Recent Advances in the Understanding of Element(Lone-Pair)…π(Arene) Interactions Operating as Supramolecular Synthons

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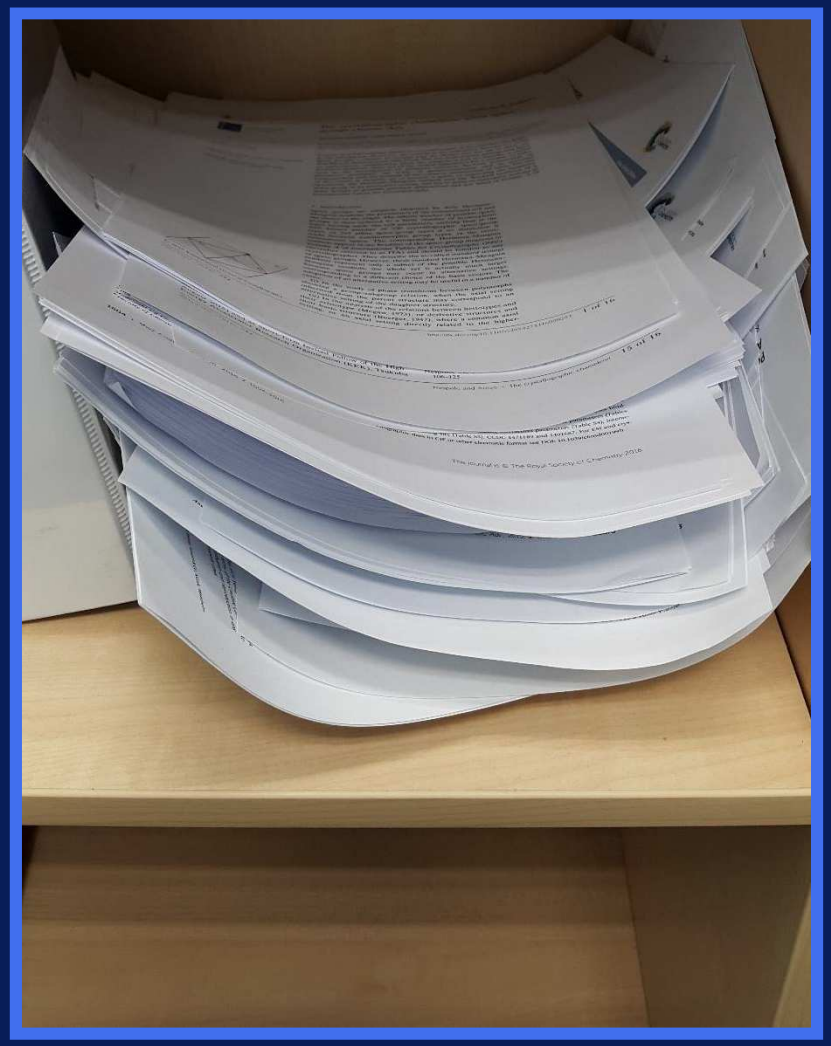
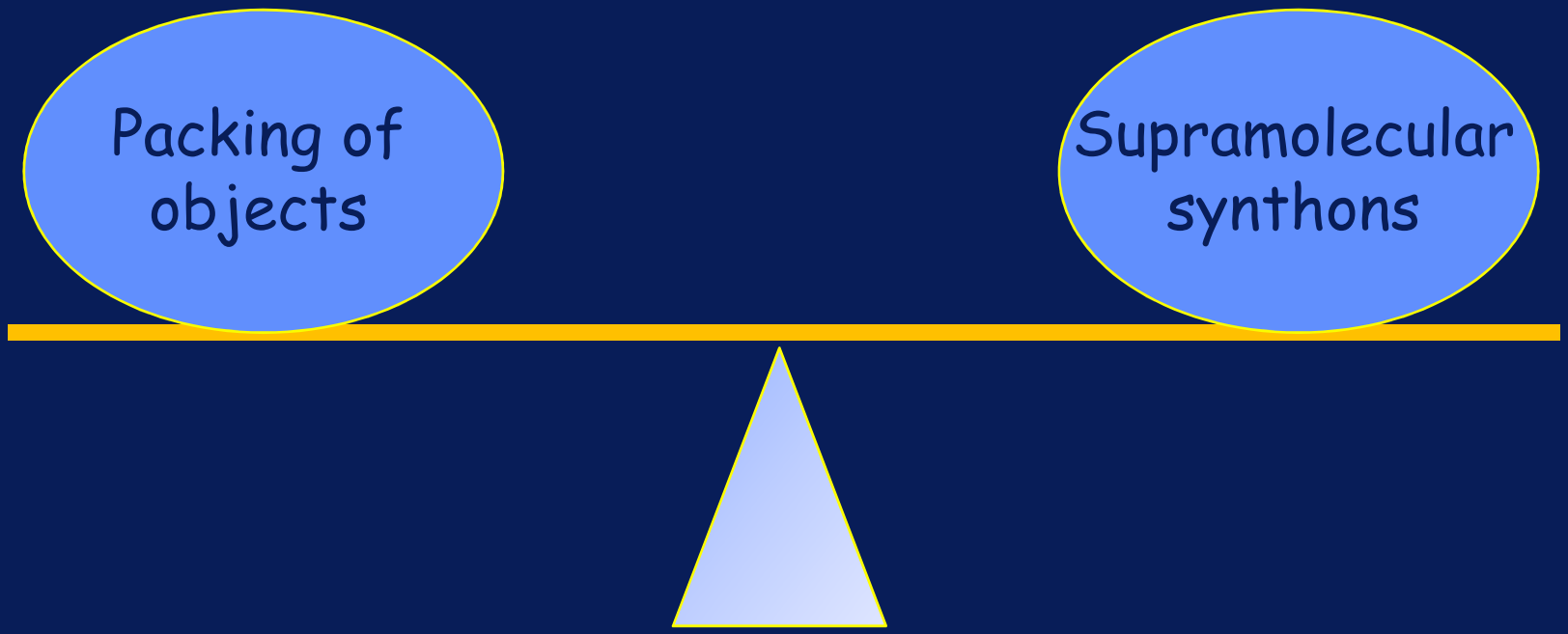
1st SEACCE, September 2016

Factors that Make SEACCE Great!



