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:
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Rm 456 (next to 3rd year inorganic lab)

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 ⇒ CavitatelClathrate (2,3)

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

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

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**Werner Complexes: Structure**

M(NCS)$_2$(4-MePy)$_4$ (M = Co(II), Ni(II), Fe(II), Mn(II), Cu(II))

- Recryst. from many non-aromatic solvents
- Dense structure

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**Clathrates of Werner Complexes: Structures**

- Recryst in the presence of aromatics (and many non-aromatics) ⇒ M(NCS)$_2$(4-MePy)$_4$.x[guest]

- $p$-xylene clathrate
- Naphthalene clathrate

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**Clathrates of Werner Complexes: Physical Properties**

- Lack of strong host-host interactions ⇒ 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.

Sorption of Hg (vap)

\[ \text{x-axis = pressure Hg} \]
\[ \text{y-axis = uptake} \]

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

\[ \text{Dense hydrogen-bonded phase with no guest inclusion} \]

Note: Hydrogen bond energy \(\sim 30 \text{ kJ/mol}\)

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

- Moderate host-host interactions
- 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:** Competitive Cocrystillisation from a Mixture of Two Guests

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**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.

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- JACS, 120, 8539 (1998); JACS, 119, 4117 (1997); JACS, 118, 5562 (1996); JACS, 117, 8341 (1995)
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.