Supramolecular Chemistry

Outline

Lecture 11: Assembly of Materials using Hydrogen Bonding
Lecture 12: Assembly of Materials using Metal Ion Complexation
Lecture 13: Applications of New Materials

Handouts:

Any questions or requests:
c.kepert@chem.usyd.edu.au
Rm 456

Discovery of Clathrates

Powell (1947): crystallisation of hydroquinone in the presence of SO₂

1D channels filled with disordered SO₂.

Application of heat or vacuum leads to the liberation of SO₂ gas and the irreversible collapse of the structure.

“Clathrate” - a host that forms a cage structure imprisoning a guest.

Classification / Categorisation

Categorise inclusion (host-guest) compounds according to two features:
(a) the type of host-guest interaction
(b) the structure of the host

Interaction:
- Coordination ⇒ Complex (1)
- VDW ⇒ Cavitate/Clathrate (2,3)

Structure:
- Lattice ⇒ Clathrate (2)
- Molecular ⇒ Cavitate (3)

For intermediate forms of interaction: “coordinatoclathrates”, “clathratocomplexes”, etc.

Bibliography

  - Vol. 6 - Solid State Supramolecular Chemistry: Crystal Engineering
  - Vol. 7 - Solid State Supramolecular Chemistry: Two and Three Dimensional Inorganic Networks
  - Vol. 8 - Physical Methods in Supramolecular Chemistry
  - Vol. 9 - Templating, Self-Assembly and Self-Organisation
  - Vol. 10 - Supramolecular Technology
  - Vol. 1 - Structural Aspects of Inclusion Compounds Formed by Inorganic and Organometallic Host Lattices
  - Vol. 2 - Structural Aspects of Inclusion Compounds Formed by Organic Host Lattices
  - Vol. 3 - Physical Properties and Applications
  - Vol. 4 - Key Organic Host Systems
### Classifying Clathrates

*Evaluating the strengths of host-host and host-guest interactions:*

- **a** - no strong interactions (“true” clathrate)
- **b** - strong host-host interactions (coordination-assisted clathrate)
- **c** - strong host-guest interactions (coordinatoclathrate)
- **d** - strong host-host and strong host-guest interactions (coordinatoclathrate in a coordination-assisted clathrate)

### Werner Complexes: Structure

\[ \text{M(NCS)\textsubscript{2}(4-MePy)\textsubscript{4}} \quad (\text{M = Co(II), Ni(II), Fe(II), Mn(II), Cu(II)}) \]

- recryst. from many non-aromatic solvents
- (dense structure)

### Clathrates of Werner Complexes: Structures

- Recryst in the presence of aromatics (and many non-aromatics)
  \[ \Rightarrow \text{M(NCS)\textsubscript{2}(4-MePy)\textsubscript{4}.x[guest]} \]

### Clathrates of Werner Complexes: Physical Properties

- Lack of strong host-host interactions
  \[ \Rightarrow \text{great structural flexibility in the up-take of guest molecules} \]
**Clathrates of Werner Complexes: Physical Properties**

- Highly unconventional behaviours arise from the great flexibility of the host.
- Properties depend strongly on the composition (and therefore structure) of the clathrate.

**Werner Complexes: Chromatographic Applications**

The rapid exchange of guest molecules from clathrates makes them suitable as stationary phases in chromatography:
- Sensitivity to chemical functionalities
- Sensitivity to size/shape

Problem: enormous flexibility of host means that the size/shape selectivity depends critically on the structure (which may change!)

- e.g., The same separation with 5 different clathrates of the Ni(II) Werner complex.

**Urea**

Crystallisation from vast majority of solvents

Dense hydrogen-bonded phase with no guest inclusion

Note: Hydrogen bond energy $\sim$ 30 kJ/mol

**Urea**

Crystallisation in the presence of long-chain molecules

Hexagonal, chiral phase with guest inclusion

Strong host-host interactions

Channel diameter = 5.25 Å
Chiral resolution may occur by several mechanisms (generally true for all chiral clathrate hosts constructed with *achiral* building units), all of which rely on the fact that the *energy of inclusion* of opposite enantiomers in a chiral lattice differs. The extent of this energy difference depends on the nature of the host-guest interaction and sets the limit for the efficiency of any chiral resolution processes.

1) **Chiral selectivity of the crystallisation process**
   - Ideally, one enantiomer crystallises out in the inclusion compound while the other remains in solution.
   - (a) seeding of crystal growth by a single crystal (single enantiomer) or by other types of chiral surface (e.g., hair, etc.)
   - (b) small excess of one enantiomer ⇒ preferential crystallisation, which may be successively increased by repetition
   - (c) presence of chiral cosolute decreases solubility of one enantiomer

2) **Guest-exchange using a chirally-resolved host**
   Growth of 100% right- or left-handed helices may be achieved using chiral templates.
   - (a) stationary phase in chromatography
   - (b) cyclic processes involving selective sorption then desorption by heating, etc.

**Enantioseparation using clathrates of chiral molecules**
As above, but simpler, since clathrate crystals are homochiral without the need for seeding or preferential crystallisation.
- e.g., cyclodextrins, ...

**Thiourea**

- **H₂NCSH₂N**
- Crystallisation in the presence of long-chain and branched molecules
- Hexagonal, achiral phase with guest inclusion
- Channel diameter = 6.1 Å

**Use of Homochiral Building Units:**
*exo-2,exo-6-Dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane*
Other Notable Molecules that form Clathrates

- Tri-o-thymotide (TOT)
- Dianin’s Compound
- Organophosphazenes
- Trimesic Acid

… plus hundreds of other molecules that don’t pack together well, have well-defined directional interactions that favour open structures, and/or have strong host-guest interactions that favour inclusion ...

Bis(resorcinol)anthracene

Bis(resorcinol)anthracene: Competitive Cocry stallisation from a Mixture of Two Guests

Heterogeneous Catalysis of Diels-Alder Reactions by Bis(resorcinol)anthracene Hosts

- Rate of catalysis depends linearly on solid volume, not surface area or extent of dissolution, so the catalysis occurs within the lattice and is driven by steric effects.
**Bis(resorcinol)anthracene: Structural Variability/Flexibility**

- Variability of the hydrogen-bonding geometry allows for different conformation of the layers, which may vary with guest-exchange

- This flexibility causes the material to collapse to a dense phase following removal of guests, as seen also with previous clathrates.

**Bis(resorcinol)anthracene: Structural Variability cont’d**

- Hydrogen bonding guests may upset the layer arrangement

---

**Tetra(carboxy)tetrathiafulvalene (TC-TTF)**

- A planar molecule with multiple hydrogen bonding sites with a very strong tendency towards π-π stacking.

---

**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
  - 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