Factors that Control Molecular Packing



Points of Contact/Recognition Between Molecules in Crystals

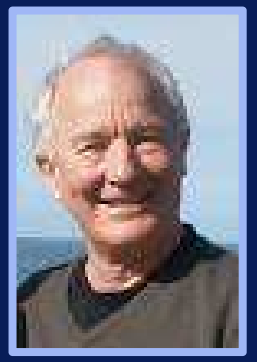
Hydrogen-bonding & coordinate bonds

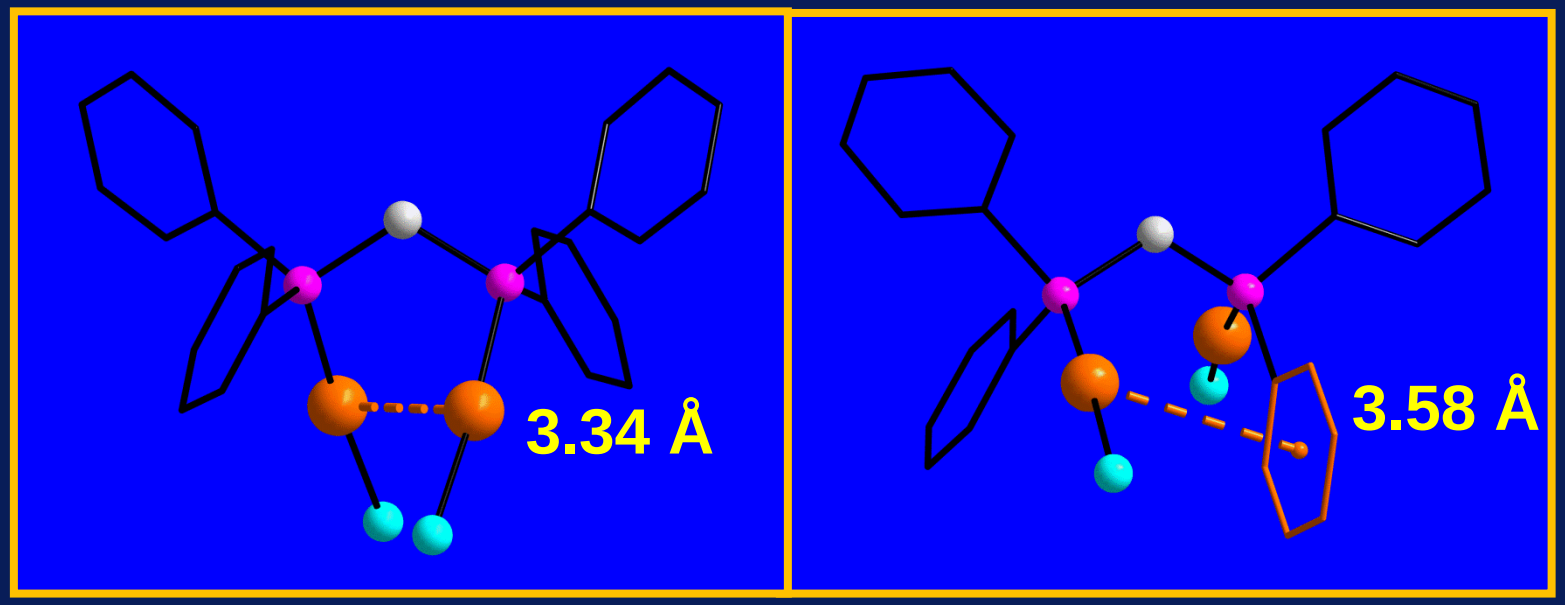
π···π, C—H···X, C—H···π, halogen bonding
M···X, M···M

Others:

C—H···π(chelate), lone-pair···π, tetrel, pnictogen, chalcogen…

Polymorphs of $(dppm)(AuCl)_2$



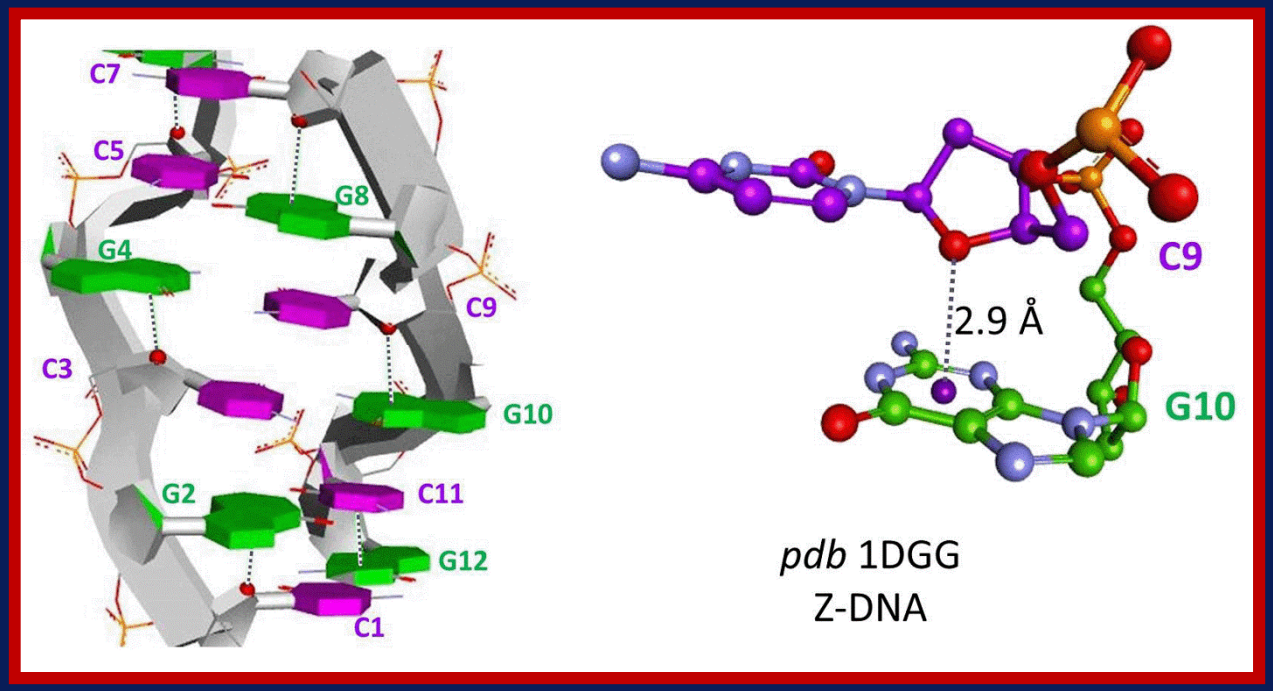


Schmidbaur *et al.* (1977)

Healy (2003)

Bio-inspiration

(O)lone pair…π(guanidinium) interaction stabilises the left-handed Z-DNA duplex



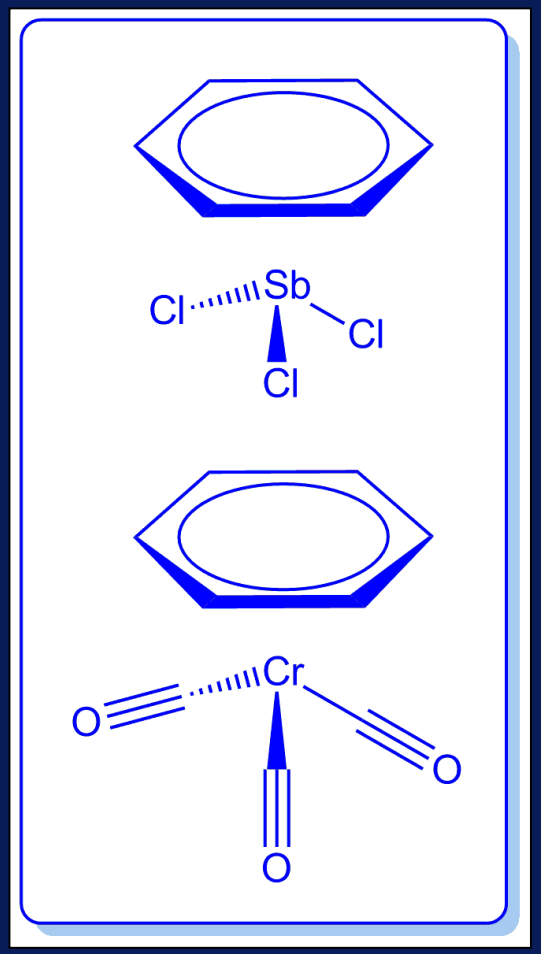
400 proteins: 1.5 kJ mol^{-1} to 5.1 kJ mol^{-1}

