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

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## Crystal Engineering

Synthetic chemists: make molecules (covalent bonding)

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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

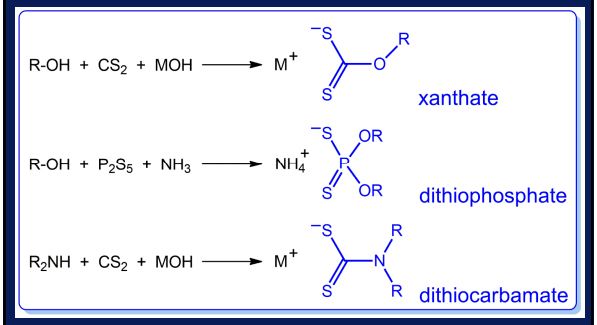
1,1-dithiolates

Secondary bonding

Extended architectures mediated by bipyridyl bridges

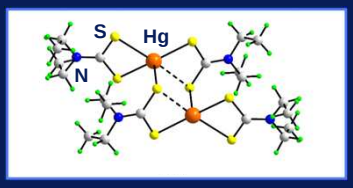
Perplexing results

## Synthesis

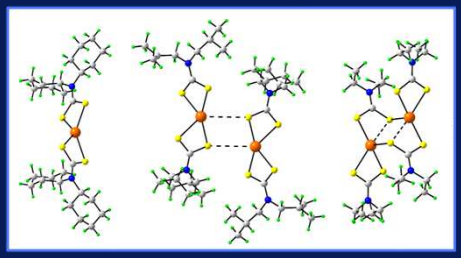



**Metathesis:** $AX_2 + 2\ MS_2COR \longrightarrow A(S_2COR)_2 + 2MX$

## Structure of $Hg(S_2CNEt_2)_2$

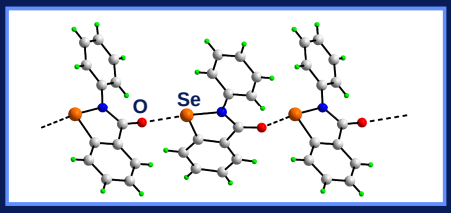



## Steric effects and secondary bonding



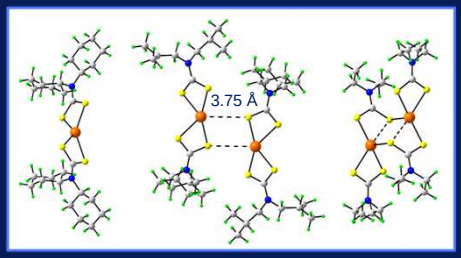
"$Hg(S_2CNR_2)_2$"

## "Secondary Bonding" (Tetrel, Pnictogen & Chaclogen)




Se···O in Ebselen®
polar gap, σ-hole; ~8 kcal/mol

## Steric effects and secondary bonding




"$Hg(S_2CNR_2)_2$"
Sum of the van der Waals radii for Hg and S = 3.35 Å

← increasing size of R

## Conclusion #1

Systematic analyses enables new design elements for crystal engineering

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

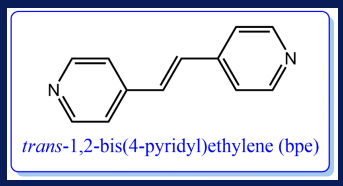
Solid-state polymers cf. solution

$A(S_2COR)_2$ + bridging ligands

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

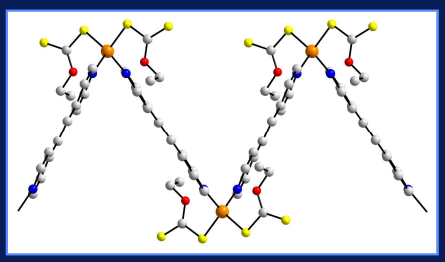
"ICASMI 2017: The Role and Innovation of Sciences in the Strengthening of Natural Resources"

## Zinc(1,1-dithiolate)$_2$ + bpe



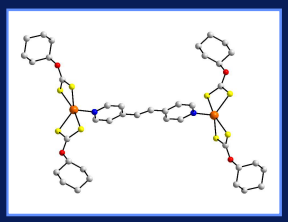

*trans*-1,2-bis(4-pyridyl)ethylene (bpe)

