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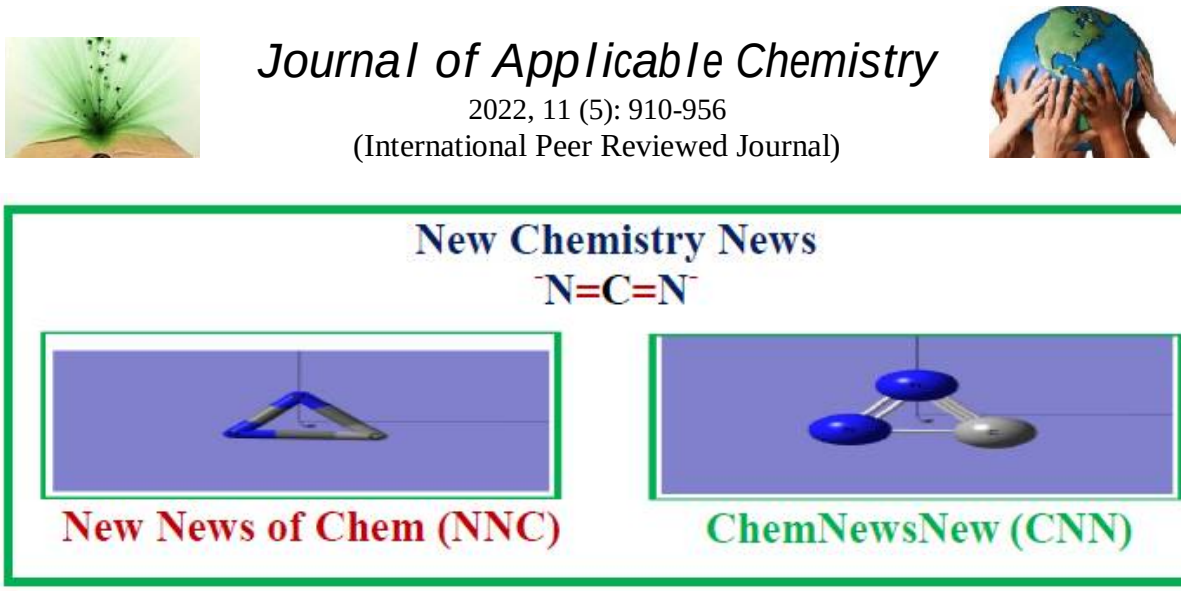

CNN – 47
Spodiumbonds

Information Source	ACS.org ; sciencedirect.com
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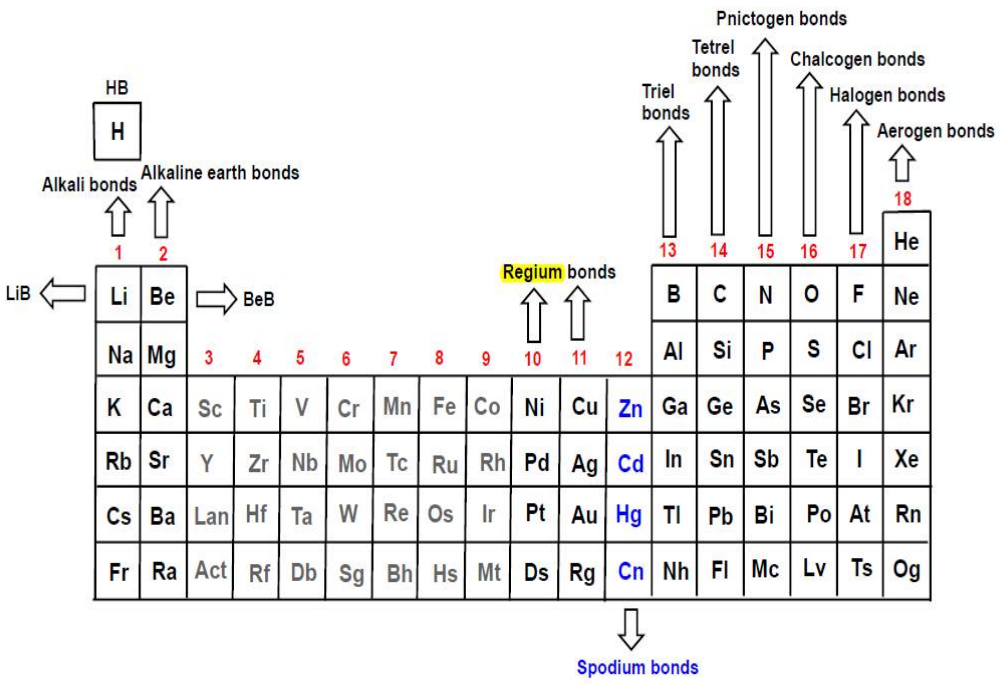
Conspectus: The term Spodium was used in the XIII century to refer to zinc oxide mixed with other metals. Spodium atoms ([SpA: [Zn, Cd; Hg; Cn]) belong to 12th group of 18 column chemical elements periodic table. SpA exhibits Lewis's acid (LA) behaviour. SpAs forms complexes or adducts with Lewis bases (LB) including molecules or species with π electron systems. The Spodium (like triel, tetrel, pnic(t)ogen, chalcogen, halogen, aerogen, hydrogen, regium) bond is also understood in terms of the σ-hole concept proposed by Politzer and Murray.

Knowledge based pipe-lines(with imbedded XI [:Artificial, eXplainable, Natural, Super Intelligence], machine learning, deep learning, deep-NNs and preliminary-consciousness tools/work flowshave beentarget/focus of our investigations of speciation in different phases and environments evolving into better and better approachesin trans-disciplinary chemical sciences. The multi-way flow/fusion with Physics, Biology based state-of-knowledge stunts will take the man-made scientific intervention towards greatest-benefit-to-human-kind.

Keywords: Interactions; Physics; Chemistry-Biology; Bonds; No-Bonds; Chemical bonds (CB); Electrovalent-B; Covalent Bond (CovB); Non-Covalent Chemical bonds (NCCB): [Nobel gas (aerogen), Halogen,Chalcogen, Pnicogen (or Pnictogen), Tetrel, Triel , Spodium, Regium (or Coinage), alkali, alkaline earth, Hydrogen [{strong, weak}, dihydrogen, hydride]], Synthesis, spectroscopy, computational quantum chemistry, Molecular dynamics

	Layout	K(nowledge)Lab
I	Spodium (12G) bonds in chemical systems	rsr.chem1979
II	Select Research Titles	
III	SupInf Fig (Sif)	

I. Spodium bonds in chemical systems



Column# Periodic table	Abbrev $$Bond	Abbrev $$Atom	$$ bonds
1G	HyB	HyA	Hydrogen

Column#	Abbrev	Abbrev	$$ bonds
18G	NgB	NgA	Nobel gas
	AeB	AeA	Aerogen
17G@	HaB	HaA	Halogen
16G@	ChB	ChA	Chalcogen
15G	PnB	PnA	Pnicogen or Pnictogen
14G	TtB	TtA	Tetrel
13G	TrB	TrA	Triel

12G	SpB	SpA	Spodium

Spodium bond is defined as non-covalent interaction between any electron donating moiety and a chemical element of group 12 group (SpA) acting as Lewis acid

11G 10G	CiB or RgB	CiA or RgA	Coinage or Regium
2G	AEB AlkEarB	AEB AlkEarA	Alkaline-Earth
1G	AkB AlkB	AkA AlkA	Alkali

Spodium bonds

σ-hole bonding	✓ Is a noncovalent interaction between a covalently-bonded atom and anegative site, e.g. A lone pair of electrons in a Lewis base, an anionor a π-system ✓ These noncovalent interactions are markedly different from coordination bonds
	✓ σ -hole arises from an anisotropic charge distribution around the polarized atom ✓ σ -holecreates a region of positive electrostatic potential (σ-hole) on the extension of one of the covalent bonds to the atom ✓ Ex.: X−Ae, X−Hal, X−Ch, X−Pn, and X−Tr
	✓ Concept of σ-hole interactions has also been extended to coinage-metal bond or regium bond and spodium bonds

Spodiumbond (SpB)	☞ Is a member of set (or family) of σ_hole (or simply σ) bonds ☞ σ-hole on the spodium atom is located approximately on the extension of the covalent bonds to this atom
	Def: Non-covalent bond arising due to interaction between ✓ a covalently-bonded Group-12 (spodium) atom (SpA) functioning as Lewis's acid (or an electron-acceptor) and electron donor playing the role of Lewis base
	✓ It is non-covalent/non-coordinative attractive interaction ✓ Antibonding (Sp–Y, where Y can be any atom) has a contribution ✓ Strength depends upon energy or force involved ✓ Coexists with other weak interactions, including hydrogen and halogen bonding
	🔔 Lewis acid property of spodium atoms arise due to existence of an electron-deficient region (called σ-hole)
	🔔 σ-hole is distributed on the outermost portion of these spodium atoms 🔔 σ-hole region characterized by a positive molecular electrostatic potential (MESP)
	✓ Very much like those of the halogen bond because of the similar misshaped electron clouds of the halogen atom

Characteristics	✓ Directional ✓ Electron rich atom is located at distances that are longer than the sum of covalent radii ✓ Considerably weaker than coordination bonds
SpB utility	✓ To differentiate the coordination bond (high covalent character) typical of transition metals from the noncovalent contact

Knowledge base for spodium bond

If	SpA : [Zn, Cd, Hg]& oxidation state = +2& coordination environment = (pseudo)tetrahedral Sp(Ligand)$_4$
Then	region of positive potential suitable to interact with a lone-pair bearing partner
→	Sp bond feasible
If	SpA : [Zn, Cd and Hg]& oxidation state = +2& coordination environment = five-coordinate coordination complexes
Then	Interactions are markedly different
→	No Sp interaction

If	former dative bonds & H < 0	
Then	Indicates high covalent character i.e. clearly a dative interaction	
	ElseIf	H > 0
	Then	Indicates Noncovalent van der Waalsinteraction
		Ex.: weakest S···Ag interaction is best described as a van der Waals interaction rather than a dative bond.
EndIf		

Applications	✓ Chemistry o Coordination polymers o Catalysis, crystal engineering ✓ Supramolecular chemistry To control o Molecular recognition o Self-assembly processes ✓ Biomolecular functional materials o Protein structure o Enzyme inhibition

Coinage metal-bond	✓ Non-covalent Interaction of polarized group11 metal (such as in AgCl or small metal clusters)with a LB ✓ To account for electrostatic interaction (Ex. goldadducts with non-negligible covalent character)

II. *Select Research Titles*

π-Hole spodium bonding in tri-coordinated Hg (ii) complexes	Dalton Transactions 50.22 (2021): 7545-7553. https://doi.org/10.1039/D1DT01235E
Gomila, Rosa M., Antonio Bauza, Tiddo J. Mooibroek, and Antonio Frontera.	
	SpB. 01

Spodium bonds: noncovalent interactions involving group 12 elements	Angewandte Chemie International Edition 59.40 (2020): 17482-17487 https://doi.org/10.1002/anie.202007814
Antonio Bauzá,Ibon Alkorta, José Elguero,Tiddo J. Mooibroek, Antonio Frontera	
	SpB. 02

Spodium bonding and other non-covalent interactions assisted supramolecular aggregation in a new mercury(II) complex of a nicotinohydrazide derivative	Inorganica Chimica Acta 519 (2021): 120279. https://doi.org/10.1016/j.ica.2021.120279
GhodratMahmoudi, EnnioZangrando, BarbaraMiroslaw, Atash V.Gurbanov, Maria G.Babashkina, AntonioFrontera, Damir A.Safin	
	SpB. 03

A new spodium bond driven coordination polymer constructed from mercury (ii) azide and 1, 2-bis (pyridin-2-ylmethylene) hydrazine	New Journal of Chemistry 44.48 (2020): 21100-21107. https://doi.org/10.1039/D0NJ04444J
Mahmoudi Ghodrat, Simon E. Lawrence, Jonathan Cisterna, Alejandro Cárdenas, Iván Brito, Antonio Frontera, and Damir A. Safin	
	SpB. 04

Insight into Spodium–π Bonding Characteristics of the MX2···π (M = Zn, Cd and Hg; X = Cl, Br and I) Complexes—A Theoretical Study	Molecules. 2022 May; 27(9): 2885. doi: 10.3390/molecules27092885
Meng Gao, Qibo Zhao,Hao Yu, Min Fu, and Qingzhong Li	
	SpB. 05

Not Only Hydrogen Bonds: Other Noncovalent Interactions	Crystals, 10.3.(2020): 180 https://doi.org/10.3390/cryst10030180
Alkorta, Ibon, José Elguero, and Antonio Frontera	
	SpB. 06

Dibismuthates as linking units for bis-zwitterions and coordination polymers	Inorganic chemistry 59.18 (2020): 13270-13280. https://doi.org/10.1021/acs.inorgchem.0c01619
Fekete, C., Barrett, J., Benkő, Z. and Heift, D	
	SpB. 07

Hydrogen and halogen bonds formed by MCO3 (M = Zn, Cd) and their enhancement by a spodium bond	Molecular Physics, 2022, https://doi.org/10.1080/00268976.2022.2102548		
Qingqing Yang,Qiaozhuo Wu,Xiaolong Zhang,Xin Yang &Qingzhong Li			
		SpB.	08

Spodium Bonds in Biological Systems: Expanding the Role of Zn in Protein Structure and Function	Journal of chemical information and modeling 61.8 (2021): 3945-3954. https://doi.org/10.1021/acs.jcim.1c00594		
Himansu S. Biswal, Akshay Kumar Sahu, Antonio Frontera, and Antonio Bauzá			
		SpB.	09

Intramolecular Spodium Bonds in Zn (II) Complexes: Insights from Theory and Experiment	International journal of molecular sciences 21.19 (2020): 7091. https://doi.org/10.3390/ijms21197091		
Karmakar, Mainak, Antonio Frontera, Shouvik Chattopadhyay, Tiddo J. Mooibroek, and Antonio Bauzá. "Intramolecular Spodium Bonds in Zn (II) Complexes: Insights from Theory and Experiment." International journal of molecular sciences 21, no. 19 (2020): 7091.			
		SpB.	10

Iribarren, Iñigo, et al. "Evaluation of electron density shifts in noncovalent interactions."	The Journal of Physical Chemistry A 125.22 (2021): 4741-4749. https://doi.org/10.1021/acs.jpca.1c00830		
Iribarren, Iñigo, Goar Sánchez-Sanz, Ibon Alkorta, José Elguero, and Cristina Trujillo			
		SpB.	11

Assessing the orbital contribution in the “spodium bond” by natural orbital for chemical valence–charge displacement analysis	Inorganic Chemistry 60.7 (2021): 4683-4692. https://doi.org/10.1021/acs.inorgchem.0c03650		
Ciancaleoni, Gianluca, and Luca Rocchigiani.			
		SpB.	12

On the importance of π-hole spodium bonding in tricoordinated Hg II complexes	Dalton Transactions 49.48 (2020): 17547-17551. https://doi.org/10.1039/D0DT03938A		
Mahmoudi, Ghodrat, Ardavan Masoudiasl, Maria G. Babashkina, Antonio Frontera, Thomas Doert, Jonathan M. White, Ennio Zangrando, Fedor I. Zubkov, and Damir A. Safin.			
		RiB.	13

Liu, Na, Qingzhong Li, and Steve Scheiner. "Spodium and tetrel bonds involving Zn (II)/Cd (II) and their interplay."	Chemical Physics 556 (2022): 111470. https://doi.org/10.1016/j.chemphys.2022.111470		
Liu, Na, Qingzhong Li, and Steve Scheiner.			
		RiB.	14

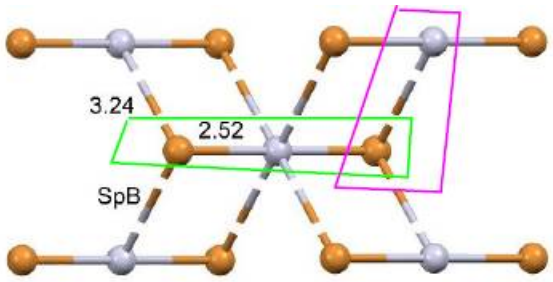
Theoretical study spodium bonding in the active site of three Zn-proteins and severalmodel systems	Physical Chemistry Chemical Physics 23.31 (2021): 16888-16896. https://doi.org/10.1039/D1CP02150H		
Llull, Rosa, Gaizca Montalbán, Ivan Vidal, Rosa M. Gomila, Antonio Bauzá, and Antonio Frontera			
		SpB.	15

III. Sup Inf Fig (Sif)
Spodium [Zn; Cd; Hg; Cn]Bond (SpB, 12G)

Spodium Bond *[Hg]*	Sp: [Zn; Cd; Hg; Cn]	SpB.	12

Partial view of the crystal structure HgBr2

ICSD refcode 36158

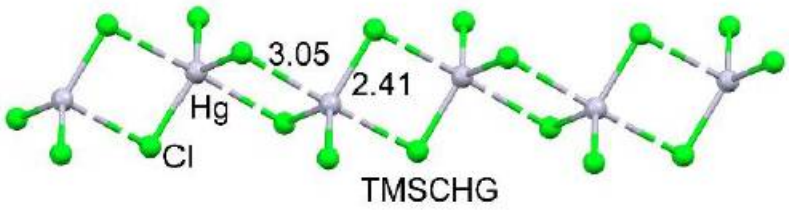


➔ Pseudo-octahedral complex ; Hg = grey, Br =brown ; distances in Å

- Linear HgBr2 solid state structure
  - ✓ Hg–Br = 2.52 Å
  - ✓ Four secondary Hg···Br SpBs of 3.24 Å

