direction
⇒ 2D layers can stack on top of each other in many different ways

This structural flexibility is reflected in the host-guest chemistry, where it is seen that a number of different sizes and shapes of molecules may be accommodated into the voids.
The Hofmann Clathrates: Guest-Exchange Properties

• Despite the flexibility in the layer stacking, the guest-exchange properties of the Hofmann clathrates are greatly more predictable & consistent than those of the Werner clathrates.
  ⇒ the chromatographic properties show no significant dependence on sample history or on which guest molecules are included in the pores.

• Large lattice energy
  ⇒ very good thermal stability (>200 °C)

⇒ Purification of benzene and many other aromatics

⇒ Separation of aromatic amines using three different Hofmann clathrates
The Hofmann Clathrates: Structural Variations

- Bridging of layers leads to the formation of 3D frameworks with improved rigidity and guest-exchange selectivity.
  - Variable bridge-length ⇒ variable pores
The Hofmann Clathrates: Structural Variations

- 3D framework formation by 90° rotation of alternating metal sites
The Prussian Blues

Building Molecular Cubes (1999)

Cyano-linkage through three \textit{cis}-positions at 90°.
Capping of other sites.

Building Cubic Molecular Lattices (1710) - the Prussian Blues

Cyano-linkage through octahedral sites at 90°.
No capping required.
The Prussian Blues: Physical Properties

Host-Guest Properties
- First observation of permanent microporosity (retention of structure following removal of guests to leave voids) in an organic-based material, attributable to the rigid 3D structure. Micropores are only large enough to house very small guest molecules.

Magnetic Properties
- Highest temperature molecule-based magnets known, and the only room temperature magnets yet made that are optically transparent.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c/K$</th>
<th>ordering</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NEt$<em>4$)$</em>{0.5}$Mn$_{1.25}$[VII(CN)$_5$]•2H$_2$O</td>
<td>230</td>
<td>FI</td>
</tr>
<tr>
<td>Cs$<em>2$Mn$</em>{II}$[VII(CN)$_6$]</td>
<td>125</td>
<td>FI</td>
</tr>
<tr>
<td>Cr$<em>{II}$[Cr$</em>{III}$(CN)$_6$]$_2$•10H$_2$O</td>
<td>240</td>
<td>FI</td>
</tr>
<tr>
<td>V$<em>{II.4}$V$</em>{III.6}$[Cr$_{III}$(CN)$<em>6$]$</em>{0.86}$•3H$_2$O</td>
<td>310</td>
<td>FI</td>
</tr>
<tr>
<td>Cs$<em>{0.75}$Cr$<em>II$</em>{1.125}[Cr$</em>{III}$(CN)$_6$]•5H$_2$O</td>
<td>190</td>
<td>FI</td>
</tr>
<tr>
<td>CsMn$<em>{II}$[Cr$</em>{III}$(CN)$_6$]•H$_2$O</td>
<td>90</td>
<td>FI</td>
</tr>
<tr>
<td>CsNi$<em>{III}$[Cr$</em>{III}$(CN)$_6$]•2H$_2$O</td>
<td>90</td>
<td>F</td>
</tr>
<tr>
<td>Mn$<em>{II.2}$[Cr$</em>{III}$(CN)$_6$]$_2$•15H$_2$O</td>
<td>66</td>
<td>FI</td>
</tr>
<tr>
<td>Ni$<em>{II.2}$[Cr$</em>{III}$(CN)$_6$]$_2$•15H$_2$O</td>
<td>53</td>
<td>F</td>
</tr>
<tr>
<td>Cu$<em>{II.3}$[Cr$</em>{III}$(CN)$_6$]$_2$•15H$_2$O</td>
<td>66</td>
<td>F</td>
</tr>
<tr>
<td>(NMe$<em>4$)$<em>2$Mn$</em>{II}$[Cr$</em>{III}$(CN)$_6$]•4H$_2$O</td>
<td>59</td>
<td>FI</td>
</tr>
<tr>
<td>K$<em>2$Mn$</em>{II}$[Mn$_{III}$(CN)$_6$]</td>
<td>41</td>
<td>FI</td>
</tr>
<tr>
<td>CsNi$<em>{III}$[Mn$</em>{III}$(CN)$_6$]•H$_2$O</td>
<td>42</td>
<td>F</td>
</tr>
<tr>
<td>Ni$<em>{II.2}$[Mn$</em>{III}$(CN)$_6$]$_2$•12H$_2$O</td>
<td>30</td>
<td>F</td>
</tr>
<tr>
<td>CsMn$<em>{II}$[Mn$</em>{III}$(CN)$_6$]•1/2H$_2$O</td>
<td>31</td>
<td>FI</td>
</tr>
<tr>
<td>Mn$<em>{II.3}$[Mn$</em>{III}$(CN)$_6$]$_2$•11H$_2$O</td>
<td>37</td>
<td>FI</td>
</tr>
<tr>
<td>(NMe$<em>4$)$<em>2$Mn$</em>{II}$[Mn$</em>{III}$(CN)$_6$]•8H$_2$O</td>
<td>29</td>
<td>FI</td>
</tr>
<tr>
<td>Mn$<em>2$[Mn$</em>{IV}$(CN)$_6$]•xH$_2$O</td>
<td>49</td>
<td>FI</td>
</tr>
<tr>
<td>Fe$<em>{II.4}$[Fe$</em>{II}$(CN)$_6$]$_3$•xH$_2$O</td>
<td>5.6</td>
<td>F</td>
</tr>
<tr>
<td>Co$<em>{II.3}$[Fe$</em>{III}$(CN)$_6$]$_2$•14H$_2$O</td>
<td>14</td>
<td>FI</td>
</tr>
<tr>
<td>Ni$<em>{II.3}$[Fe$</em>{III}$(CN)$_6$]$_2$•14H$_2$O</td>
<td>23</td>
<td>F</td>
</tr>
<tr>
<td>Cu$<em>{II.3}$[Fe$</em>{III}$(CN)$_6$]$_2$•12H$_2$O</td>
<td>14</td>
<td>FI</td>
</tr>
<tr>
<td>Mn$<em>{II.3}$[Fe$</em>{III}$(CN)$_6$]$_2$•15H$_2$O</td>
<td>9</td>
<td>FI</td>
</tr>
</tbody>
</table>
Use of Larger Connecting Units: Extended Networks with 4,4’-Bipyridine