## Zinc(xanthate)$_2$ + bpe



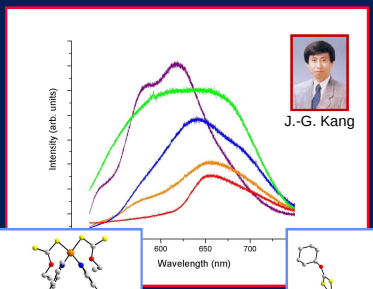
R = Et

## Zinc(xanthate)$_2$ + bpe



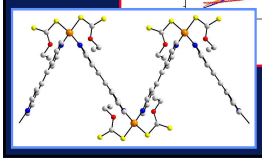
R = Cy

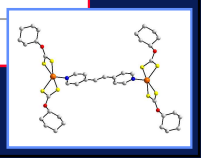
## Implications for solid-state luminescence





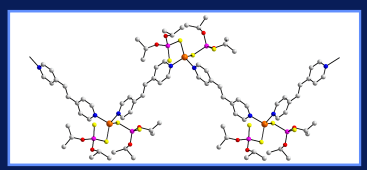

J.-G. Kang

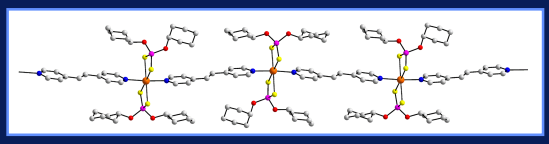




## Zinc(dithiophosphate)$_2$ + bpe

R = iPr

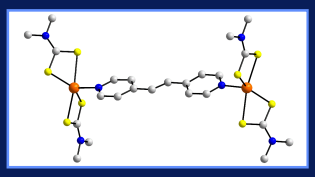




R = Cy

## Zinc(dithiocarbamate)$_2$ + bpe

R = Me

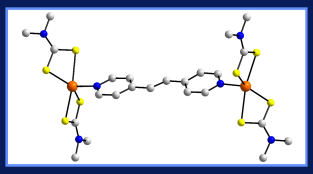


## Zinc(dithiocarbamate)$_2$ + bpe

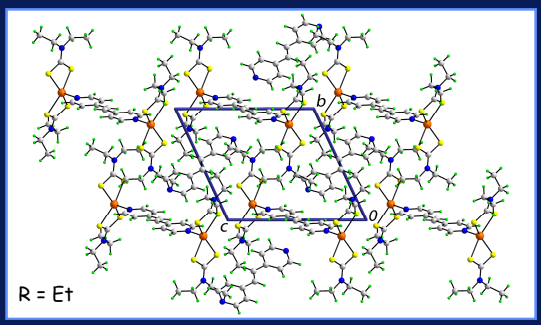
R = Me

R = Et

R = iPr

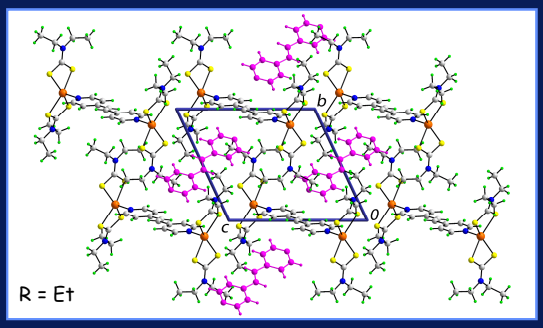


## Zinc(dithiocarbamate)$_2$ + bpe



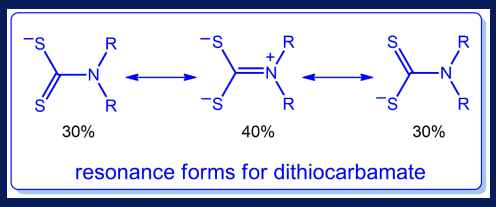

Crystallisation with an excess bpe leads to a lattice adduct

## Zinc(dithiocarbamate)$_2$ + bpe




Crystallisation with an excess bpe leads to a lattice adduct

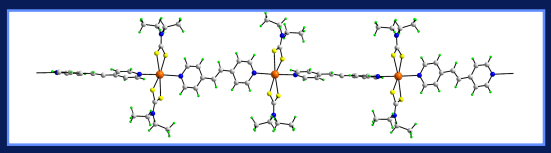
## Explanation: electronic effects




Effective chelator for metals and reduces Lewis acidity

## Cadmium(dithiocarbamate)$_2$ + bpe # 1

R = Et



Increase the size of the metal centre

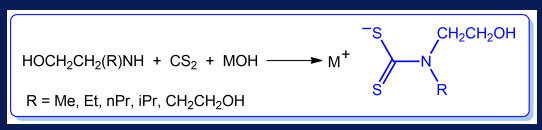