CSD ref. code TMSCHG

[HgCl3]– units

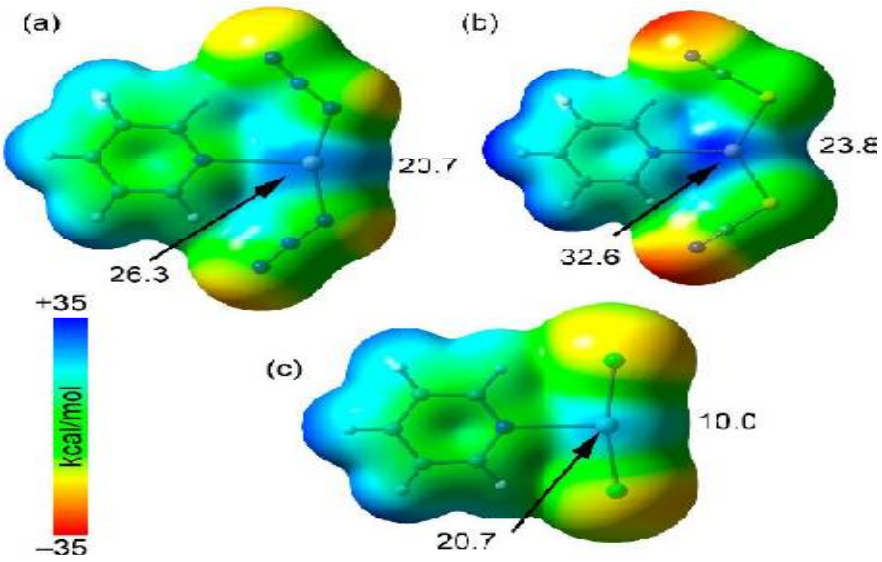


Hg = grey, Cl = green

- Planar [HgCl3]– anions in crystal structures stack close together in a slipped parallel arrangement
- Strong noncovalent SpBs formed between Hg π–hole of one unit and Cl atom of an adjacent unit
- Anion···anion SpBs work in tandem with crystal packing forces → stabilizing {[HgCl3]–···[HgCl3]–}n polymeric chains

MESP

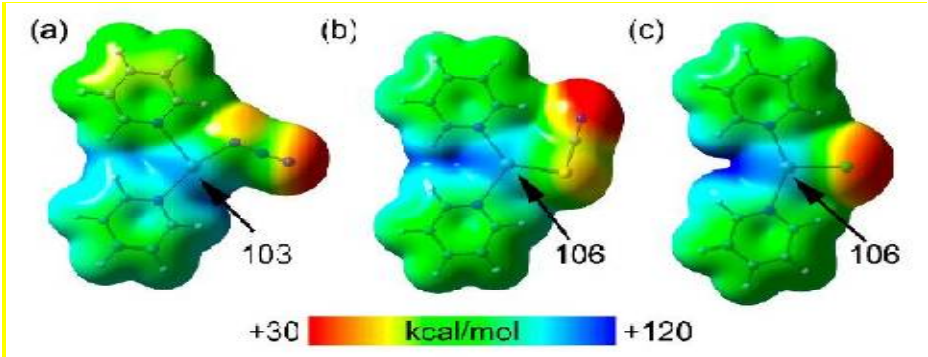
PBE0- D3/def2-TZVP



HgPy(N3)2 (a), HgPy(SCN)2 (b) and HgPy(Cl)2 (c)

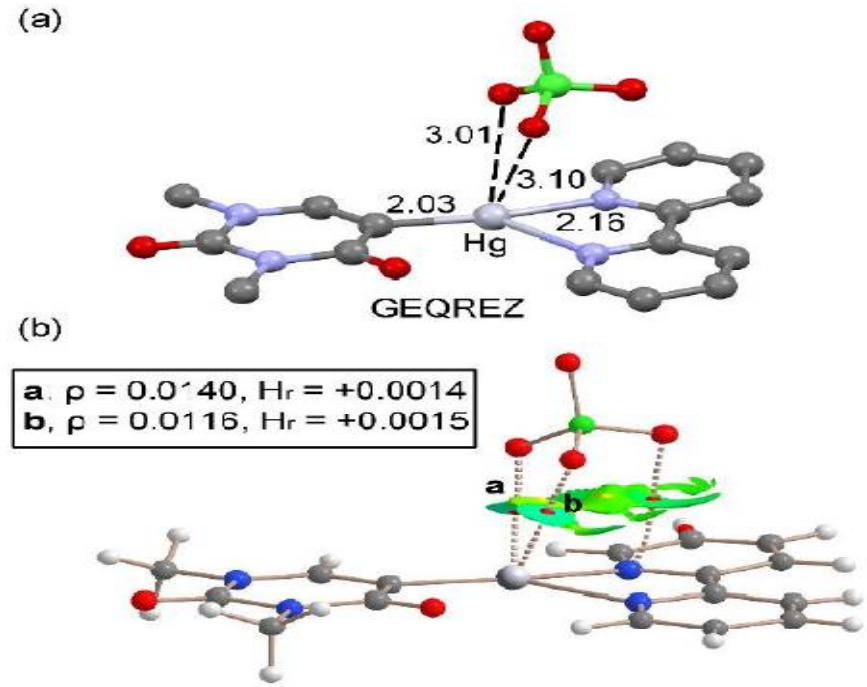
SP

PBE0- D3/def2-TZVP



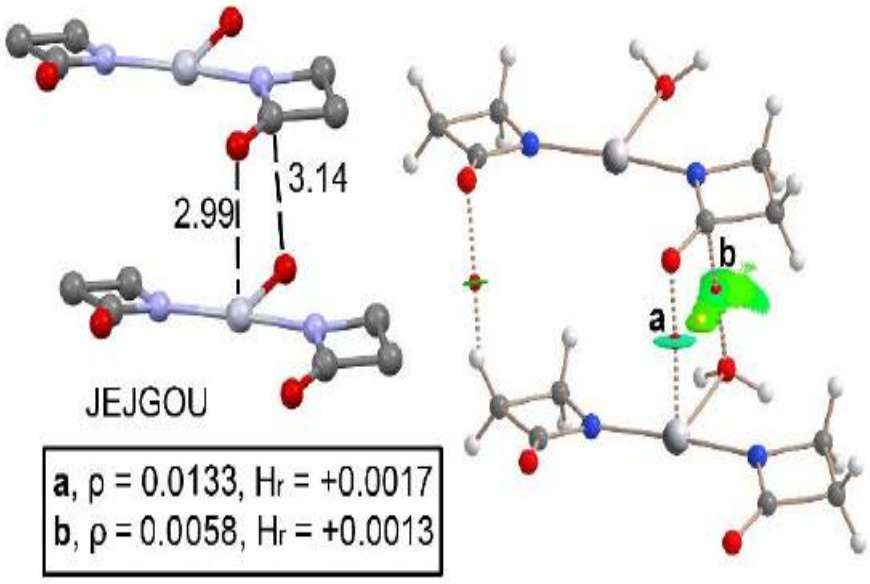
HgPy2(N3) (a), HgPy2(SCN) (b) and HgPy2Cl (c)

(a) Partial view of crystal structure GEQREZ



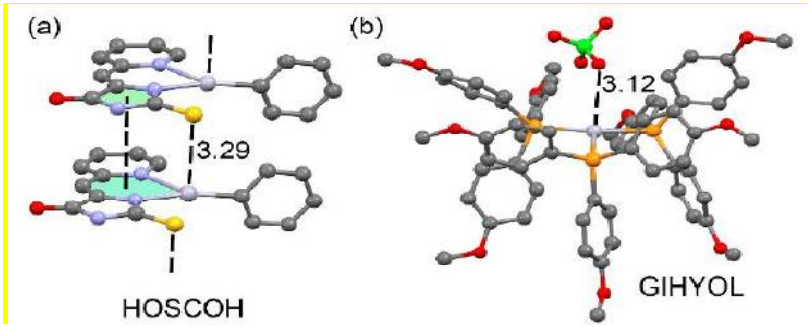
- (b) QTAIM analysis of bond (red) and ring (yellow spheres) CPs
- Bond paths overlapped
  - NCIplot surface Constructed using
    - 0.5 a.u. RDG isosurface,
    - Density cut-off is 0.04 a.u
    - Colour range is $-0.035 \leq (\text{sign}\lambda 2)\rho \leq 0.035$
    -

(a) Partial view of the crystal structure JEJGOU



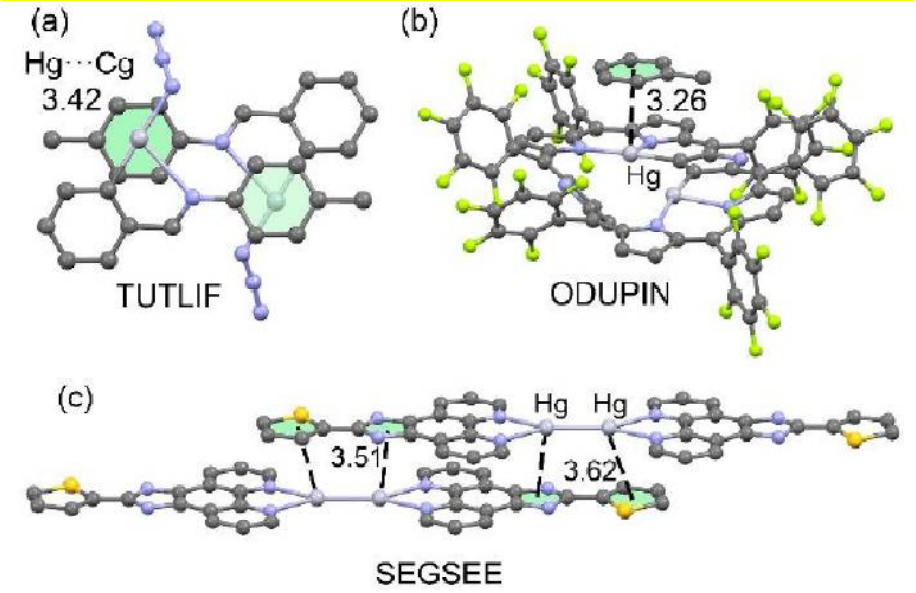
- (b) QTAIM analysis of bond (red) and ring (yellow spheres) CPs
- Bond paths overlapped with the
  - NCIplot surface Constructed using
    - 0.5 a.u. RDG isosurface,
    - Density cut-off is 0.04 a.u
    - Colour range is $-0.035 \leq (\text{sign}\lambda 2)\rho \leq 0.035$

Partial views of the crystal structures HOSCOH (a), and GIHYOL (b)

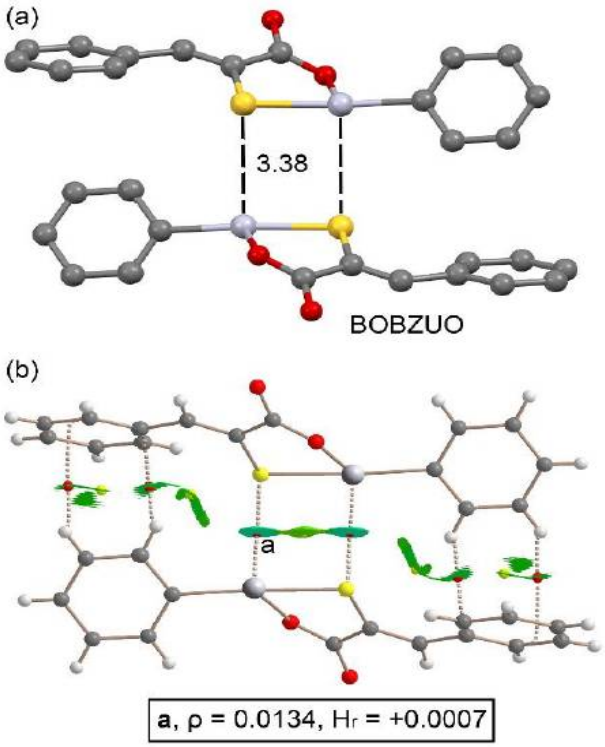


Partial views of crystal structures

TUTLIF (a), ODUPIN (b) and SEGSEE (c)



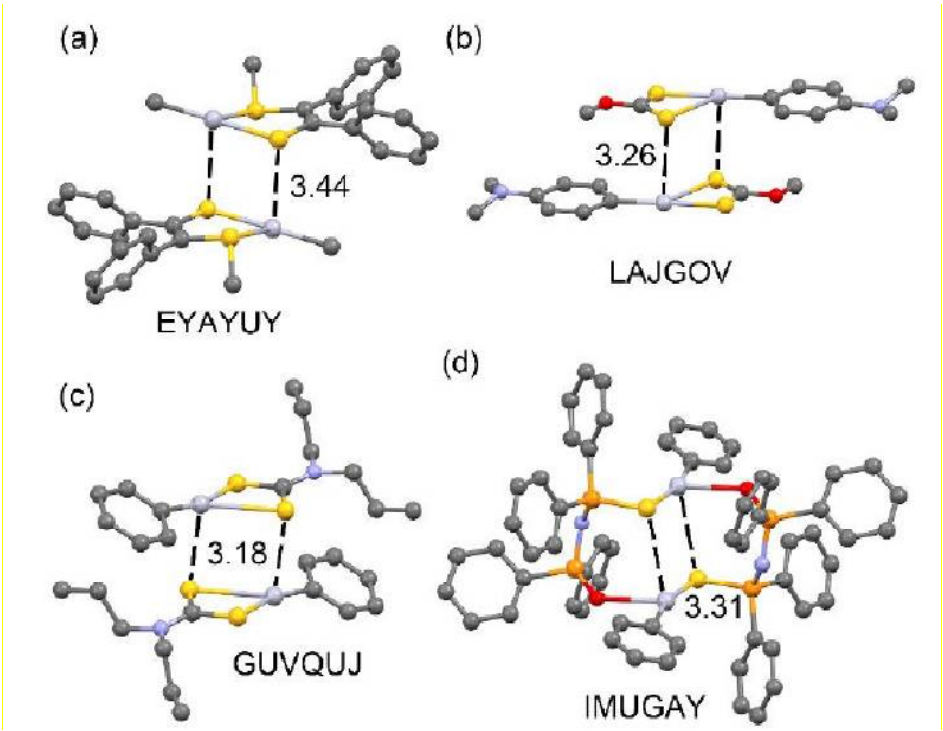
(a) Partial view of the crystal structure BOBZUO



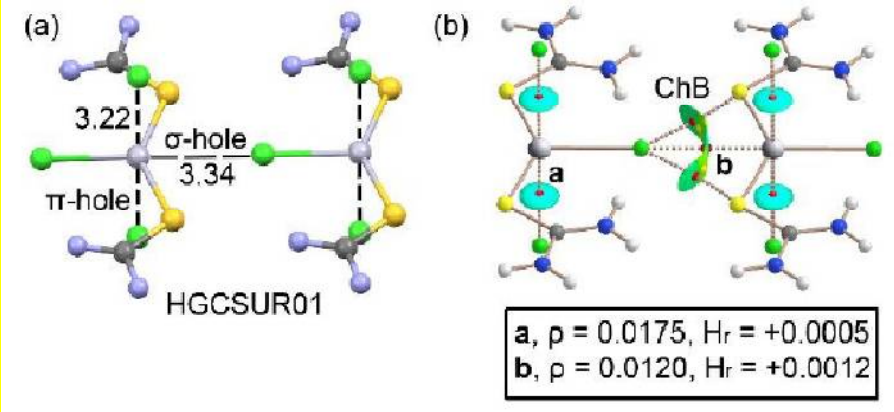
(b) QTAIM analysis of bond and ring CPs

Partial views of crystal structures

EYAYUY (a), LAJGOV (b), GUVQUJ (c) IMUGAY (d).