Egli & Gessner, *PNAS*, 1995, **92**,180; Jain *et al*., *Protein Sci*., 2009, **18**, 595

The pre-bio-inspiration

Menšutkin complexes

1874 - 1938

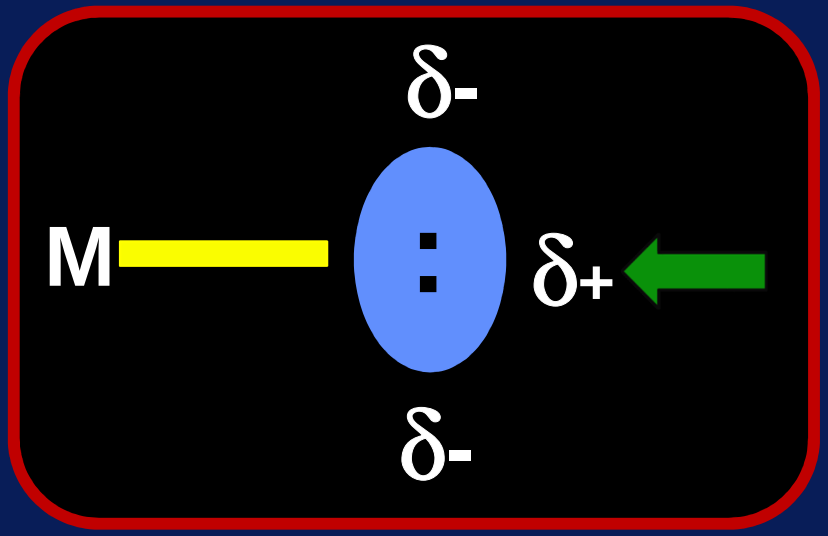


Davies, *J. Chem. Educ.*, 1938, **15**, 203; Schmidbaur & Schier, *Organometallics*, 2008, **27**, 2361.

Bonding Considerations

M….π(arene) - HOMO donating to metal

M(lp)….π(arene) - cf. halogen bonding



i.e. polar positive hole

As to Bi: 6-9 kJ.mol^{-1}

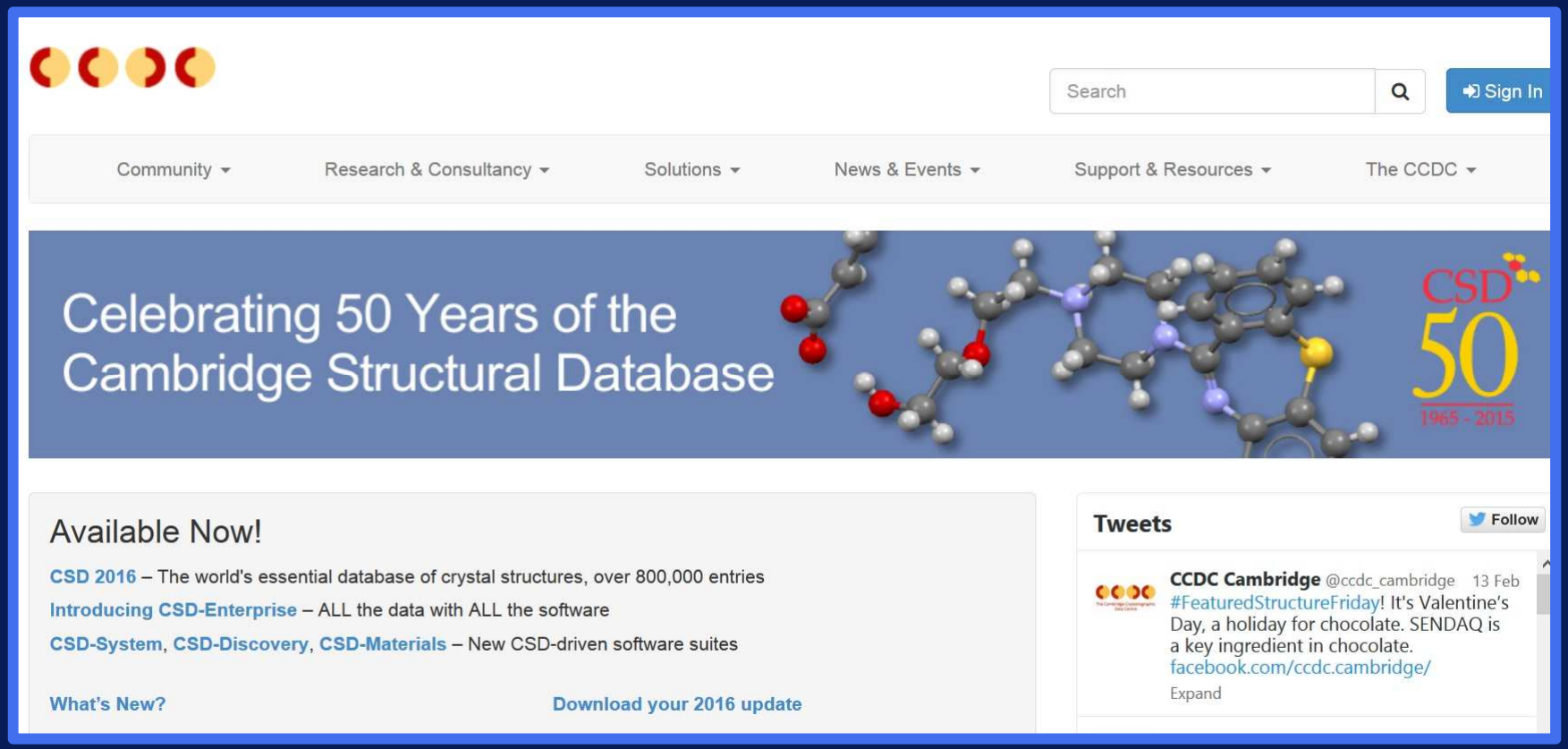
Expt'l (Sb): 20-40 kJ.mol^{-1}

ChemPhysChem, 2012, **14**, 14061.

Energy considerations:

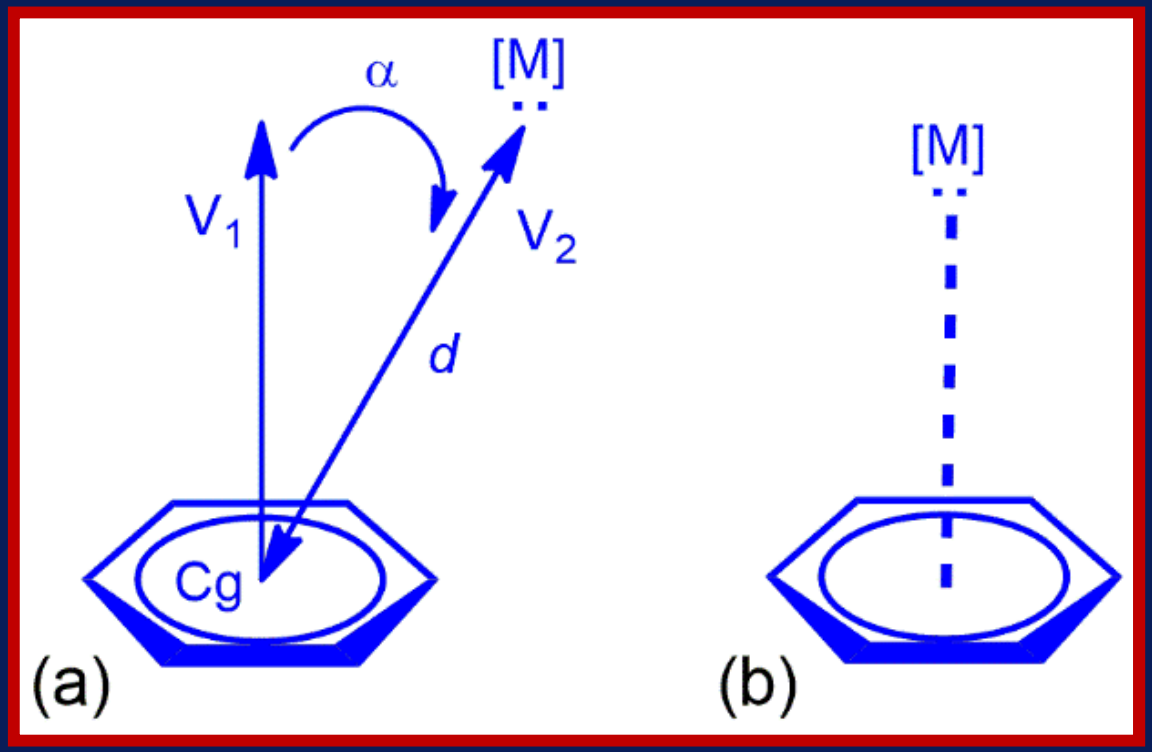
	kJ mol^{-1}
O—H···O	20 - 65
π···π	8 - 40
C—H···O	4 - 16
C—H···π	1 - 8

