Chalcogen Bonding and Perplexing Coordination Behaviour of Bipyridine Donors in the Coordination Chemistry of Zinc-Triad 1,1-Dithiolate Compounds

Edward R.T. Tiekink
Research Centre for Crystalline Materials
Faculty of Science and Technology

INTERNATIONAL CONFERENCE ON APPLIED SCIENCES MATHEMATICS AND INFORMATICS (ICASMI)

Crystal Engineering

Synthetic chemists: make molecules (covalent bonding)

CE's: design crystals (parts of crystals) by controlling intermolecular interactions, e.g. hydrogen-bonding, halogen-bonding, secondary bonding, π-π, C-H…O, C-H…π, "emerging" interactions, etc.

Why molecules pack as they do

1,1-dithiolates
Secondary bonding
Extended architectures mediated by bipyridyl bridges
Perplexing results

Synthesis

Metathesis: $AX_2 + 2MS_2COR \rightarrow A(S_2COR)_2 + 2MX$
Structure of $\text{Hg} \left( \text{S}_2 \text{CN} \text{Et}_2 \right)_2$

Steric effects and secondary bonding

"$\text{Hg} \left( \text{S}_2 \text{CN} \text{R}_2 \right)_2$"

"Secondary Bonding" (Tetrel, Pnictogen & Chalcogen)

Steric effects and secondary bonding

$\text{Se}$: $\text{O}$ in Ebselen®

polar gap, $\sigma$-hole: $\sim 8$ kcal/mol

Sum of the van der Waals radii for $\text{Hg}$ and $\text{S} = 3.35 \, \text{Å}$

increasing size of $\text{R}$

Conclusion #1

Systematic analyses enables new design elements for crystal engineering

Coordination polymers (MOF's) of zinc-triad elements

Solid-state polymers cf. solution

$\text{A} \left( \text{S}_2 \text{COR} \right)_{n}$ + bridging ligands

Applications: gas storage/sensing; catalysis; luminescence; energy storage; crystal sponge...

"ICASMI 2017: The Role and Innovation of Sciences in the Strengthening of Natural Resources"
Implications for solid-state luminescence

J.-G. Kang
Crystallisation with an excess bpe leads to a lattice adduct

Zinc(dithiocarbamate)$_2$ + bpe

$R = \text{Me}$

$R = \text{Et}$

$R = \text{iPr}$

Crystallisation with an excess bpe leads to a lattice adduct

Zinc(dithiocarbamate)$_2$ + bpe

Explanation: electronic effects

Cadmium(dithiocarbamate)$_2$ + bpe #1

$R = \text{Et}$

Increase the size of the metal centre

Conclusions #2

One can control supramolecular aggregation in metal 1,1-dithiolates by:

- electronic effects
- size of the central element
Introducing hydrogen-bond functionality into dithiocarbamate ligands

\[ \text{Cadmium(dithiocarbamate)}_2 + \text{bpe #2} \]

Product regardless of the ratio of reagents 2:1, 1:1 and 1:2

\[ \text{R} = \text{iPr} \]

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Conclusions #3

Perplexing!

- unexpected reaction products
- stoichiometry "doesn't matter"
- hydrogen-bonding is competitive with coordinate-bonding
- more experiments are needed!