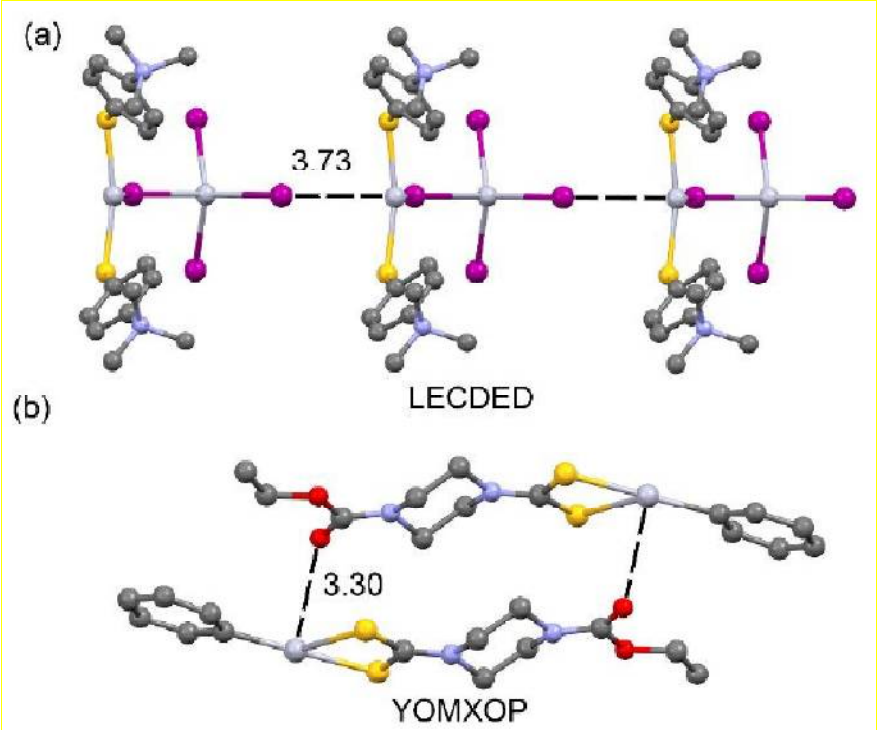
(a) Partial view of crystal structure HGCSUR01



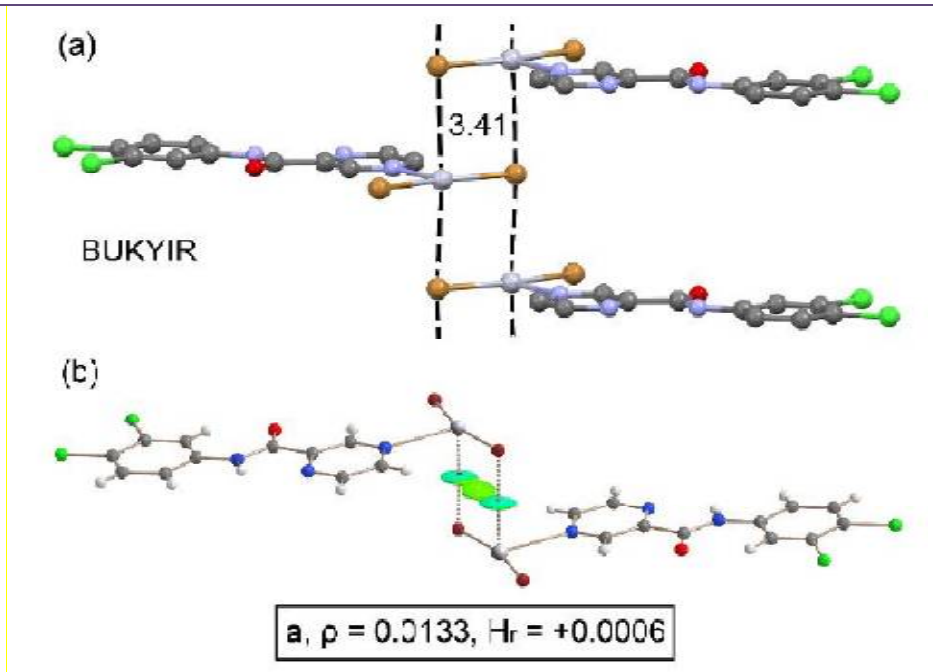
(b) QTAIM analysis of bond and ring CPs

Partial views of crystal structures

LECDED (a), I and YOMXOP (b)

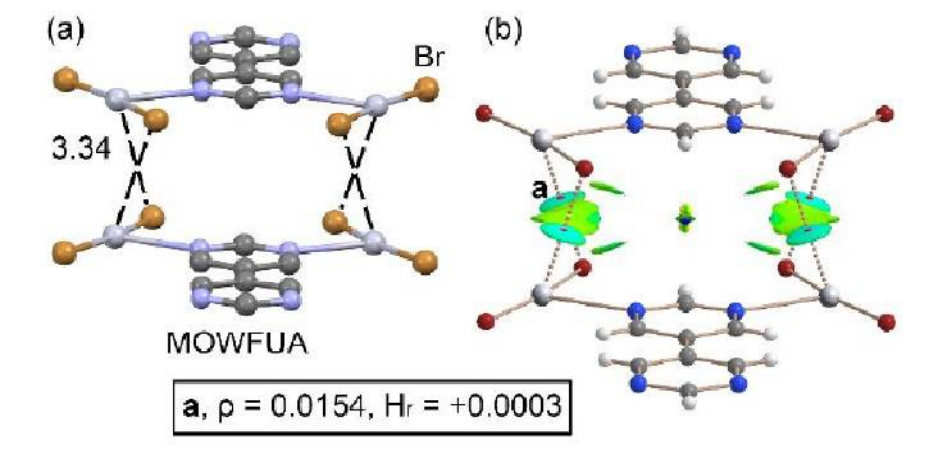


Partial view of crystal structure BUKYIR

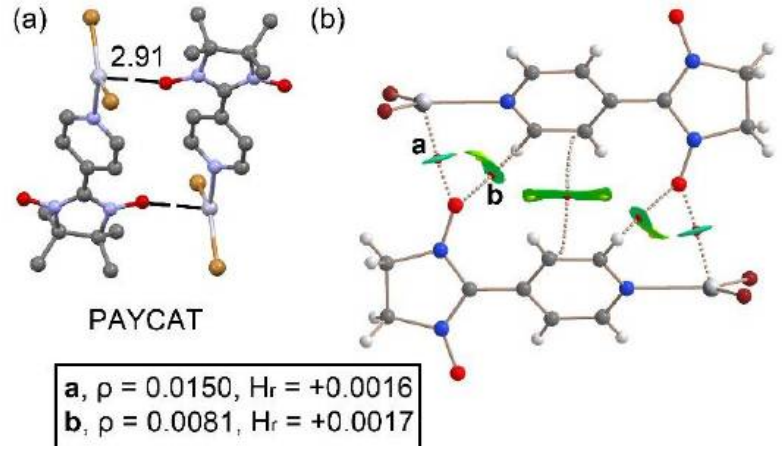


(b) QTAIM analysis of bond and ring CPs

(a) Partial view of crystal structures BUKYIR

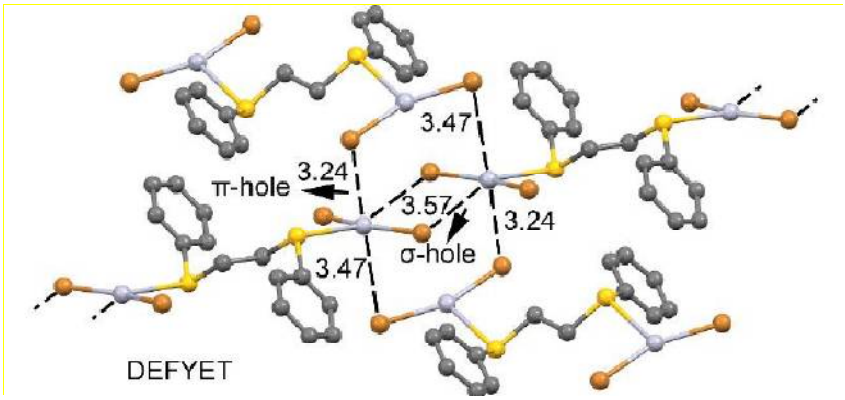


(a) Partial view of crystal structure PAYCAT

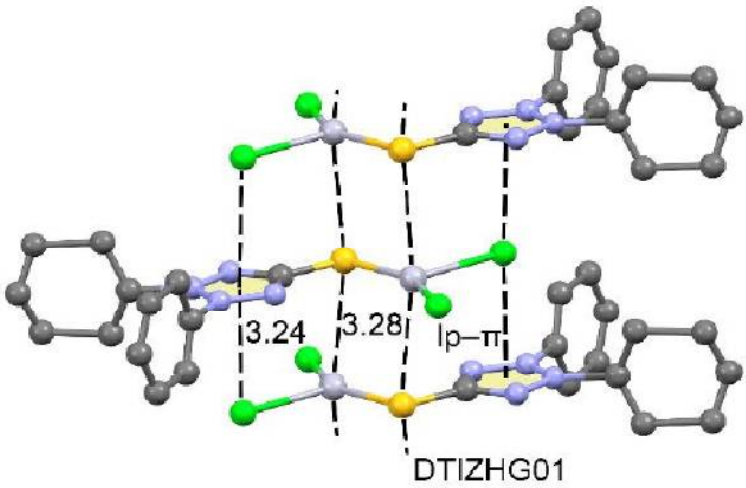


(b) QTAIM analysis of bond and ring CPs

Partial view of crystal structures DEFYET

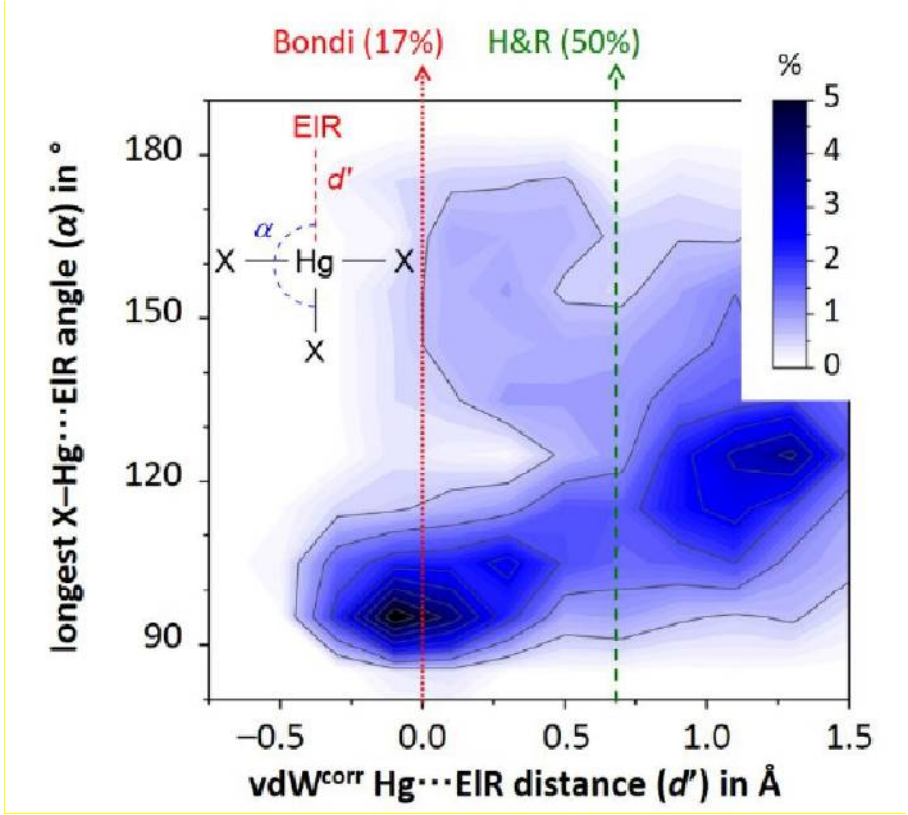


Partial view of crystal structures DTIZHG01



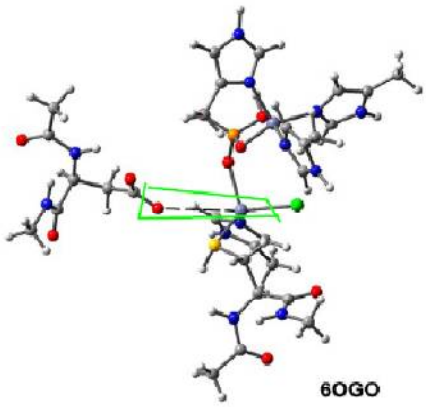
Heat plot (in % from light to dark blue)

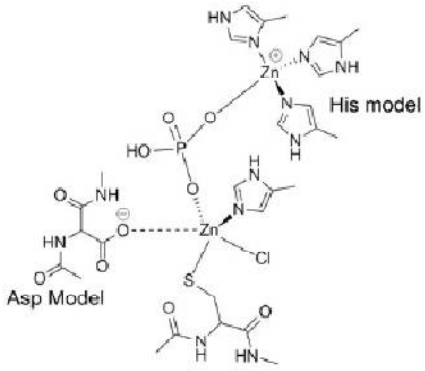
Parameters α and d'. Ntotal = 2,174 within 529 CIFs.

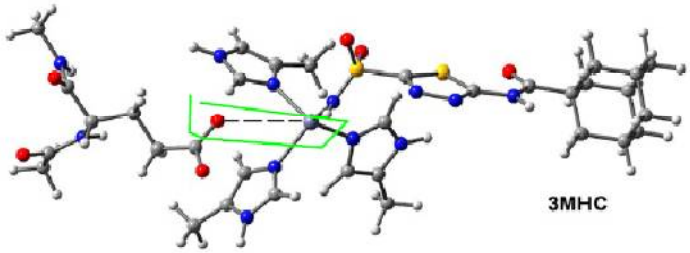


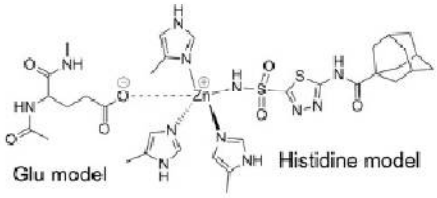
Heat plot (in % from light to dark blue) of the longest X–Hg···ElR angle (α) as a function of the van der Waals corrected Hg···ElR distance in Å (d') using Bondi's vander Waals radii

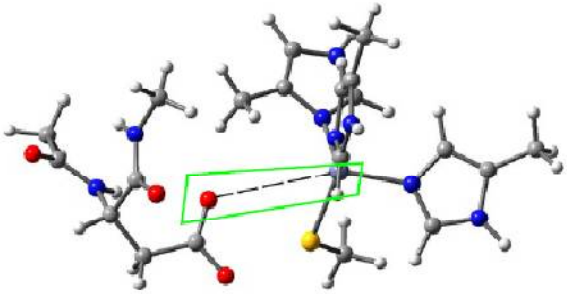
Active sites Models

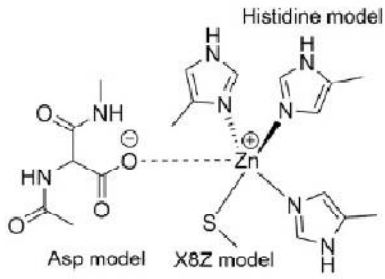






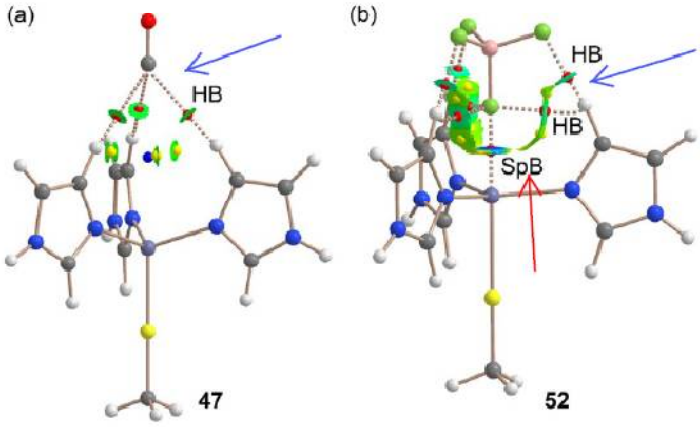






QTAIM

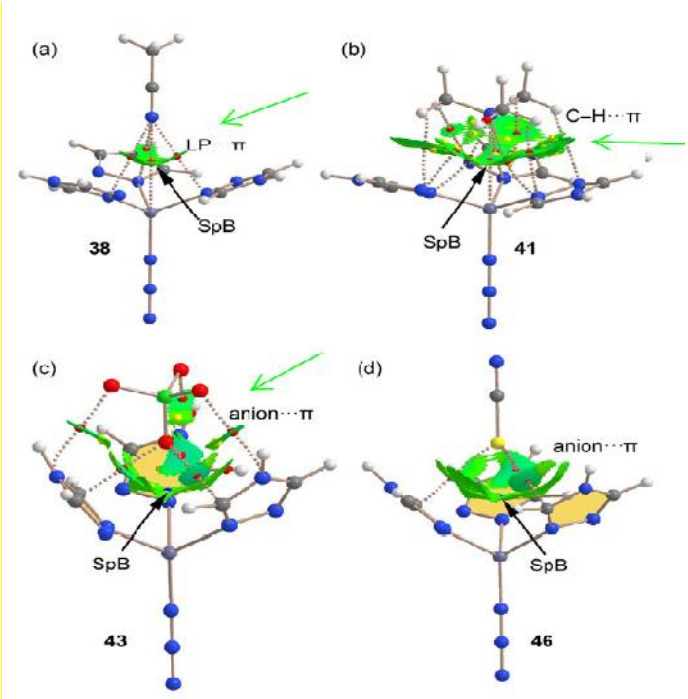
PBE0-D3/def2-TZVP



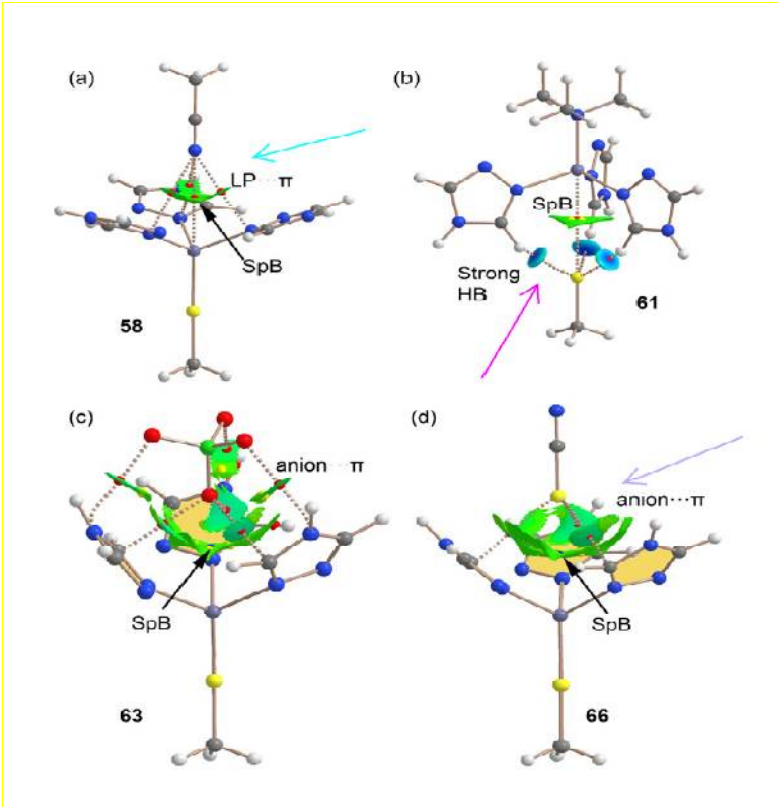
- ✓ NCIplot analysis using RGD isosurface 0.4
- ✓ Colour scale $-0.04 \leq (\text{sign}\lambda 2)\rho \leq 0.04$ a.u