Data mining: > 800,000 deposited structures

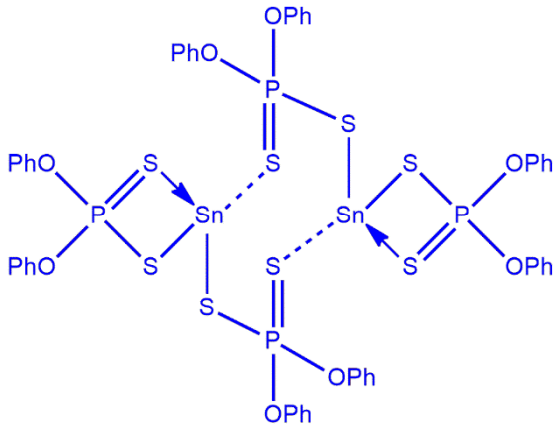


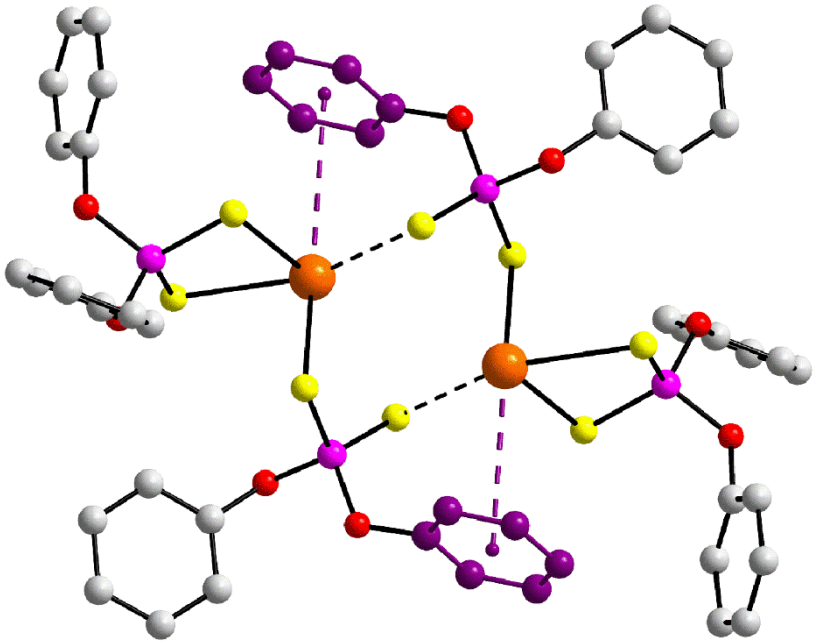
http://www.ccdc.cam.ac.uk/

Search Protocols

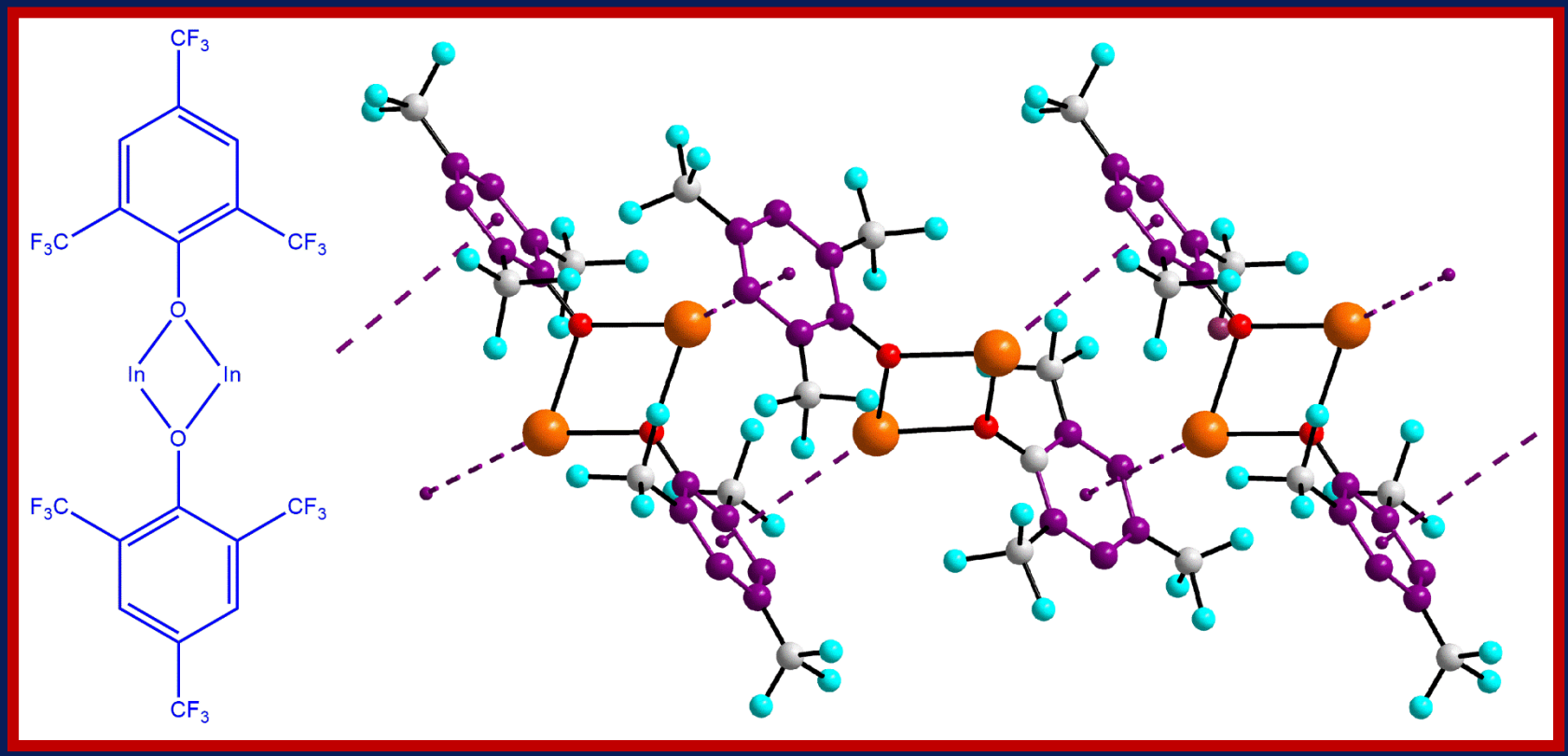


Search Protocols

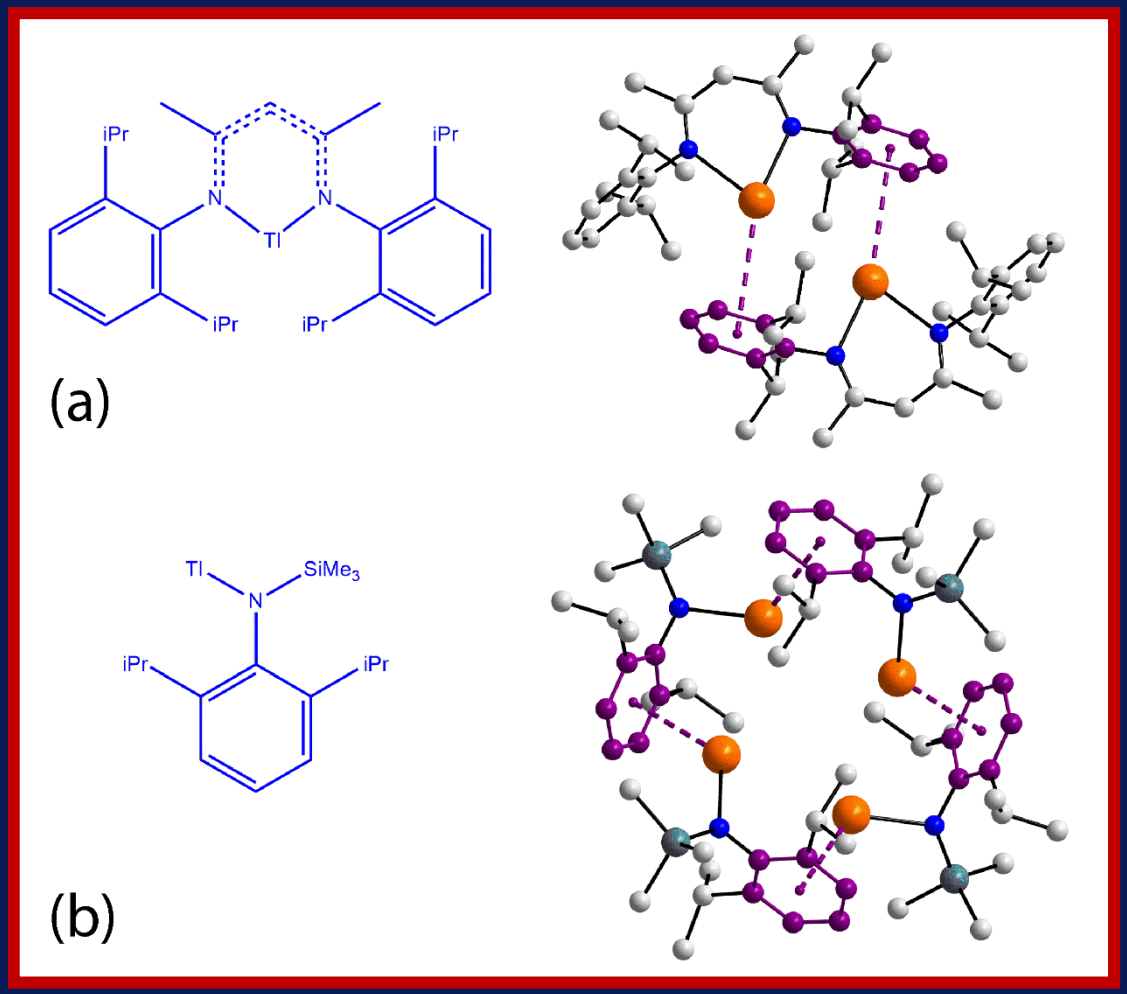