- Hofmann-type structures form with square planar coordination. Larger squares (~ 11 Å, cf. 5 Å for Hofmann) permits guest migration through the layers
  ➞ increased rate of guest-exchange
  ➞ better size-selectivity

- The first observation of heterogeneous catalysis by a porous molecular solid (cyanosilation of aldehydes)
Use of Larger Connecting Units: Extended Networks with Carboxy Ligands

A large number of metal ion complexes of carboxy ligands are known, with a wide range of geometries. These can be linked together if multiply coordinating carboxy ligands are used.
MOF-5: Prussian Blue-type Structure with Terephthalate (1,4-benzene dicarboxylate, bdc)

- The \([\text{Zn}_4\text{O(O}_2\text{CR})_6]\) complex is an octahedral species with very high thermal stability.

  Linkage of \([\text{Zn}_4\text{O(O}_2\text{CR})_6]\) centres through bdc “struts”

Microporous material with 19 Å cavities that is stable to 300 °C
MOF-5: Microporosity

Up-take and release of guest molecules is fully reversible (removal of guests leaves lattice intact)

Table 1 Gas and liquid vapour sorption in desolvated MOF-5

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>$T$ ($^\circ$C)</th>
<th>Amount sorbed (mg g$^{-1}$)</th>
<th>Sorbate molecules per unit cell</th>
<th>Free volume (cm$^3$ g$^{-1}$)</th>
<th>Free volume (cm$^3$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>-194</td>
<td>1,492</td>
<td>230</td>
<td>1.03</td>
<td>0.61</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-194</td>
<td>831</td>
<td>183</td>
<td>1.04</td>
<td>0.61</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>22</td>
<td>1,211</td>
<td>88</td>
<td>0.93</td>
<td>0.55</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>22</td>
<td>1,367</td>
<td>71</td>
<td>0.94</td>
<td>0.55</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>22</td>
<td>802</td>
<td>63</td>
<td>0.94</td>
<td>0.55</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>22</td>
<td>1,472</td>
<td>59</td>
<td>0.94</td>
<td>0.56</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>22</td>
<td>703</td>
<td>51</td>
<td>0.92</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Zn$_3$(btc)$_2$(OH$_2$)$_3$.x[guest]
(btc = 1,3,5-benzenetricarboxylate)

Square Planar + Triangular Connectors:

[Zn$_2$(Ac)$_4$] + btc → Pt$_3$O$_4$ network
POST-1: Chiral Framework Formation using Chiral Ligands

stacking of 2D layers through which run 13 Å cavities
POST-1: Enantioselective Catalysis

Transesterification of Esters

Replacement of EtOH with racemates of chiral alcohols leads to enantioselective catalyses to produce products with ee ~ 8%