



## Non-conventional Interactions in Molecular Crystals

Edward R.T. Tiekink  
Research Centre for Crystalline Materials

The 43rd Congress on Science and  
Technology of Thailand (STT 43)

## Molecular packing

Well known...

Hydrogen bonding  
Halogen bonding

"Emerging"

Secondary bonding  
M-M interactions  
M-H interactions  
Interactions involving chelate rings

"Non-conventional", "Weak", "Second tier",  
"Not really important cf. (HB)<sup>2</sup>"



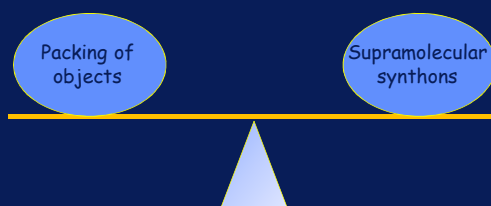
## Factors that Control Molecular Packing

Supramolecular synthon approach

versus

Global crystal packing approach

## Factors that Control Molecular Packing



## Factors that Control Molecular Packing

IMF interactions form to  
arrange molecules into  
the crystal

Packing of  
objects

Supramolecular  
synthons

## Factors that Control Molecular Packing

Molecules pack and,  
then, IMF interactions  
form

Packing of  
objects

Supramolecular  
synthons

## "Egg Causality Dilemma"



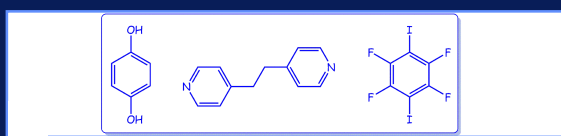
atom...atom or molecule...molecule interactions

## Molecular packing

Well known...

Hydrogen bonding  
Halogen bonding

## Hydrogen Bonding versus Halogen Bonding



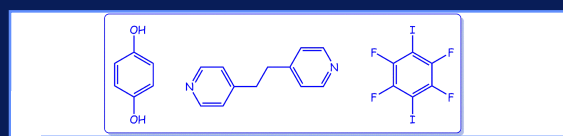
### Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly Processes<sup>\*,†</sup>

Eleonora Corradi, Stefano V. Meille, Maria T. Messina, Pierangelo Metrangola,<sup>\*</sup> and Giuseppe Resnati<sup>†</sup>

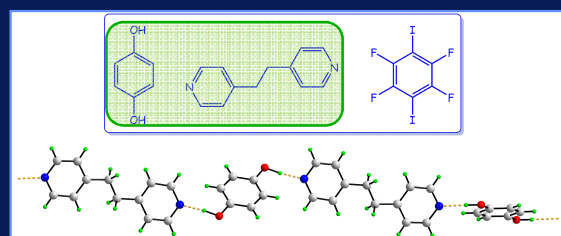
1782

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2000 0970-0833/00/3910-1782 \$ 17.50+ .50 Angew. Chem. Int. Ed. 2000, 39, No. 10

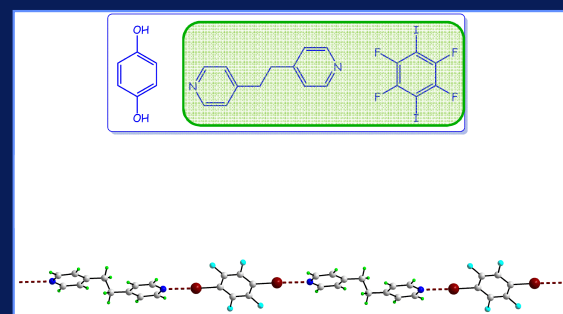
## Hydrogen Bonding versus Halogen Bonding



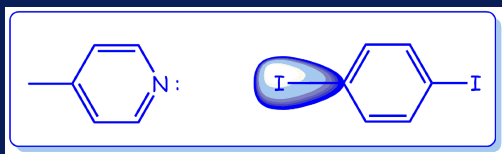
## Hydrogen Bonding versus Halogen Bonding



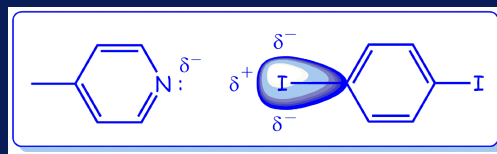
## Hydrogen Bonding versus Halogen Bonding