QTAIM

PBE0-D3/def2-TZVP

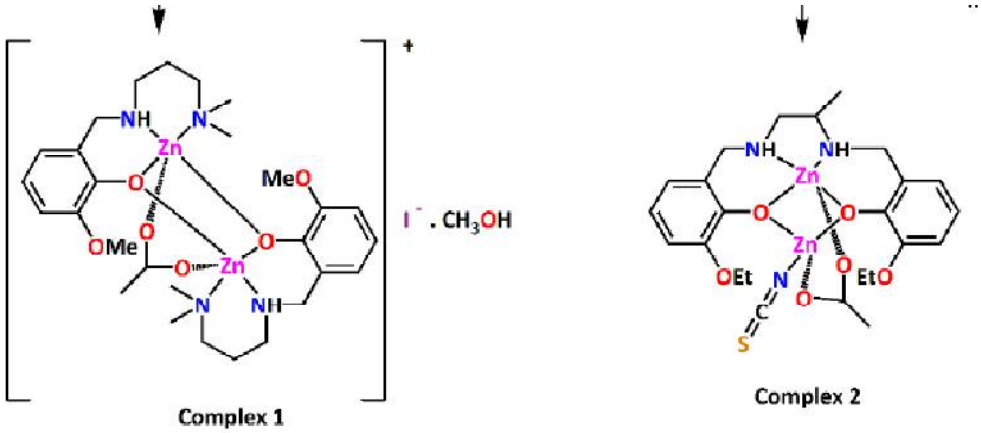


QTAIM distribution of bond, ring and cage CPs

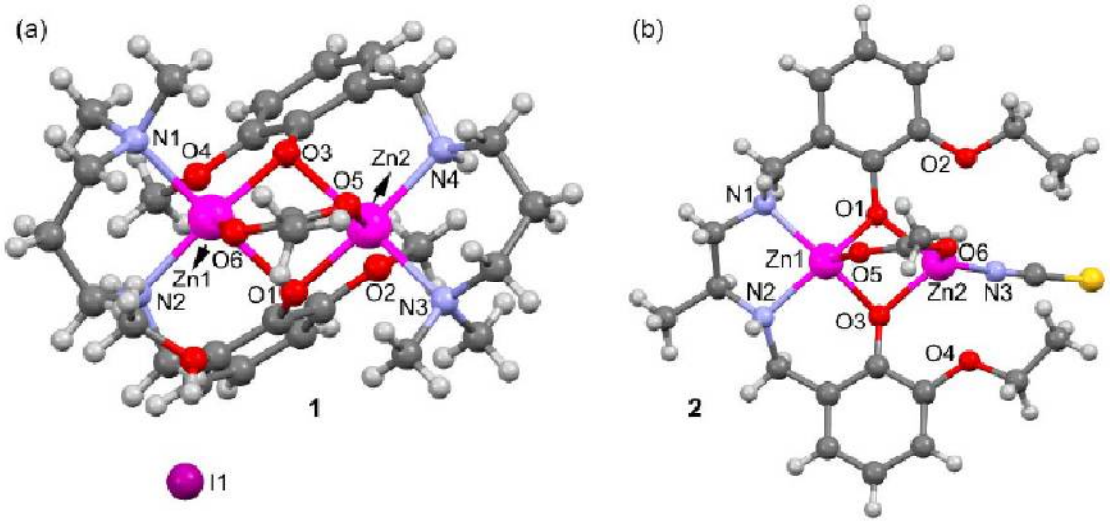


Spodium Bond *[Hg]*		SpB.	10

Complexes 1 and2



Perspective ball and stick view of the complexes

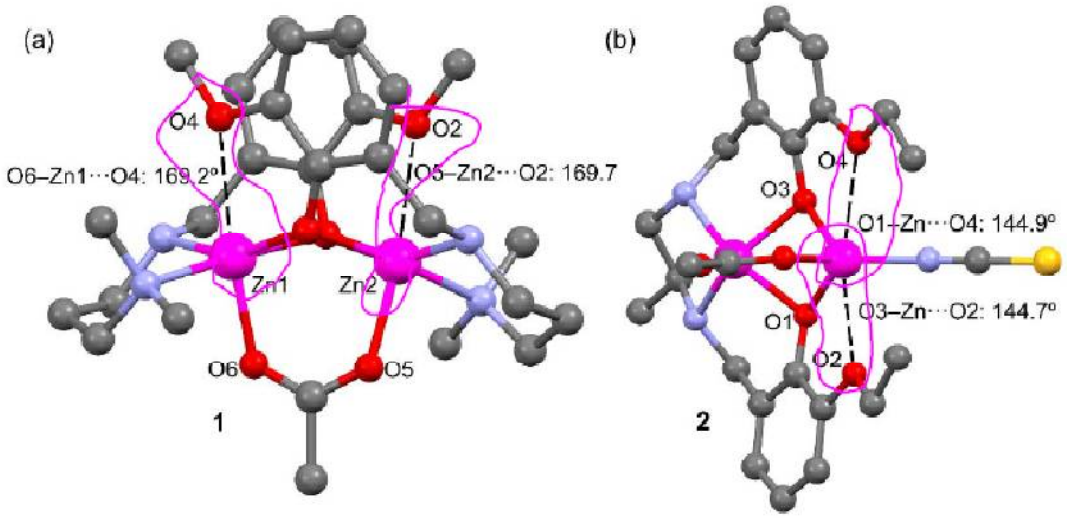


Selected bond lengths (A°)

	1		
Zn1–N1 (coord.) [1]	2.169(5)	Zn2–N3 (coord.)	2.160(5)
Zn1–N2 (coord.)	2.074(4)	Zn2–N4 (coord.)	2.085(4)
Zn1–O1 (coord.) [2]	2.212(4)	Zn2–O1 (coord.)	1.983(4)
Zn1–O3 (coord.)	1.977(3)	Zn2–O3 (coord.)	2.165(3)
Zn1–O6 (coord.)	2.051(4)	Zn2–O5 (coord.)	2.075(4)
Zn1–O4 (SpB)	*2.688(5)*	*Zn2–O2 (SpB)*	*2.667(4)*
Zn1···Zn2	3.047(1)		
	2		
Zn1–N1 (coord.)	2.091(2)	Zn2–N3 (coord.)a	1.922(2)
Zn1–N2 (coord.)	2.099(2)	Zn2–O1 (coord.)	2.017(1)
Zn1–O1 (coord.)	2.058(2)	Zn2–O3 (coord.)	2.007(2)
Zn1–O3 (coord.)	2.042(2)	Zn2–O6 (coord.)	1.976(2)
Zn1–O5 (coord.)	1.978(2)	*Zn2–O2 (SpB)*	*2.692(2)*
Zn1···Zn2	2.9025(5)	*Zn2–O4 (SpB)*	*2.664(2)*

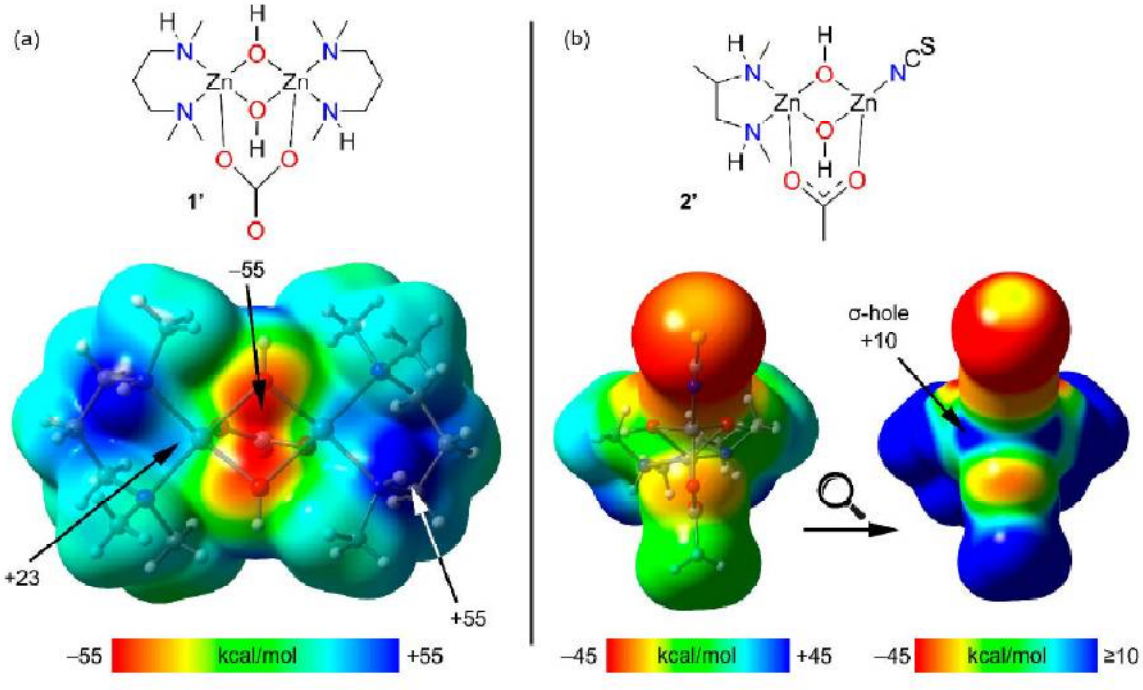
[1] Sum of Zn and N covalent radius: 1.93 Å; [2] Sum of Zn and O covalent radius: 1.86 Å.

Spodium bonds (black dashed lines)



ESP

PBE0-D3/def2-TZVP

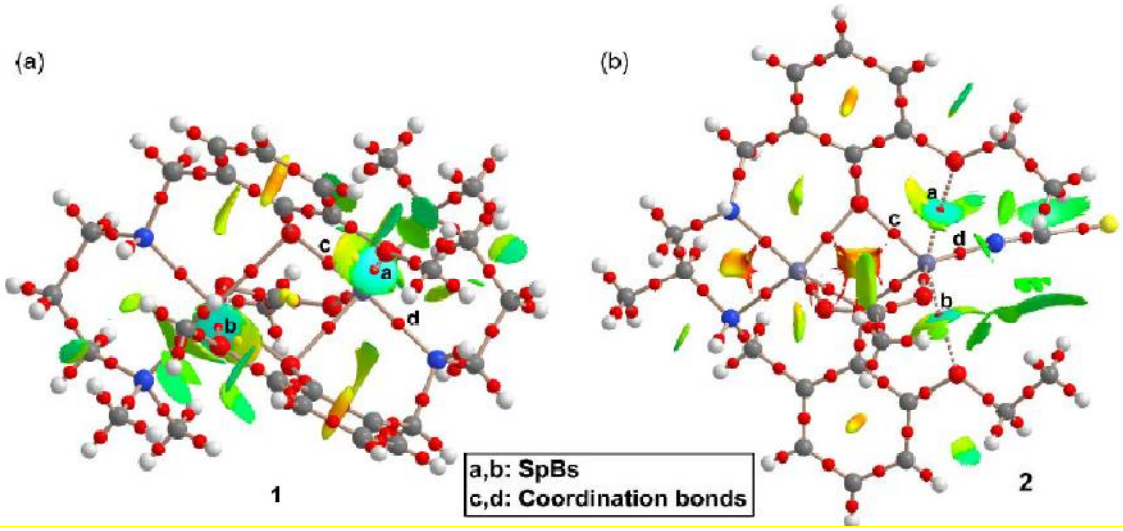


- Most positive MEP is located at the NH group.
- Two regions of positive potential are present at extension of the O–Zn bonds (+23 kcal/mol),

Compounds 1 (a) and 2 (b)

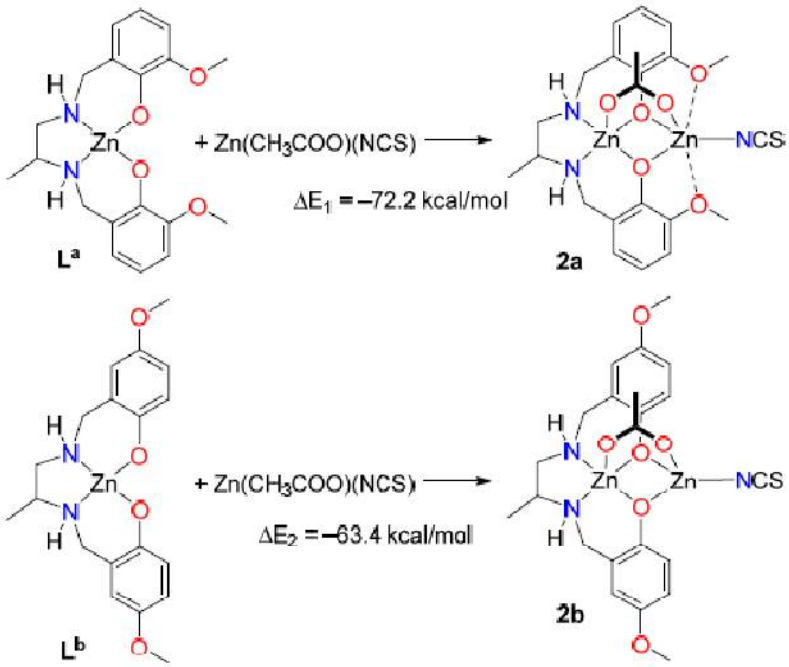
Methods: Quantum theory of atoms in molecules (QTAIM) +

Noncovalent interaction (NCI)