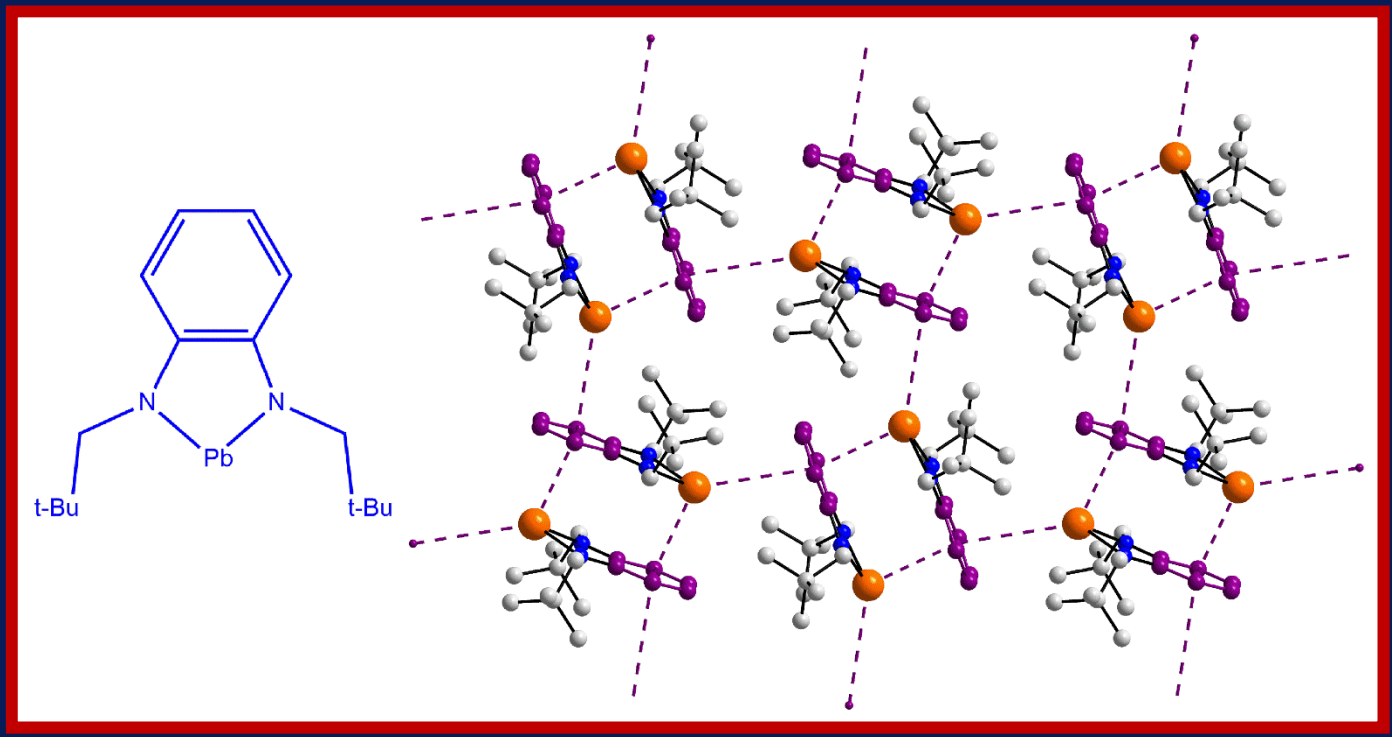
Cooperation: EXCLUDED



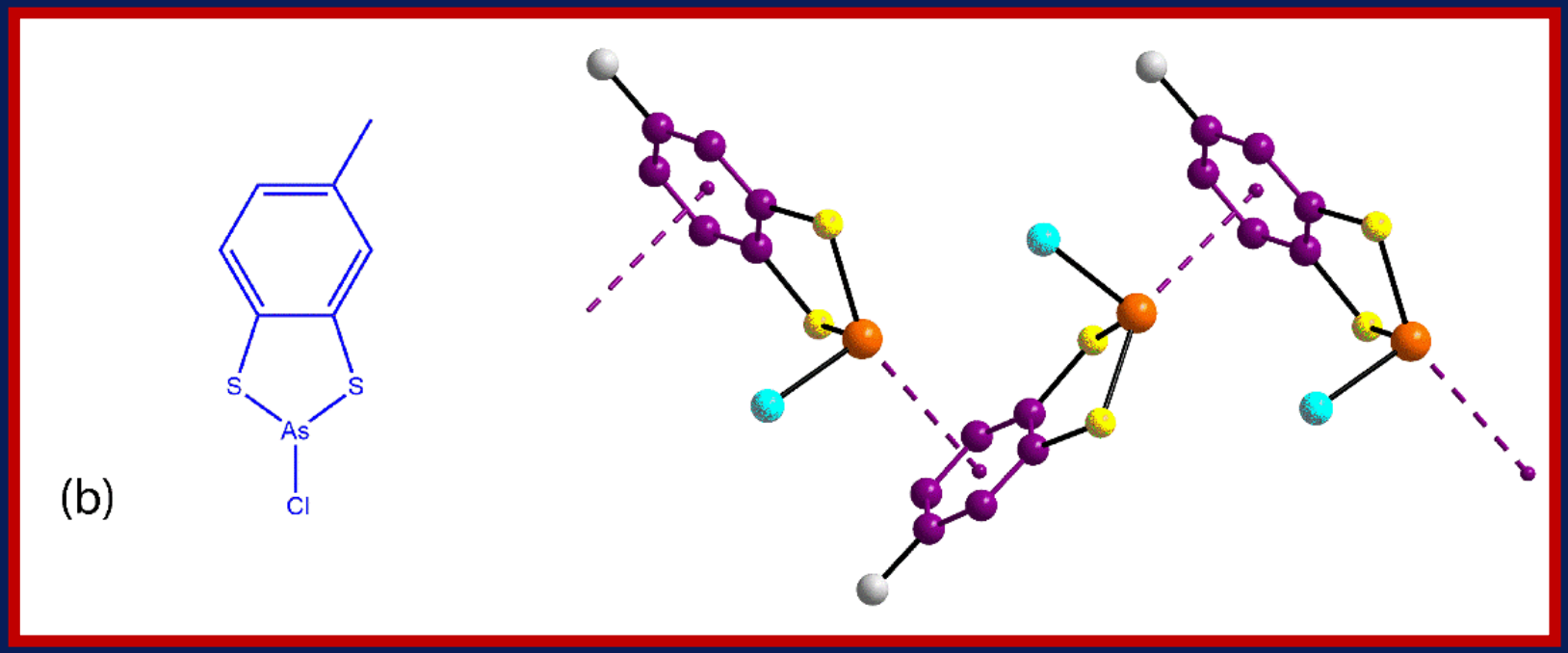
Binuclear, indium(I): 1-D



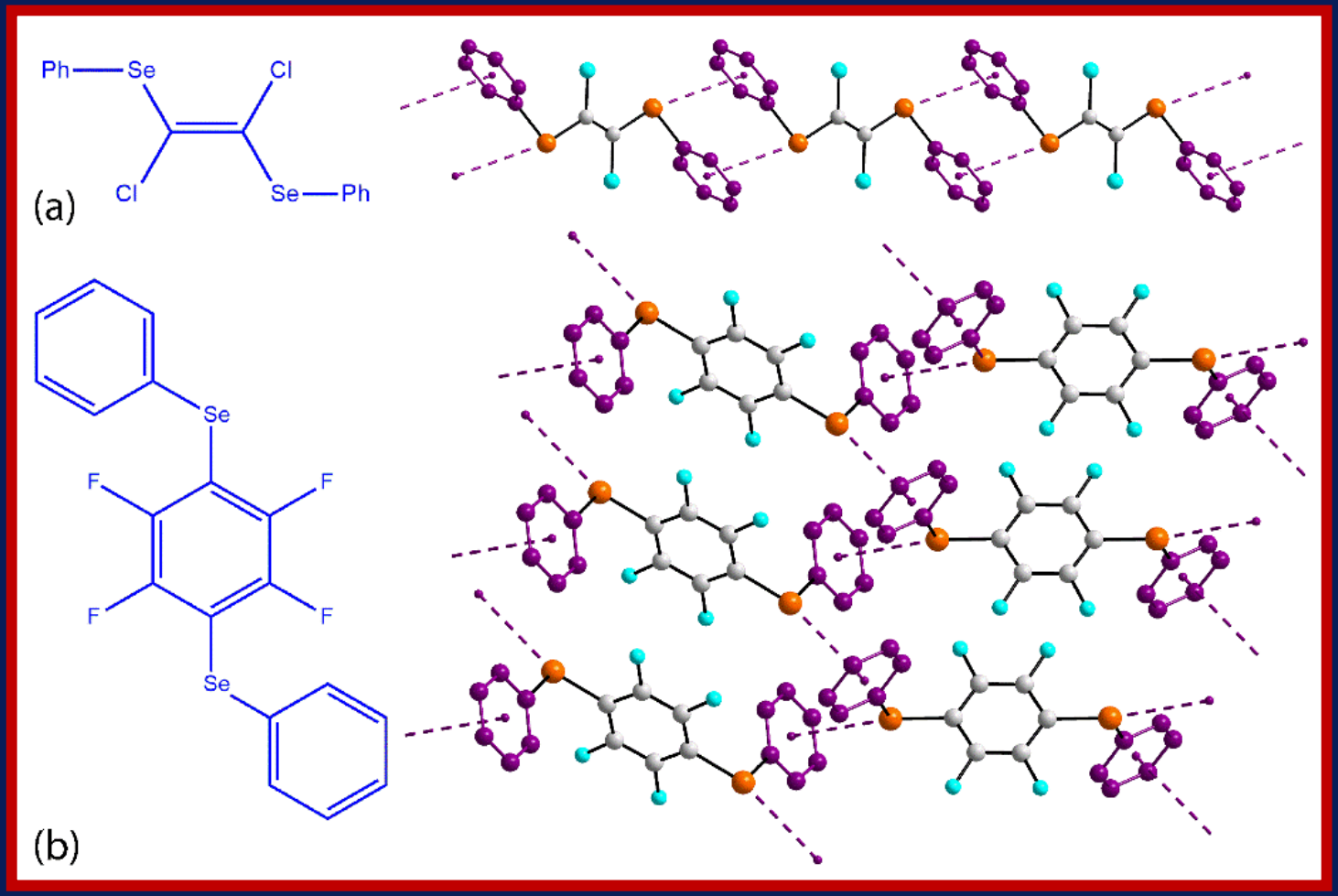
Mononuclear, thallium(I): 0-D



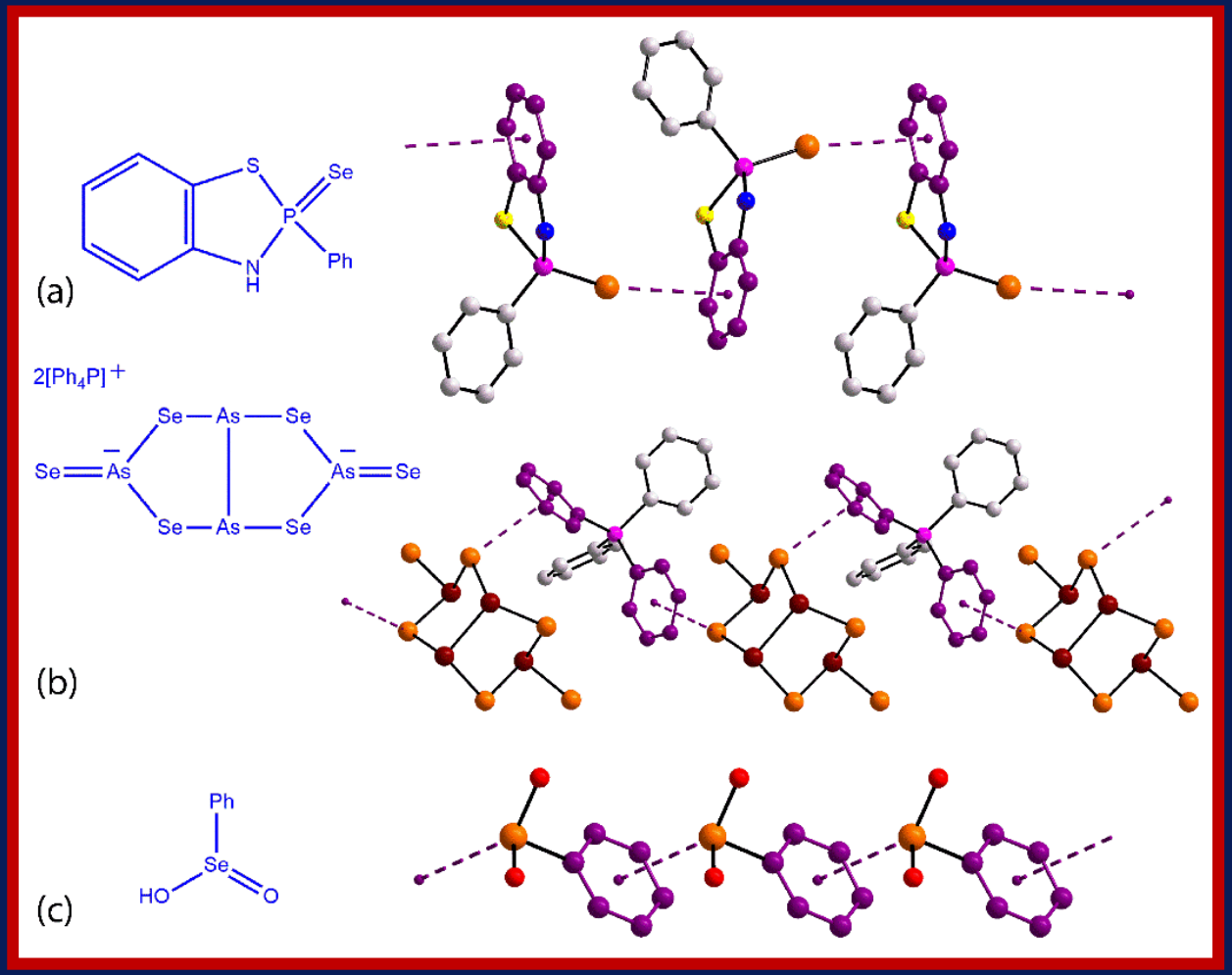
Mononuclear, lead(II): 2-D



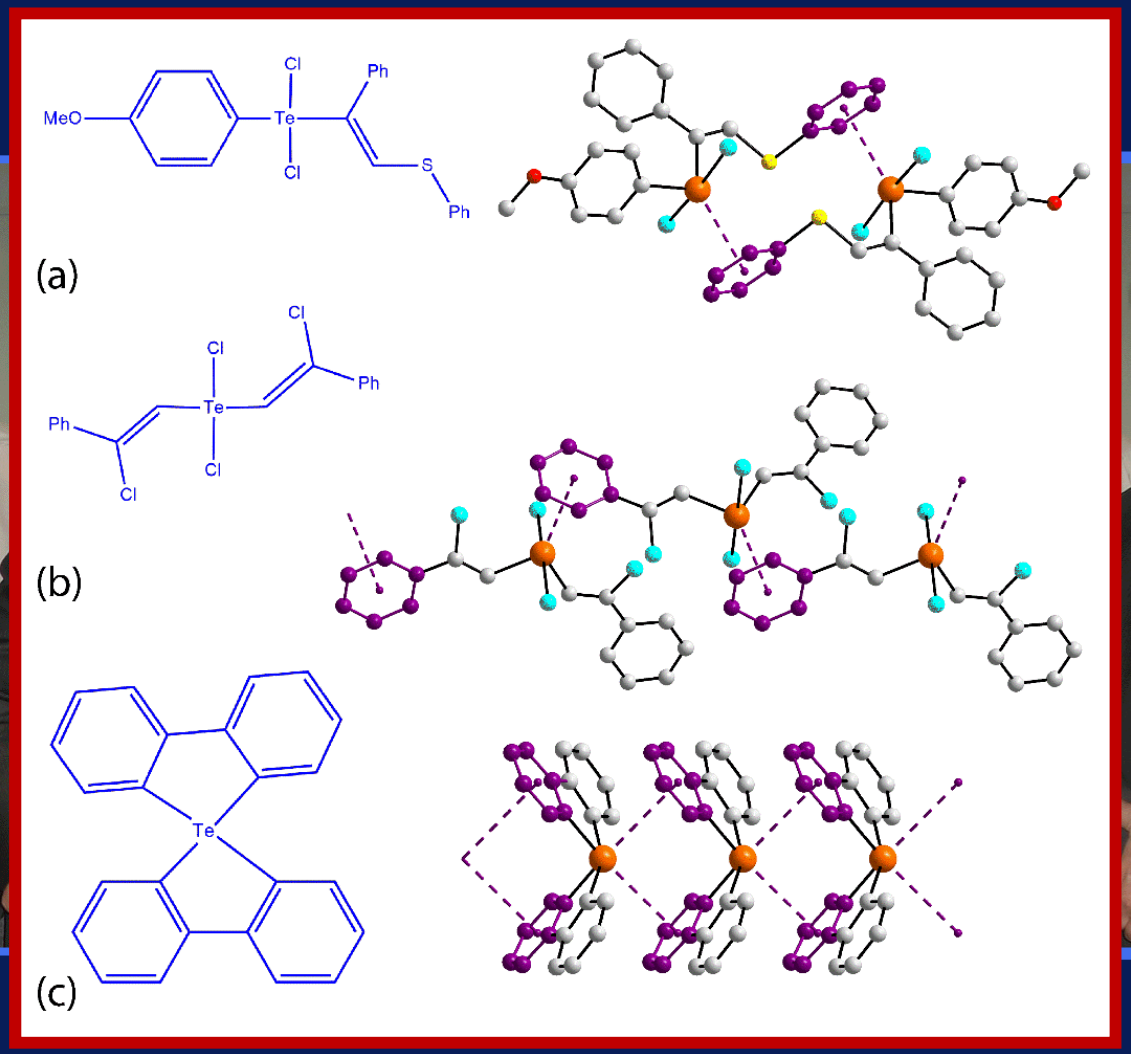