## Conclusions #2

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

electronic effects

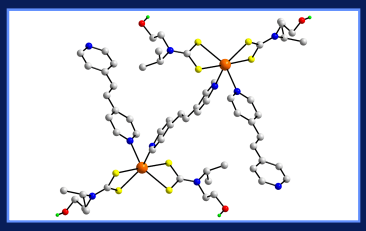
size of the central element

## Introducing hydrogen-bond functionality into dithiocarbamate ligands




## Cadmium(dithiocarbamate)$_2$ + bpe #2

R = iPr



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

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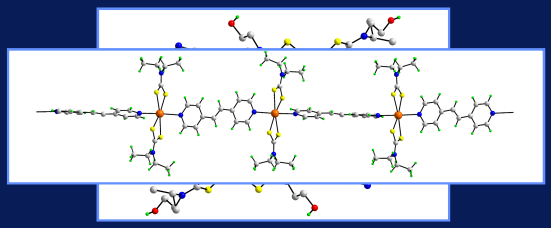
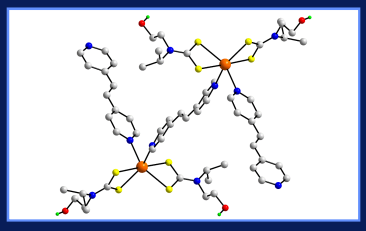
R = iPr



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

## Cadmium(dithiocarbamate)$_2$ + bpe #2

R = iPr



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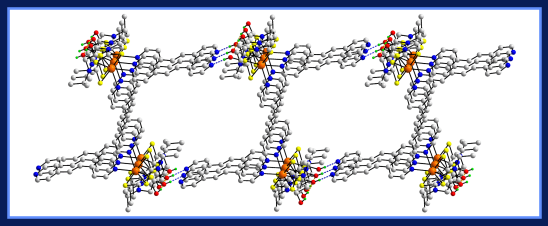
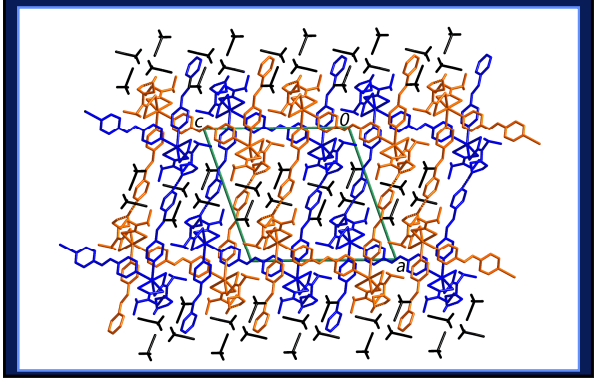
## Cadmium(dithiocarbamate)$_2$ + bpe #2

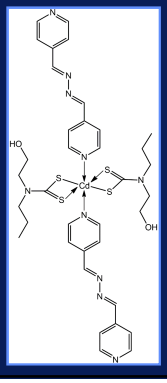
R = iPr



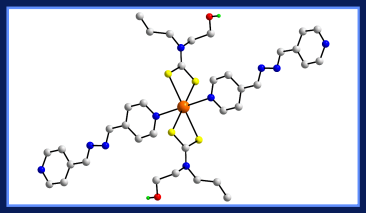
## Cadmium(dithiocarbamate)$_2$ + bpe #2



## $Cd[S_2C(iPr)CH_2CH_2OH]_2$ + 4-pyridinealdazine



1:1



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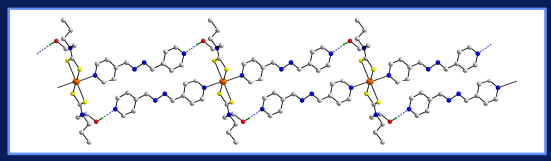

## Conclusions #3

Perplexing!

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

## Sunway University

Fortuna Eruditis Favet ("*Fortune favours the prepared mind*")