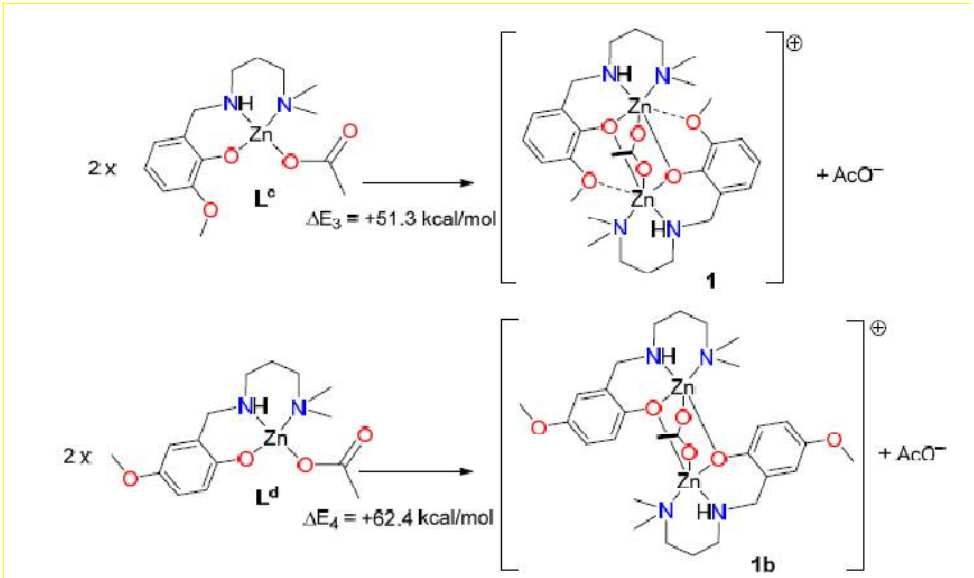


! Dashed lines : Noncovalent bond paths

Reactions used to evaluate the SpB energy in compound 2

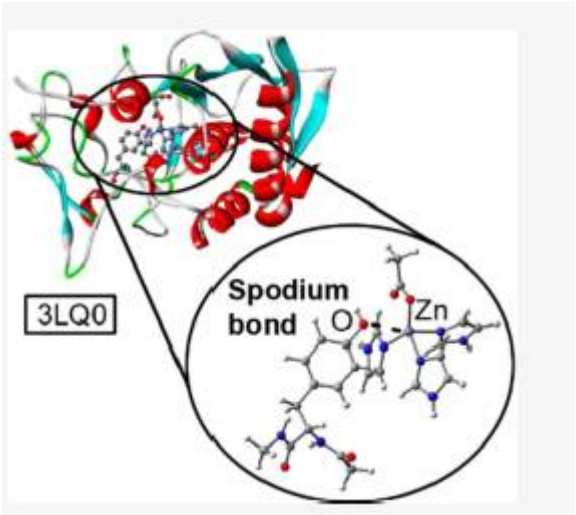


Reactions used to evaluate the SpB energy in compound 1.1

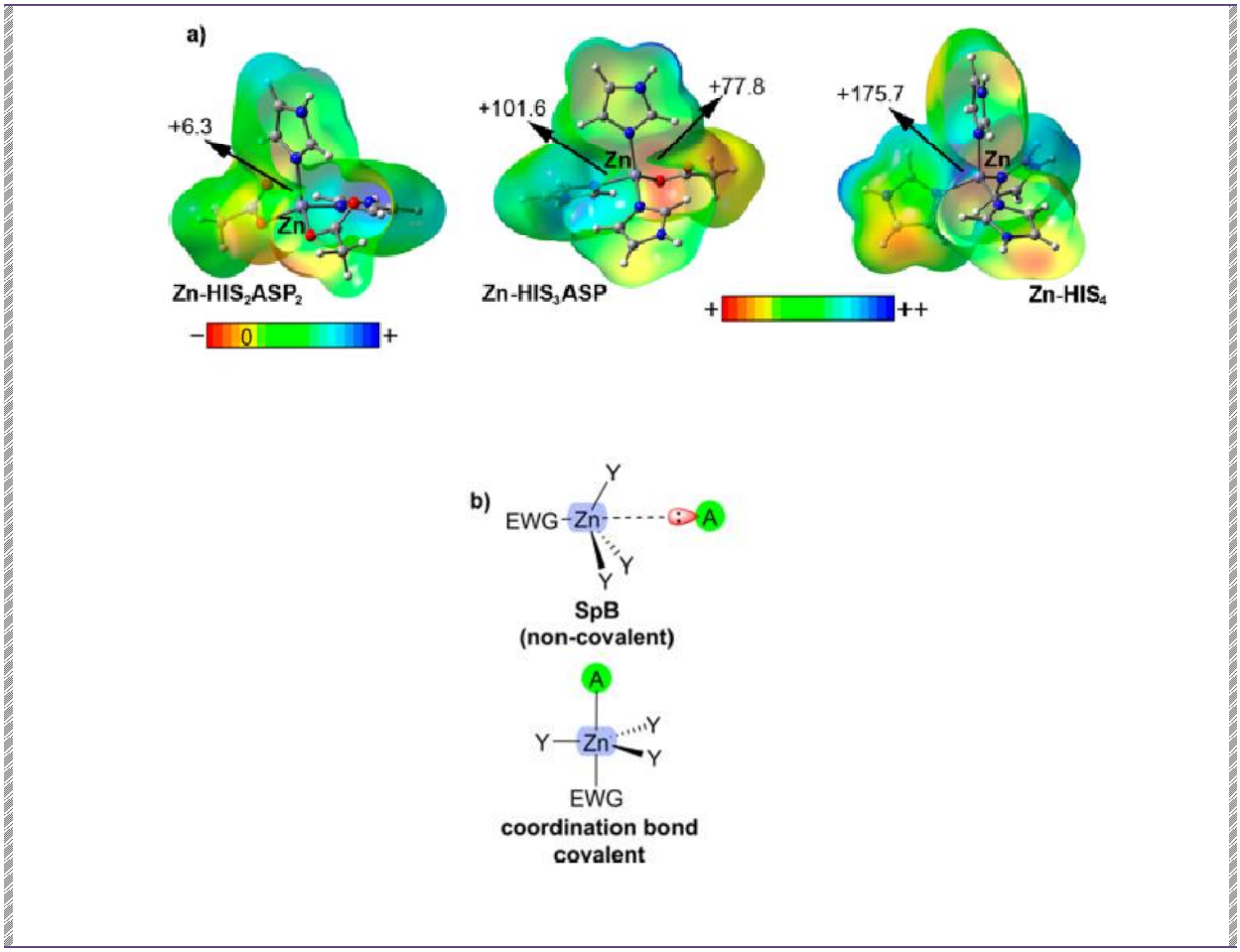


Spodium Bond [Hg]		SpB.	09

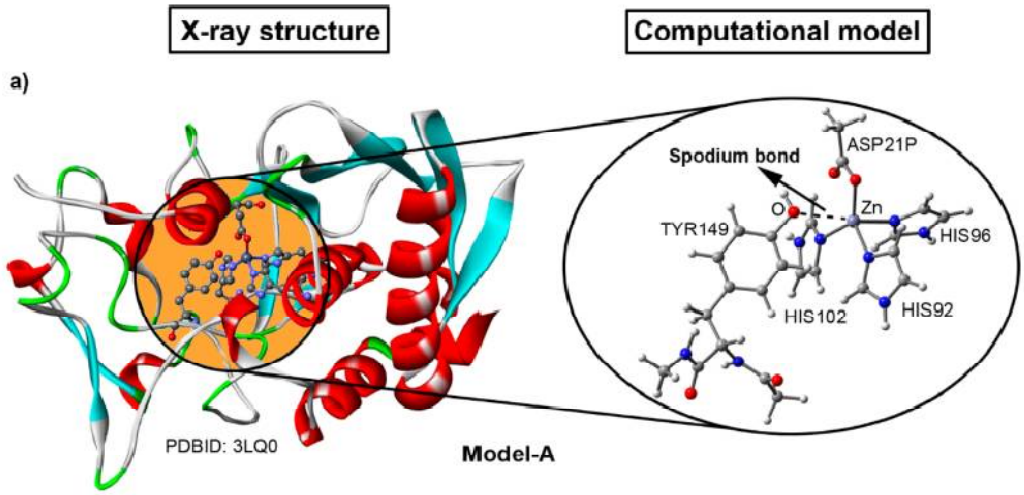
Spodium Bond



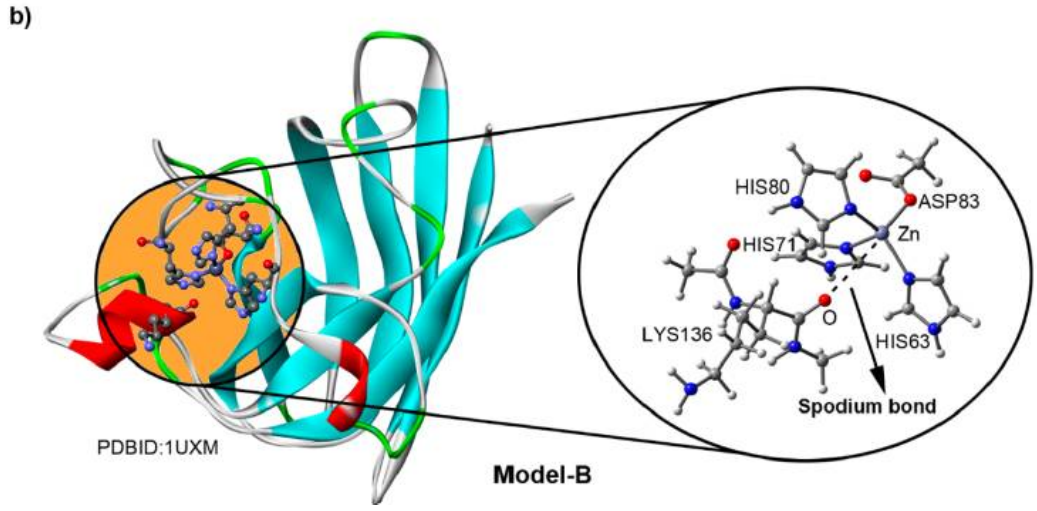
MESP



(a) Partial views of the X-ray crystal structures of 3LQ0 1UXM

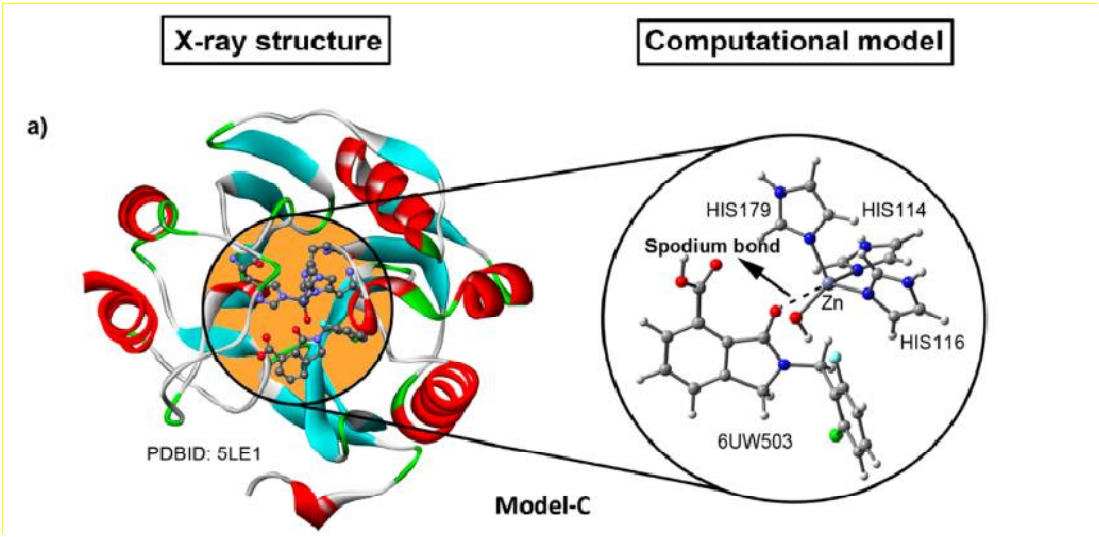


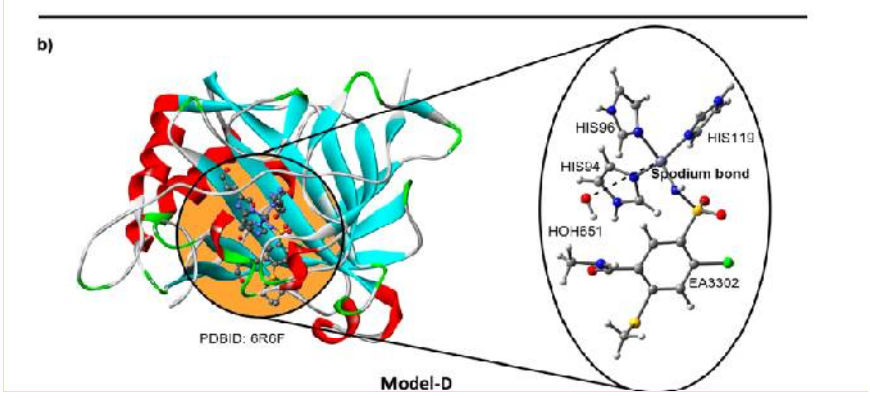
- ✓ SpB's: Zn and its tetrahedral coordination environment
- ✓ Interacting electron-rich partner [an amino acid residue (model A) or an O atom belonging to the carbonyl group of the protein backbone model



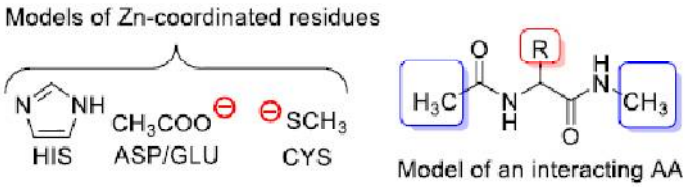
✓ SpBs represented by dashed lines connecting the O atoms and the Zn center

Sp…Bonds

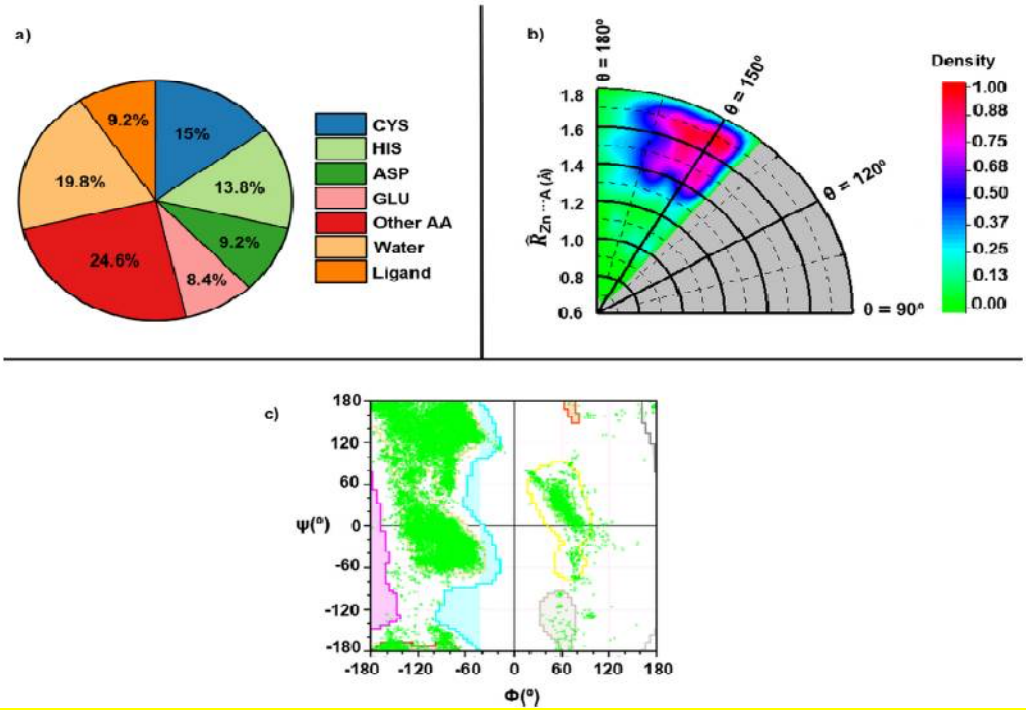




Computational models



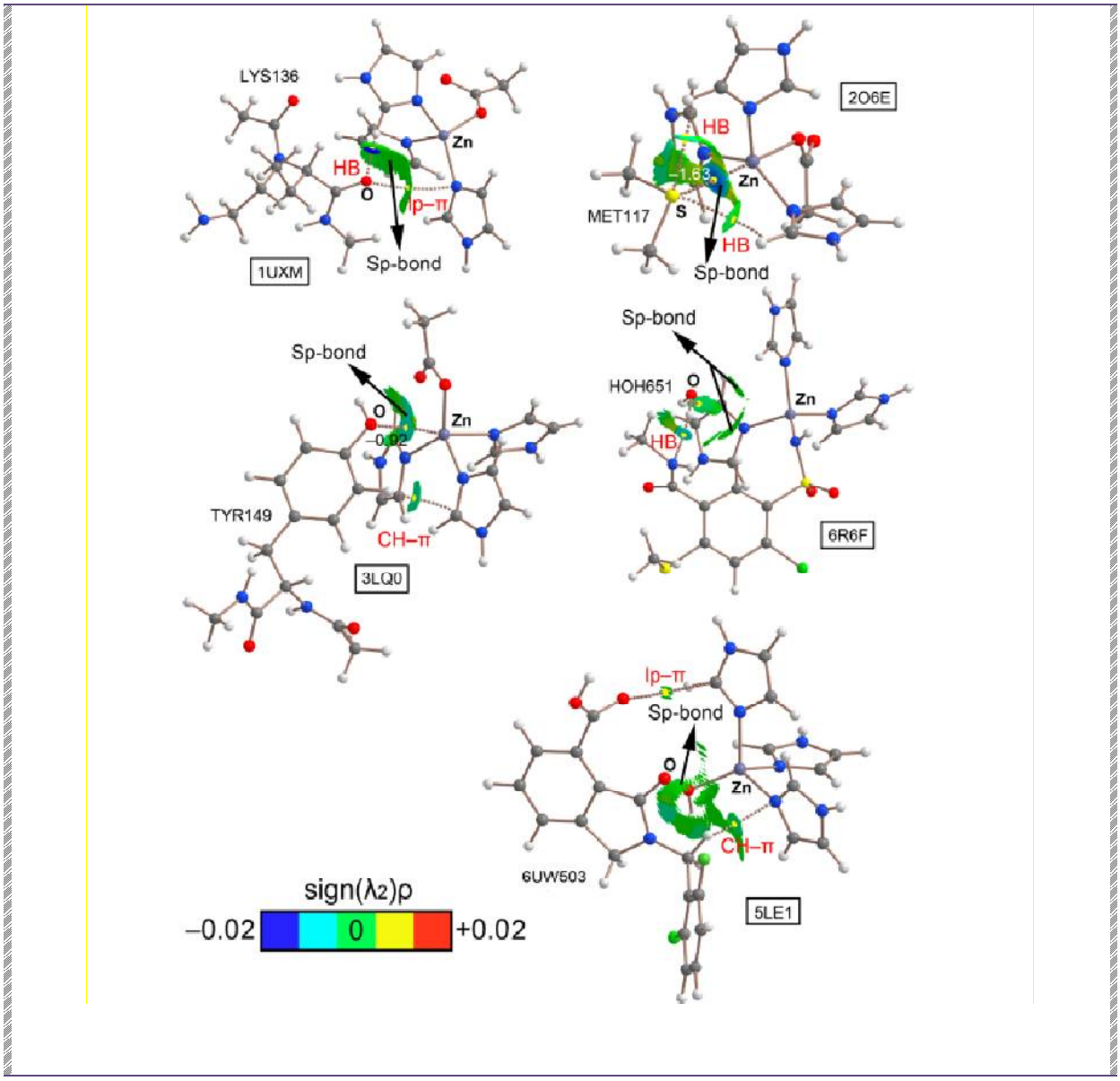
Zn···A SpB's in proteins. The angle (θ) made by A



(a) Pie chart for electron-rich partners involved in the SpB
(b) Radial distribution of Zn···A SpB's in proteins
The angle (θ) made by Awith respect to the Zn−R bond is plotted against the distance of Zn to Zn to A (R Zn···A) atom
(b) Ramachandran plot of combined N/O/S atoms belonging to the amino acid residue

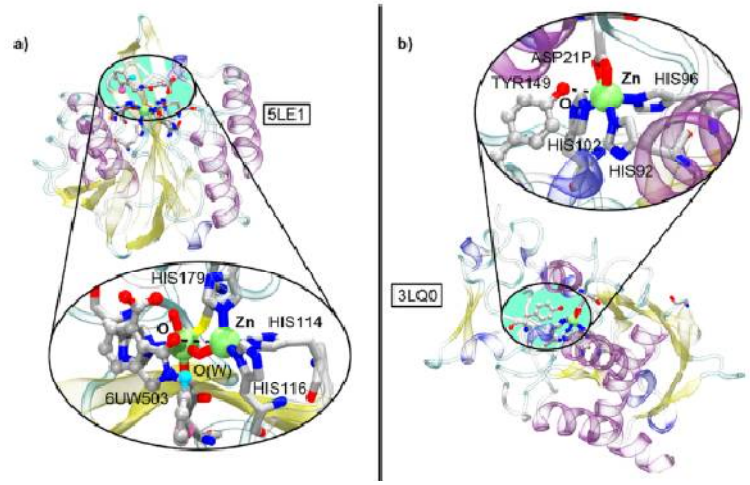
Distribution of intermolecular BCPs (yellow dots) and bond paths