### ? Halogen Bonding ?

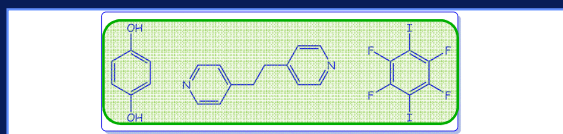


### ? Halogen Bonding ?

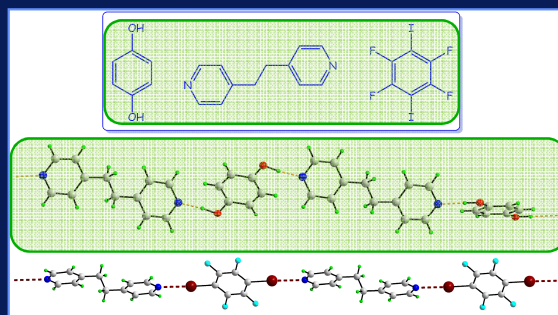


polar gap,  $\sigma$ -hole

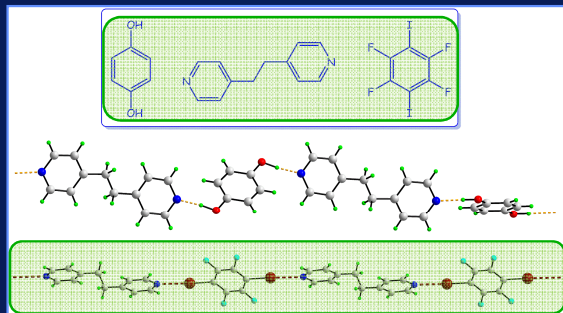
### Hydrogen Bonding versus Halogen Bonding



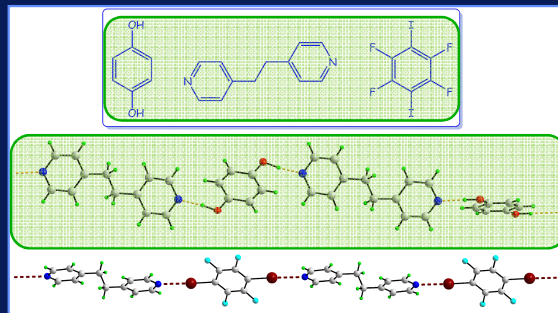
### Hydrogen Bonding versus Halogen Bonding



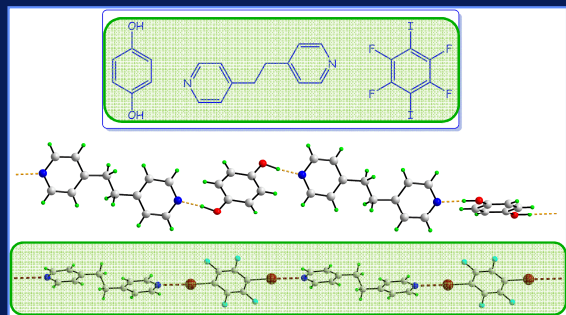
### Hydrogen Bonding versus Halogen Bonding



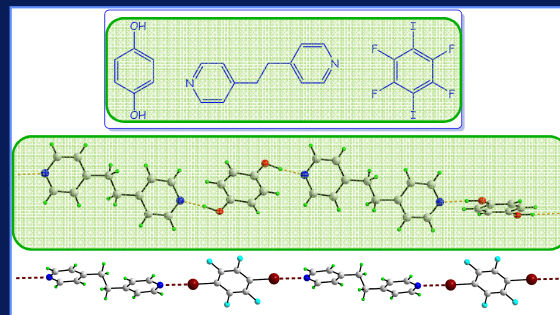
### Hydrogen Bonding versus Halogen Bonding



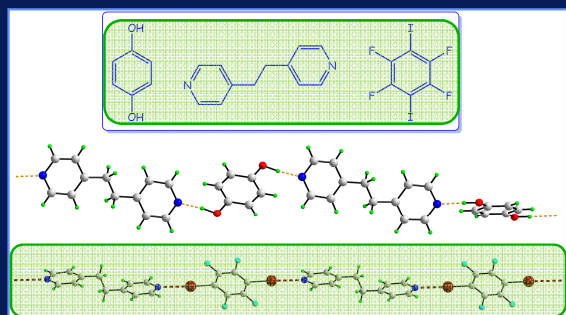
## Hydrogen Bonding versus Halogen Bonding



## Hydrogen Bonding versus Halogen Bonding



## Hydrogen Bonding versus Halogen Bonding



## Molecular packing

Well known...

Hydrogen bonding  
Halogen bonding

HB<sup>2</sup>: Similar in energy = 5 - 15 kcal/mol

## Molecular packing

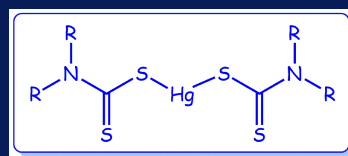
Well known...

Hydrogen bonding  
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"Emerging"

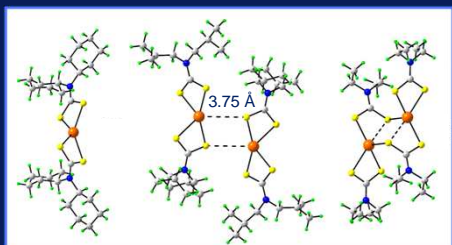
Secondary bonding  
M-M interactions  
M-H interactions  
Interactions involving chelate rings

## Steric effects and Secondary Bonding



"Hg(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>"

## Steric effects and Secondary Bonding



"Hg(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>"  
Sum of the van der Waals radii for Hg and S = 3.35 Å  
← increasing size of R

Inherently weak interactions

How weak?

Inherently weak interactions

How weak?