Mononuclear, arsenic(III): 1-D



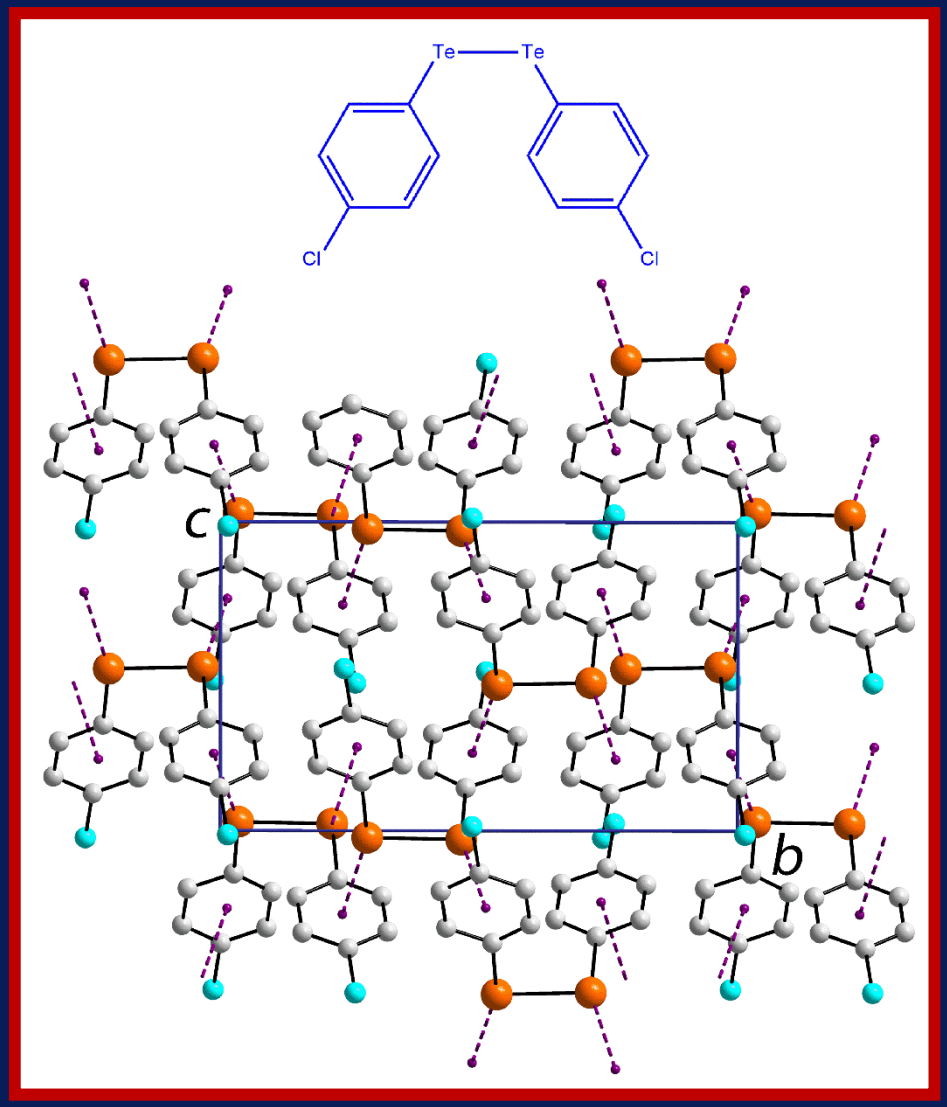
Binuclear, selenium(IV): 1-D & 2-D



Selenium(II, IV): 1-D



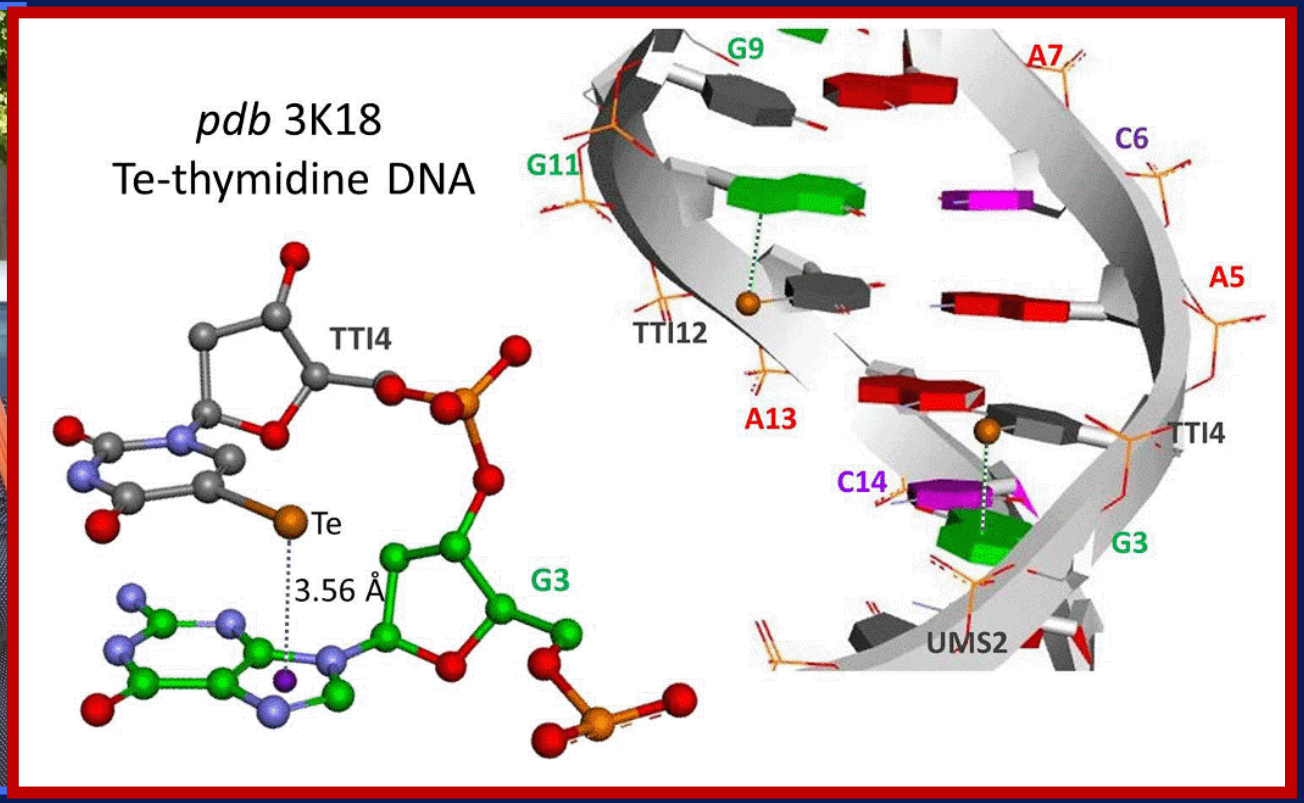
Tellerium(IV): 0-D & 1-D



Tellerium(II): 3-D

Biological Example

Ignez Caracelli



Overview

Maximum adoption: 14% Tl

Often:

occur in co-operation with other synthons

intramolecular

No distance/angle correlations

Included in the PLATON output

Complete description of molecular packing should include M(lone-pair)…π(arene) interactions

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