Sp… bonds

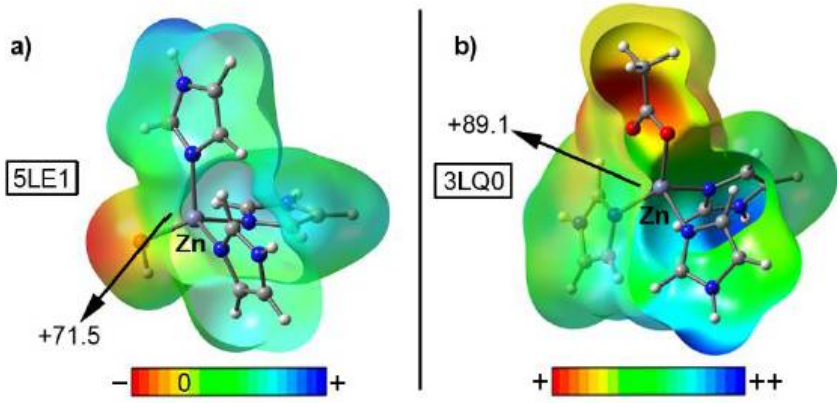

LYS136
Zn
HB
O
lp–π
Sp-bond
1UXM
2O6E
HB
−1.63
Zn
MET117
S
HB
Sp-bond
Sp-bond
O
−0.02
Zn
TYR149
CH–π
3LQ0
Sp-bond
HOH651
O
Zn
HB
6R6F
lp–π
Sp-bond
O
Zn
CH–π
6UW503
5LE1
sign(λ2)ρ
−0.02
0
+0.02

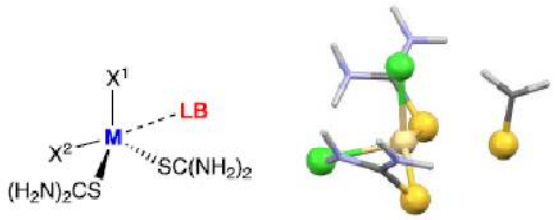
Partial views of X-ray structures

Sp…bond interaction magnified inside the circular parts of figure



MEP



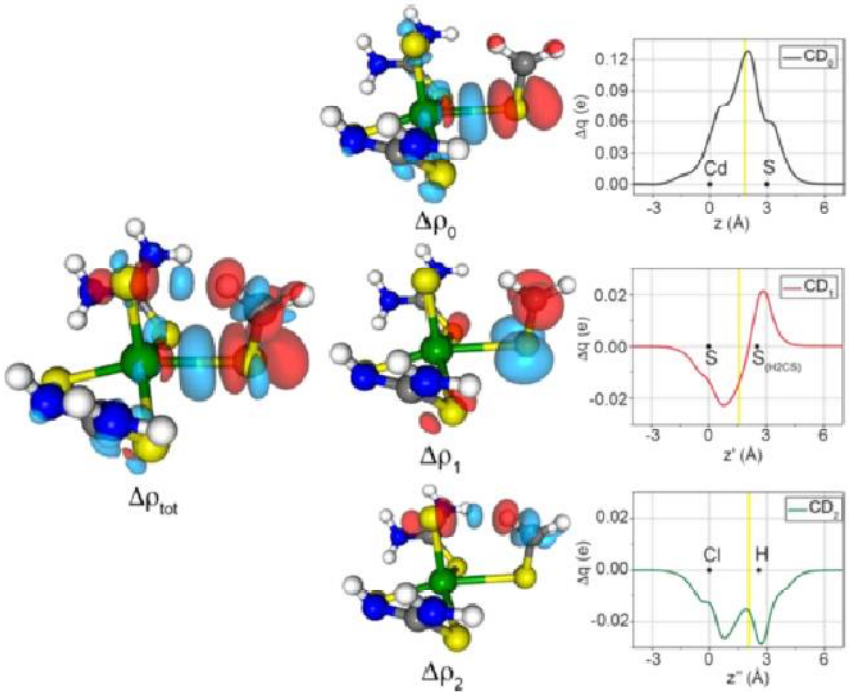


Scheme 1. Numbering of the Model Complexes Studied andOptimized Structure of 1CH2S

1: M = Cd, $X^1 = X^2$ = Cl, **2**: M = Cd, $X^1 = X^2$ = I,
3: M = Zn, $X^1 = X^2$ = Cl, **4**: M = Zn, X^1 = F, X^2 = Cl,
5: M = Hg, $X^1 = X^2$ = Cl, LB = CH_2S, CH_2O, CO, CH_3CN

Isodensity surface

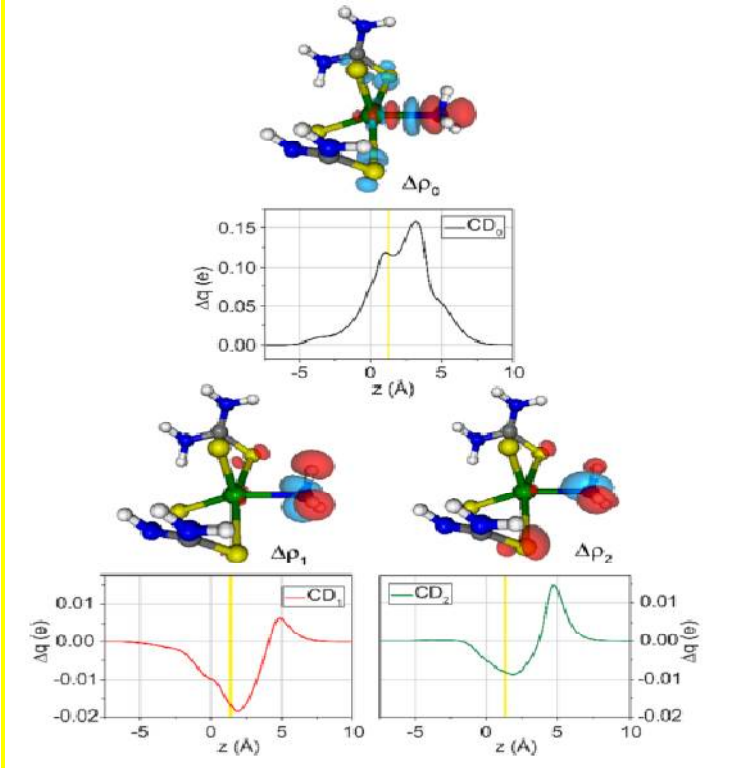
[1]···[CH2S] interaction



- Deformation maps relative toΔρtot and Δρk (k = 0, 1, and 2) of the [1]···[CH2S] interaction
- Charge flux is red → blue.
- Aside each Δρk map, corresponding charge displacement function shown
- Black dots indicate the position on the axis of atomic nuclei
- A yellow vertical band indicates boundary between the fragments

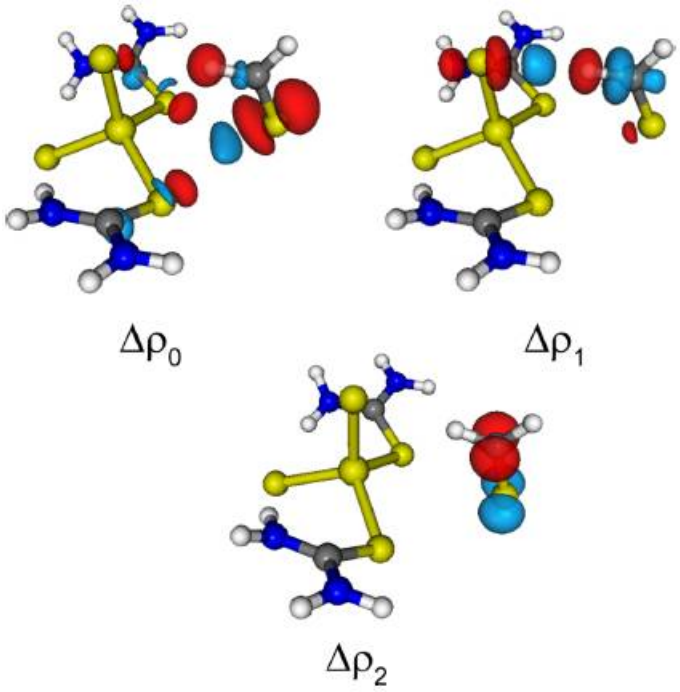
Isodensity surface

1NH3 adduct



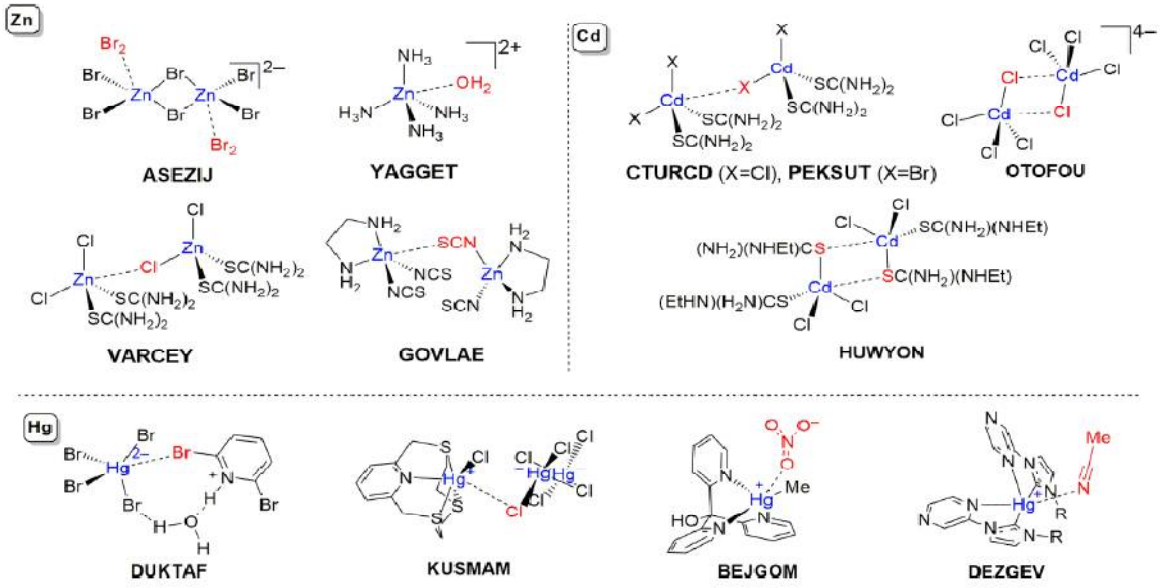
Isodensity surface

3CH2S adduct

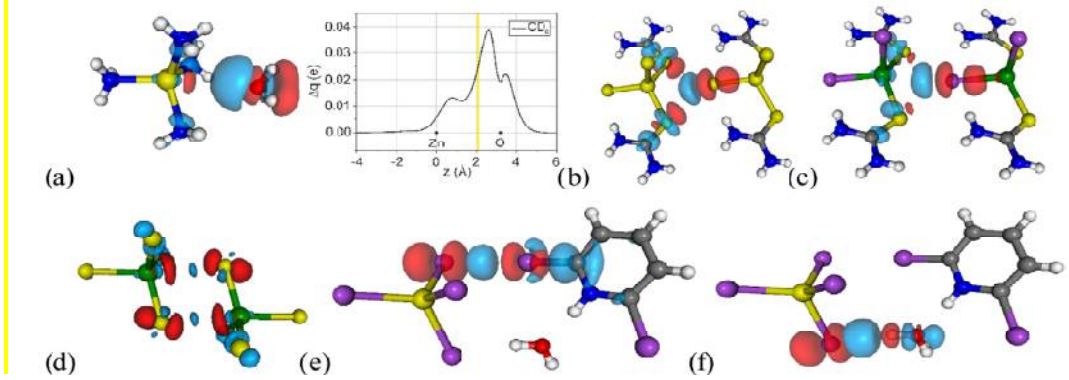


ETS–NOCV–CD Analysis

Dashed Lines : Putative SpB Interactions



Isodensity surface



Adducts

(a) $\Delta\rho_0$ of the YAGGET

(b) $\Delta\rho_0$ of the VARCEY

(c) $\Delta\rho_0$ of the PEKSUT

(d) $\Delta\rho_0$ of the OTOFOU

(e) $\Delta\rho_1$ of the DUKTAF

(f) $\Delta\rho_2$ of the DUKTAF

- ✓ Charge flux is red →blue

Eigen values

	υ_0	υ_1	υ_3	υ_4	υ_5
1CH$_3$CN	0.14	0.10	0.06	0.05	0.04
1CO	0.12	0.08	0.06	0.02	0.02

EDA results, in kcal/mol

Adduct	E_{int}	E_{orb}	E_{st}	E_{disp}
1CH$_3$CN	-9.4	-6.2	-2.2	-0.9
1CO	-4.4	-2.8	-1.2	-0.4

Orbital Energies (in kcal/mol) and CT Values (inme) Relative to the Different Bond Components

adduct	E_{orb}	E_{SpB} (CT_{SpB})	E_{HB} (CT_{HB})	E_{ChB} (CT_{ChB})
1CH$_3$CN	−6.2	−2.5 (42)	−1.4 (−17)	−0.3 (5)
1CO	−2.8	−0.7 (15)		−0.3 (−2)

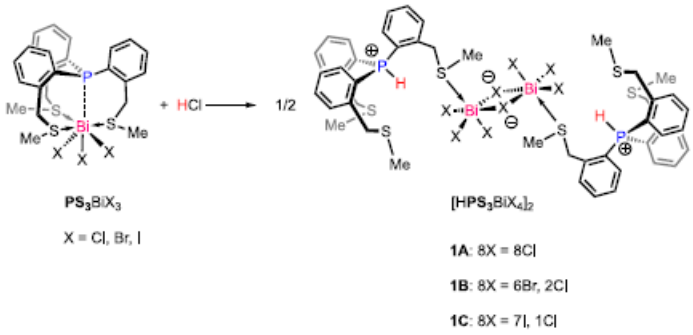
EDA Results (in kcal/mol) and CT Values (in me) Relative to the Different Bond Components for Experimental Solid-State Dimers from CSD

adduct	E_{int}	E_{orb}	E_{st}	E_{disp}	E_{SpB} (CT_{SpB})	E_{HB} (CT_{HB})	E_{ChB} (CT_{ChB})	E_{XB} (CT_{XB})	refs
					M = Zn				
ASEZIJ-a	−8.8	−6.1	−2.3	−0.4				−4.5 (−77)	41
ASEZIJ-b	−15.2	−14.8	0.0	−0.5				−12.9 (−136)	41

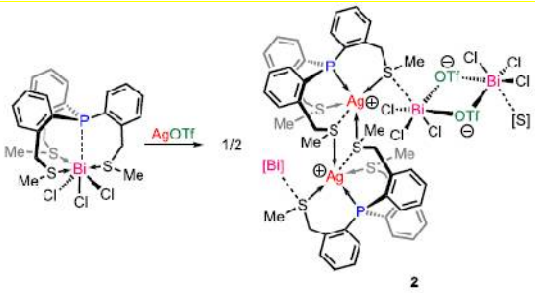
Spodium Bond
[Zn]

SpB. 07

Zwitterions 1A–C



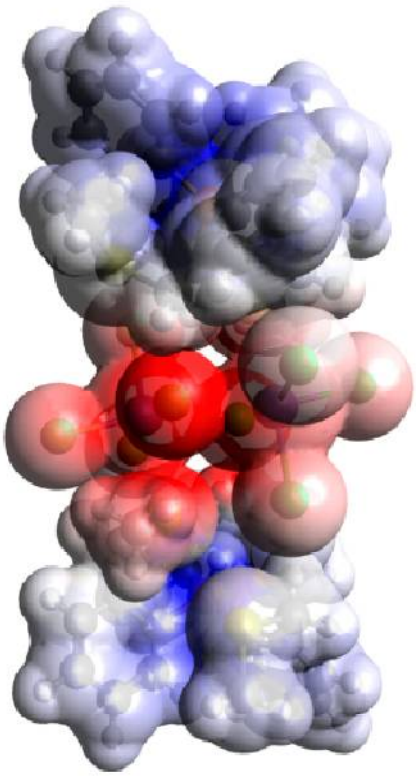
Compound 2



Scheme 2. Reaction of $PS3BiCl_3$ with Silver Triflate, Delivering Compound 2[a]
[a][Bi] and [S] denote the continuation of the polymeric chain.

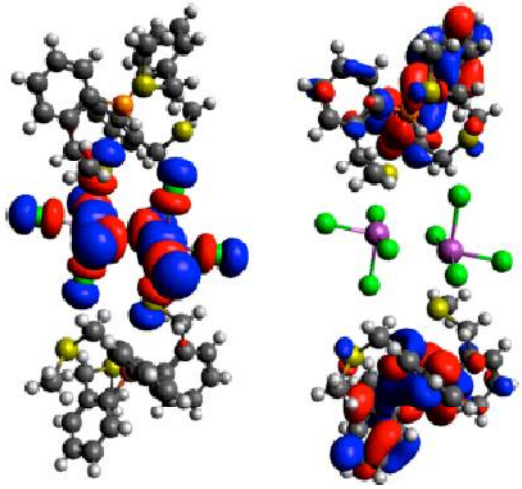
MESP

ωB97XD/def2-SVP(PCM)



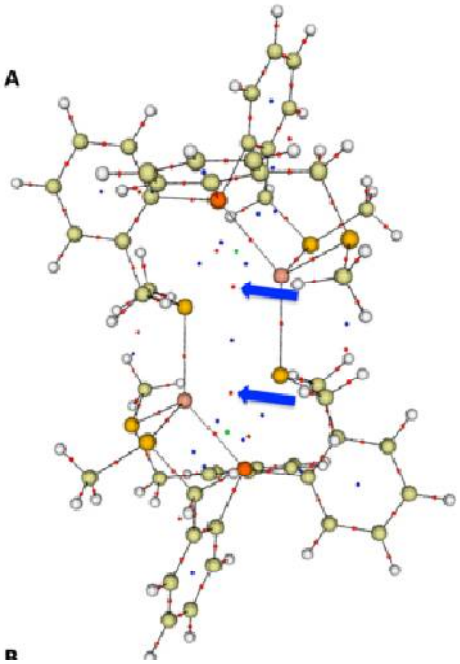
Red and blue areas: attractive and repulsive electrostatic potentials toward a positive point charge

. Kohn–Sham HOMO (left) and LUMO (right)
B3LYP/def2-SVP

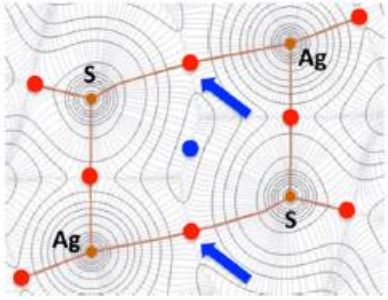


AIM analysis of dimer $[Ag(PS3)]_2^{2+}$

ωB97XD / def2-SVP(PCM = CH_2Cl_2)



B



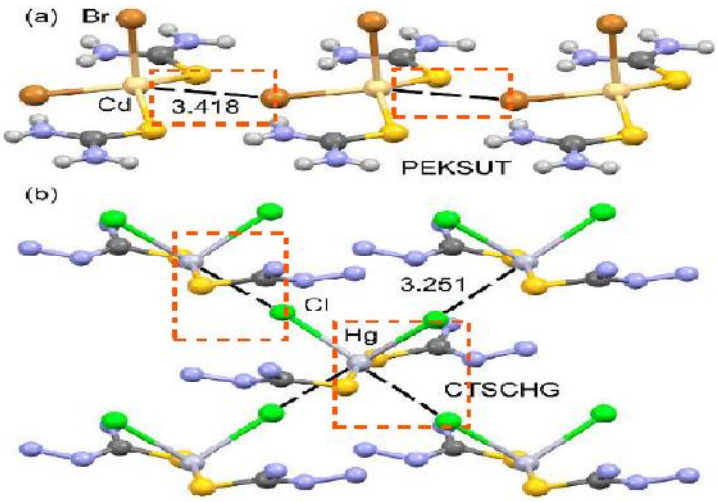
- Blue arrows show the weak S···Ag interactions
- Red, blue, and green dots : bond, ring cage critical points

- ✓ (A) Three-dimensional representation of bond, ring, and cage critical points.
- ✓ (B) Contour plot of the electron density in the Ag_2S_2 plane

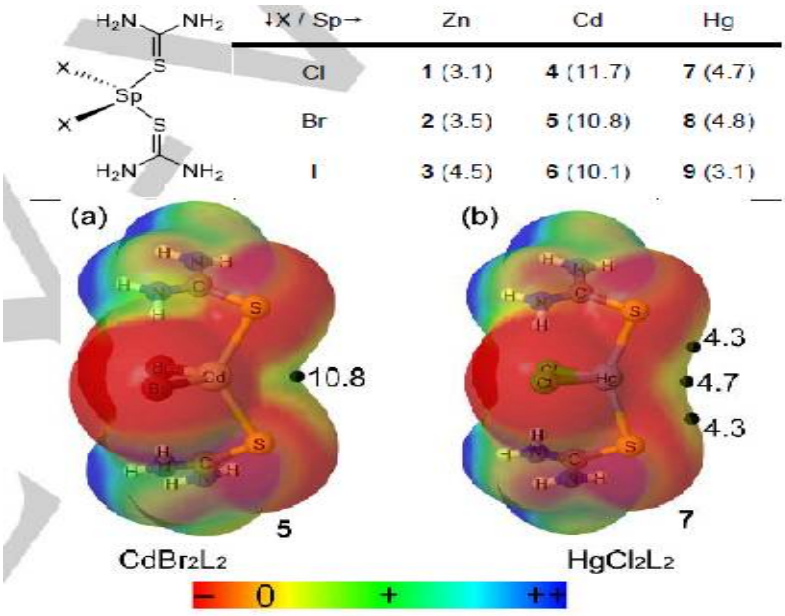
Spodium Bond
[Zn Cd Hg [Cn]]

SpB. 02

X-ray structure

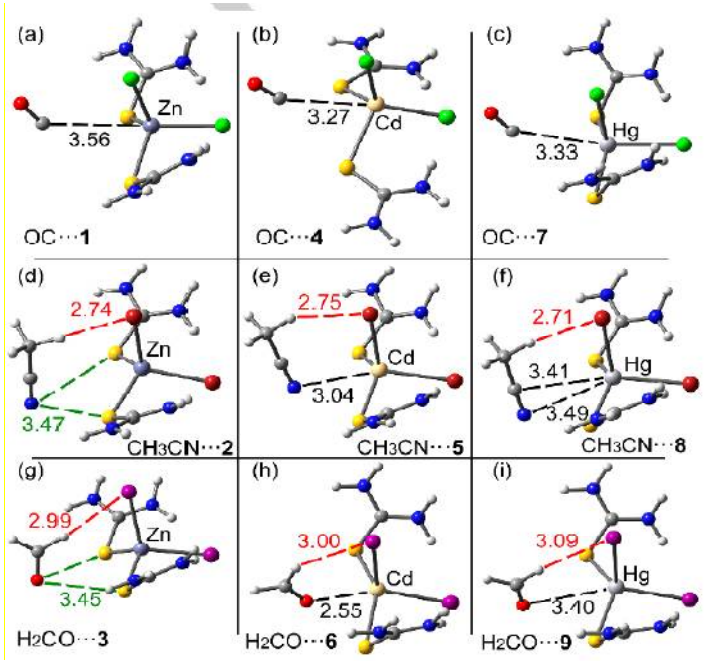


MESP

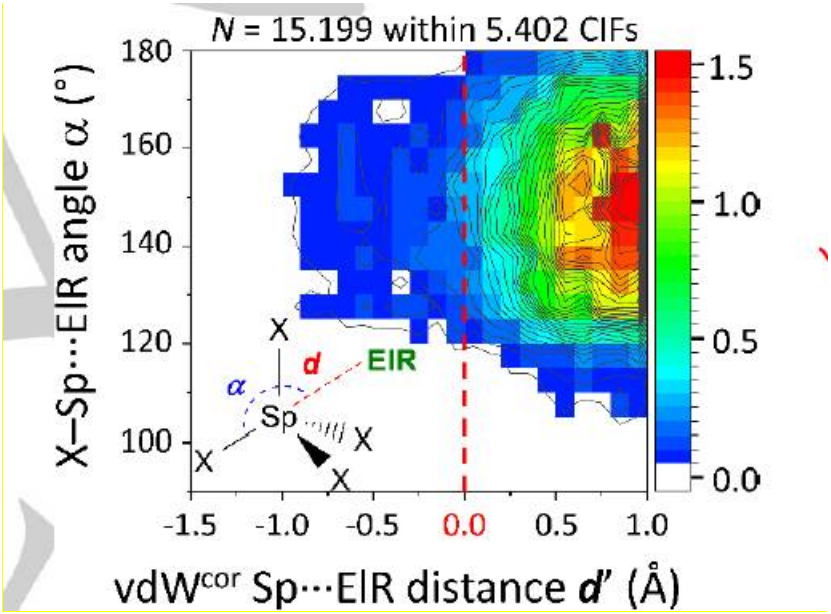


CdBr2L2 (L = thiourea)

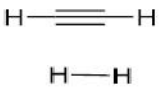
RI-MP2/aug-cc-pVTZ geometries



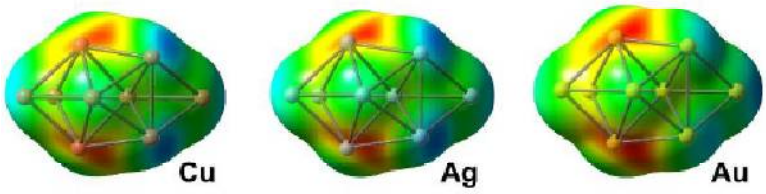
Heat plots of the largest X–Sp···ElR angle



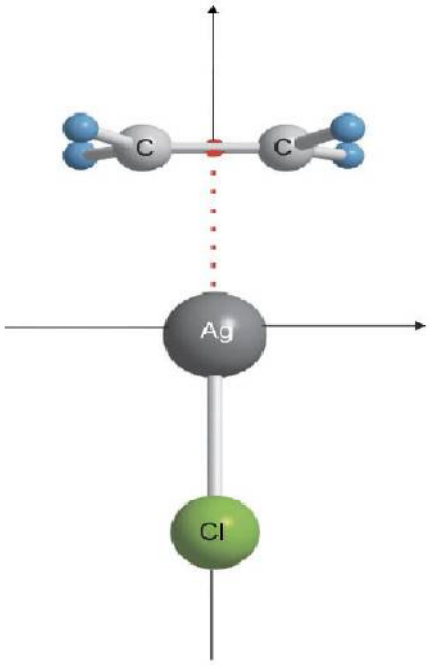
Lewis Bases
LB

Anions	Neutral molecules			
	Atoms	Bonds	Rings	Groups
H^- F^- CN^- 	He			 $BrCH_3$

Coinage metal clusters

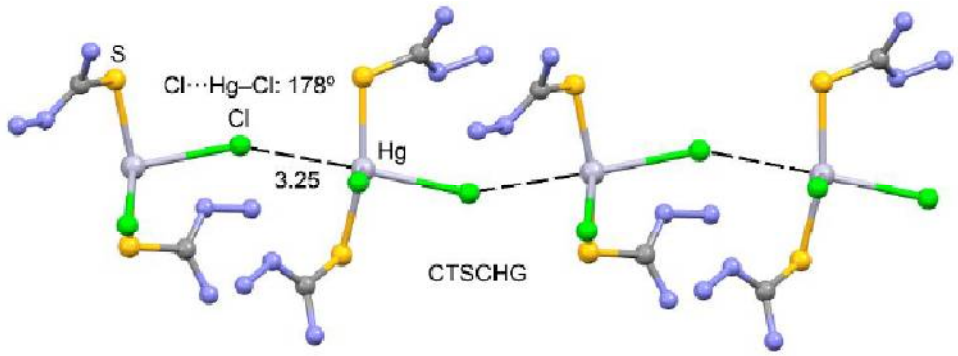


Experimental microwave (MW) structure of complex C2H4… Ag–Cl



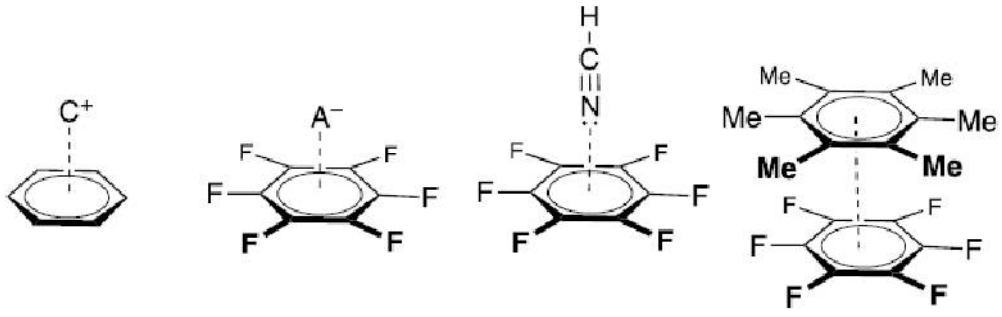
Spodium Bond [Zn]		SpB.	06

ZnCl2



NCI Bond		SpB.	06

Cation-pi, anion-pi, lone pair–pi and pi-pi stacking



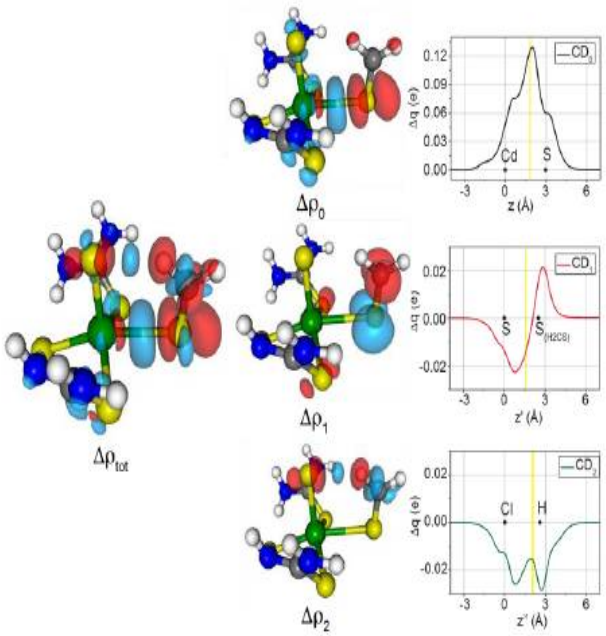
Spodium Bond [Zn Cd Hg]		SpB.	05

1: M = Cd, $X^1 = X^2$ = Cl, 2: M = Cd, $X^1 = X^2$ = I,
3: M = Zn, $X^1 = X^2$ = Cl, 4: M = Zn, X^1 = F, X^2 = Cl,
5: M = Hg, $X^1 = X^2$ = Cl, LB = CH_2S, CH_2O, CO, CH_3CN

ETS-NOCV analysis

M06-D0/TZVP/ZORA level

Isodensity surface plots



(ETS-NO-CV-CD)

Extended Transition State-(ETS)

Natural Orbital (NO) for

Chemical Valence-(CV)

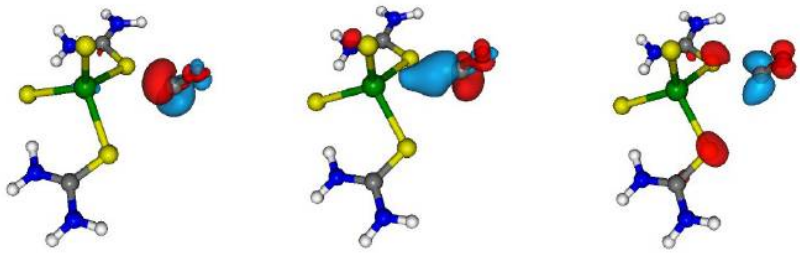
Charge Displacement analysis (CD)

Adduct
1CH$_3$CN
1CO
1CH$_2$O
1CH$_2$S
2CO
3CH$_3$CN
3CO
3CH$_2$O
3CH$_2$S
4CH$_2$O
5CH$_3$CN
5CO
5CH$_2$O
5CH$_2$S

Functional/basis set
M06-D0/ZORA-TZVP
B3LYP-D3/ZORA-TZVP
PBE0-D3/ZORA-TZVP
TPSSh-D3/ZORA-TZVP
TPSS-D3/ZORA-TZVP
BLYP-D3/ZORA-TZVP
BP86-D3/ZORA-TZVP
B3LYP-D3/ZORA-sVP
BP86-D3/ZORA-sVP

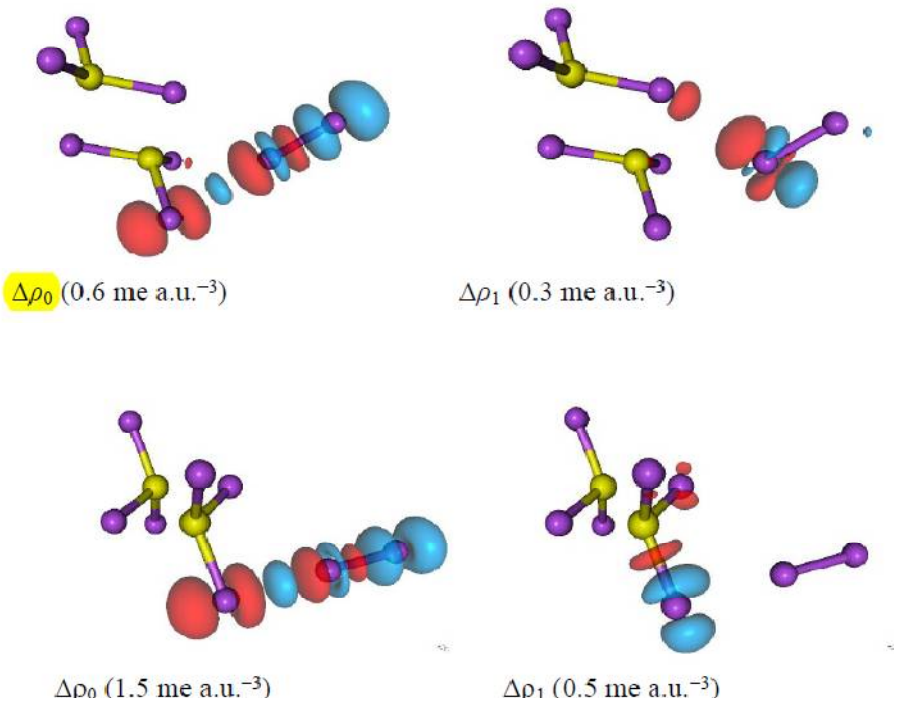
Isodensity surfaces

1CO adduct



$\Delta\rho_0$ (0.8 me a.u.$^{-3}$) $\Delta\rho_1$ (0.6 me a.u.$^{-3}$) $\Delta\rho_2$ (0.2 me a.u.$^{-3}$)

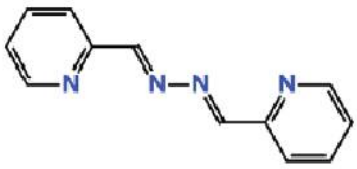
ASEZIJ adduct



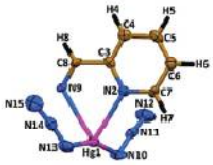
Isodensity surfaces for the deformation maps relative to Δρk (k = 1 and 2)

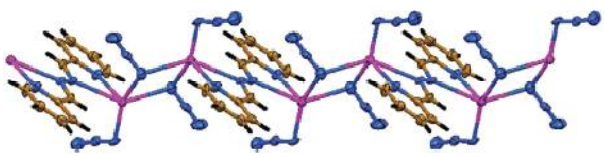
Spodium Bond [Hg]		SpB.	04

ligand L



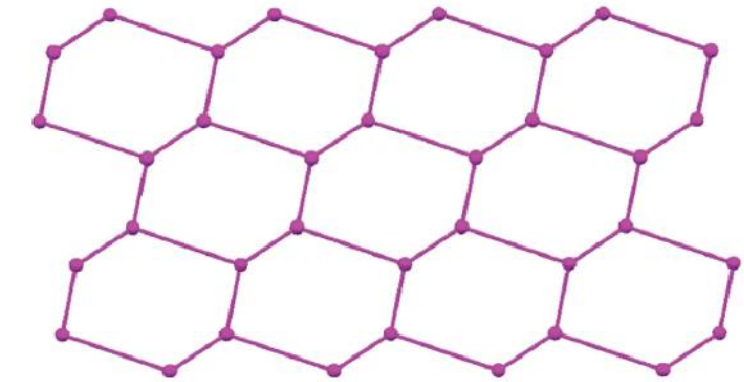
(top) Asymmetric unit in the crystal structure of 1

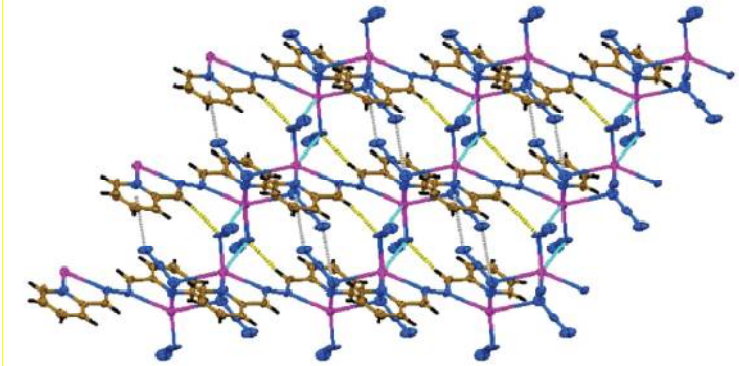




(bottom) A 1D zig-zag polymeric chain in the crystal structure of 1

2D supramolecular polymeric layer in the crystal structure of 1

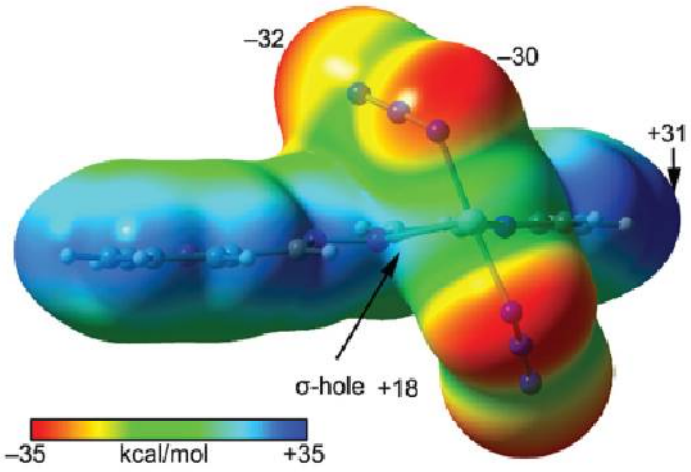




Constructed from 1D polymeric chains linked through the Hg N spodium bonds

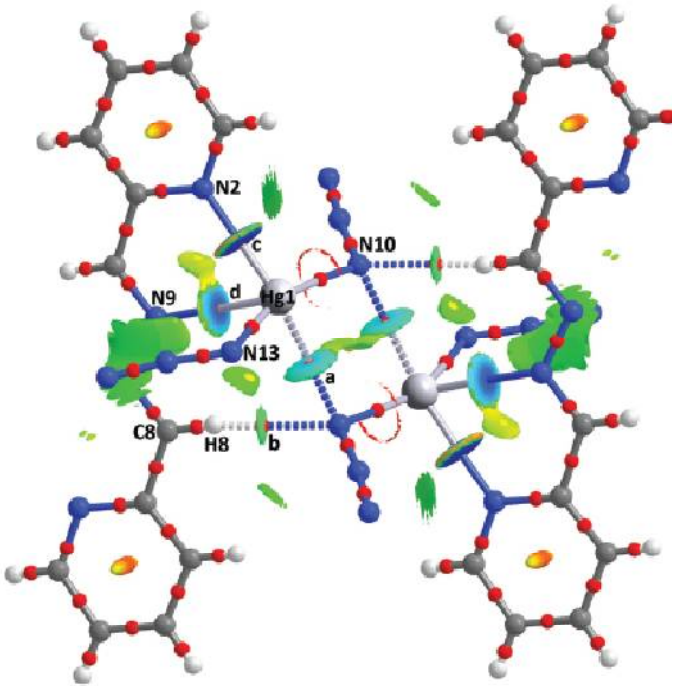
M E S P

PBE1PBED3/def2-TZVP



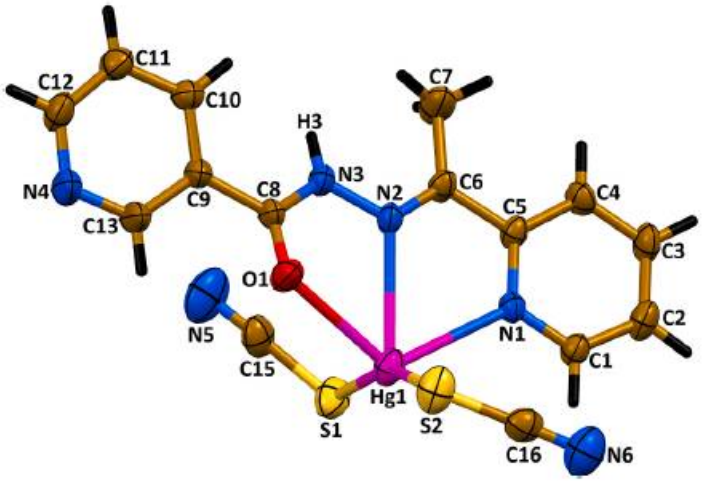
QTAIM +NCIplot analyses

[HgL(N3)2]2of 1

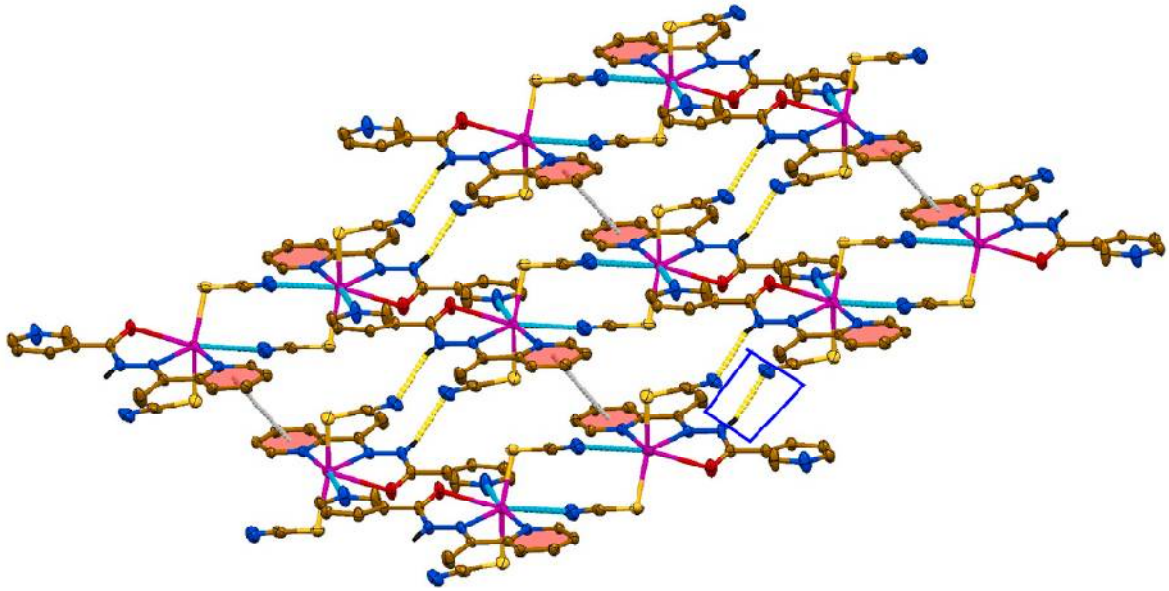


Spodium Bond *[Hg]*		SpB.	03

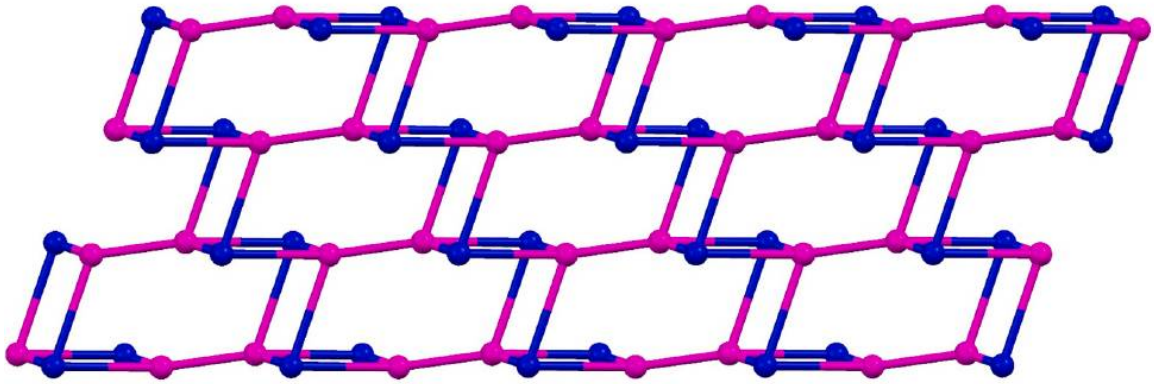
Molecular structure of [Hg(HL)(SCN)2]



(top) The 2D supramolecular polymeric layer in the crystal structure of [Hg(HL)(SCN)2]



simplified network of [Hg(HL)(SCN)2]

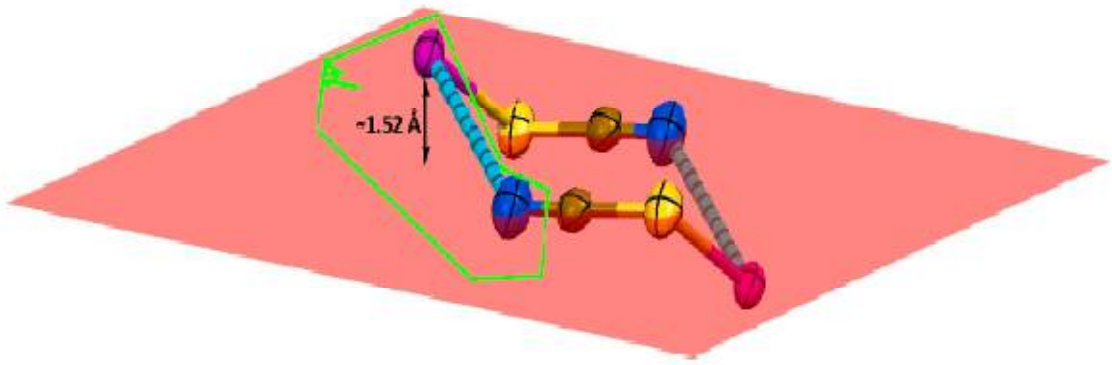


Binodal 3,4-connected hcb topology

- Hg···N spodium bonds
- N–H···N hydrogen bonds

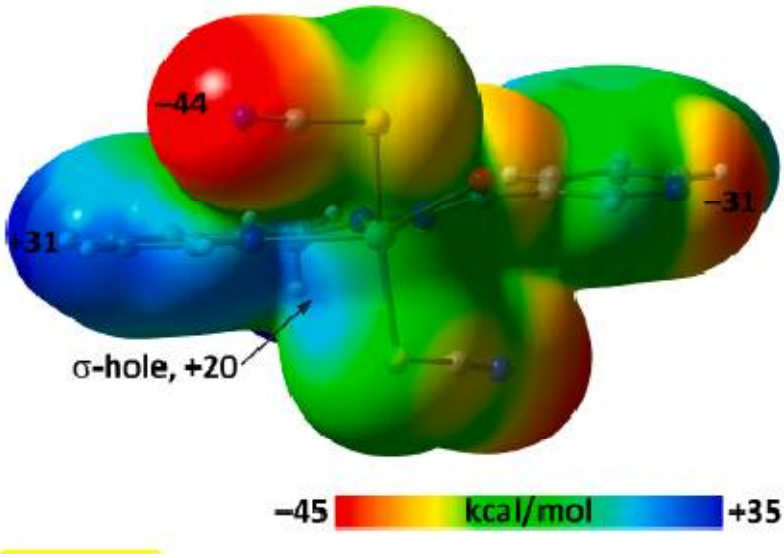
Eight-membered [Hg2(SCN)2]2+ motif, adopting a chair conformation

Hg···N spodium bonds

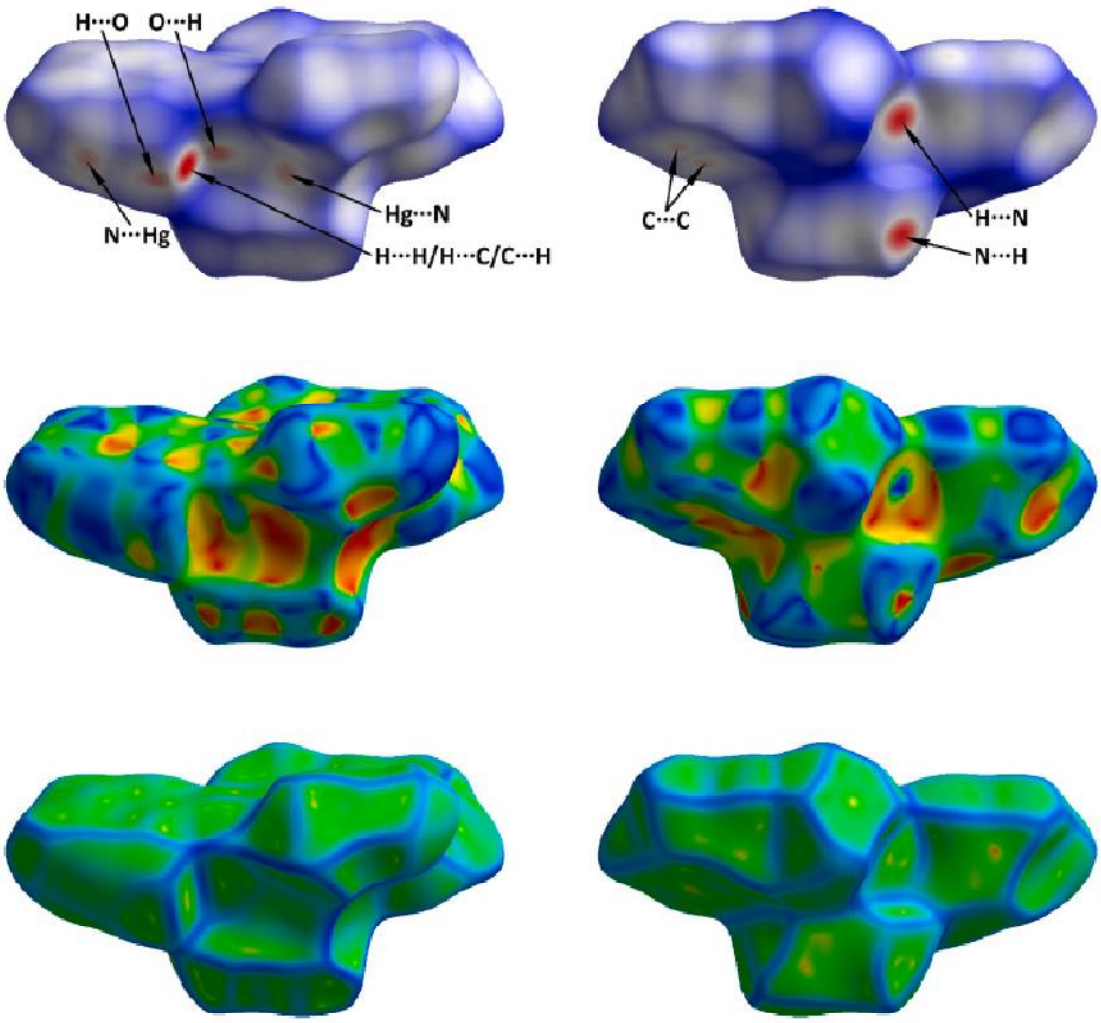


ESP [Hg(HL)(SCN)2]

PBE0-D3/def2-TZVP

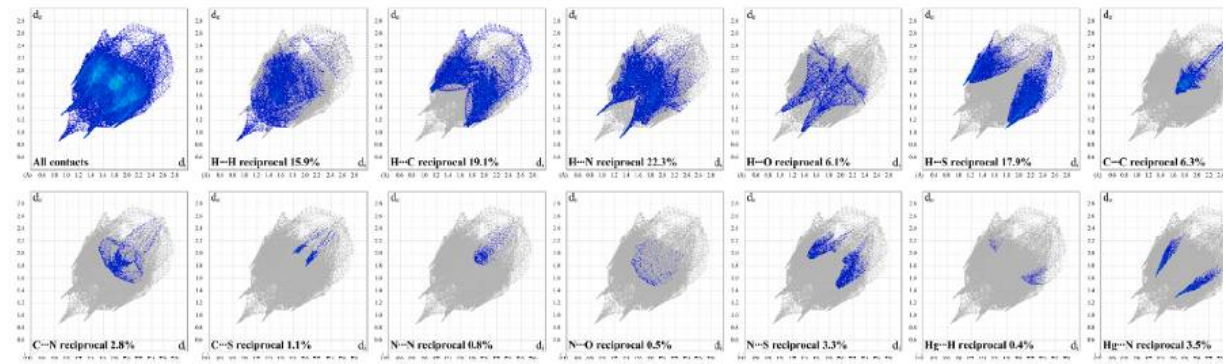


Molecular Hirshfeld surfaces
[Hg(HL)(SCN)2]



➔ Top, middle, bottom : [normalized distance;shape index ; curvedness]

Hirshfeld contact surfaces
[Hg(HL)(SCN)2]



- (top) 2D and decomposed 2D fingerprint plots of observed contacts
- (bottom) Hirshfeld contact surfaces and derived "random contacts" and "enrichment ratios"

[Hg(HL)(SCN)2]
SpB