Repackaging:

Tetrel, pnictogen and chalcogen bonds

Electrophilic sites from Groups 14, 15 & 16, resp.

THE JOURNAL OF  
PHYSICAL CHEMISTRY A

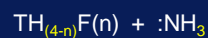
Article  
pubs.acs.org/JPCA

### Systematic Elucidation of Factors That Influence the Strength of Tetrel Bonds

Steve Scheiner\*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

DOI: 10.1021/jp101604a0000  
J. Phys. Chem. A 2011, 115, 1000–1008



T = C, Si, Ge & Sn

n = 0	0.9 kcal/mol
n = 1*	6 – 9 kcal/mol
SnF <sub>4</sub>	25.5 kcal/mol

THE JOURNAL OF  
PHYSICAL CHEMISTRY A

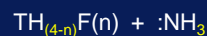
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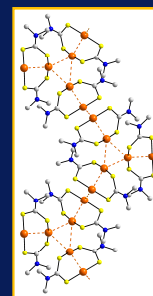
## Aurophilic interactions

Au–Au separations in molecular  
Crystal structures: 2.50 ~ 3.50 Å

Radius from ccp-Au: 2.89 Å

Sum of van der Waals radii: 3.80 Å

5d<sup>10</sup> closed shell interactions -  
relativistic effects



Yam et al. *Inorg. Chim. Acta* **358** (2005) 4191.

## Gold Chemistry

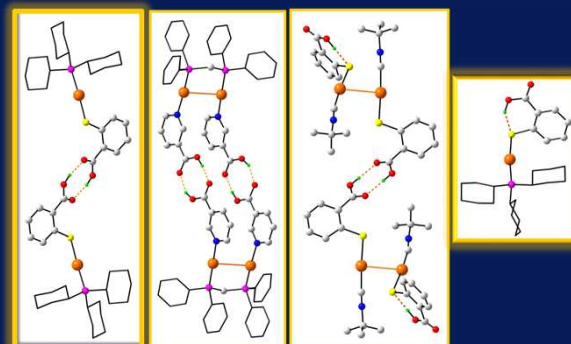
Competition between

- i)  $\text{Au}\cdots\text{Au}$  and hydrogen bonding



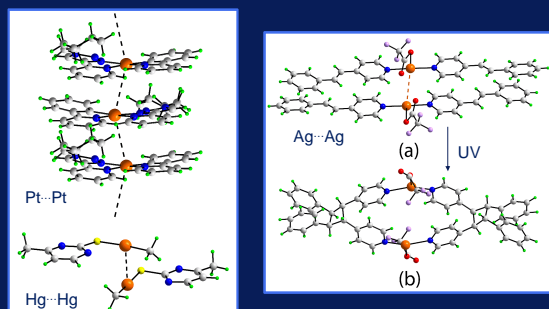
Comparable in energy

## Gold structures with carboxylic acids



*Coordination Chemistry Reviews*, 275 (2014) 130 – 153

## Heterometallophilic ( $M\cdots M'$ ) interactions



Krikorian *et al.*, 2014; Bravo *et al.*, 1986; Chu *et al.*, 2005

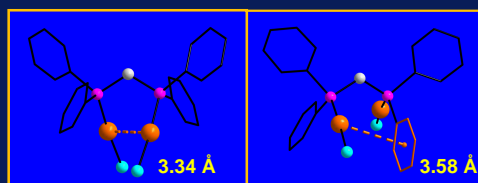
## Gold Chemistry

Competition between

- i)  $\text{Au}\cdots\text{Au}$  and hydrogen bonding
- ii)  $\text{Au}\cdots\text{Au}$  and  $\text{Au}\cdots\pi(\text{arene})$



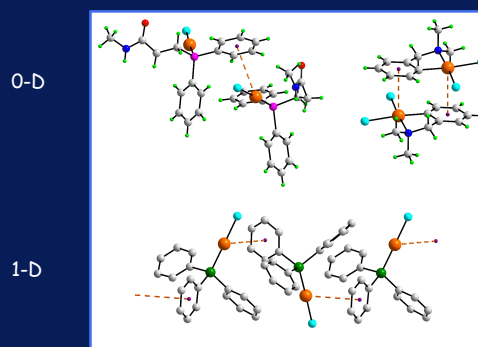
## Polymorphs of $(\text{dppm})(\text{AuCl})_2$



Schmidbaur *et al.* (1977)

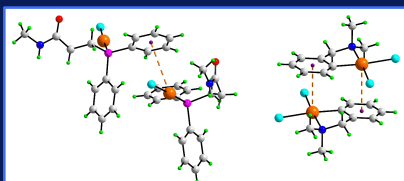
Healy (2003)

## Intermolecular $\text{Au}\cdots\pi(\text{arene})$ interactions

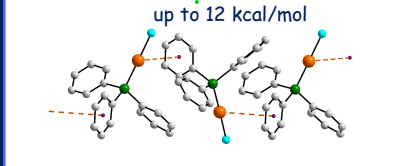


## Intermolecular $\text{Au} \cdots \pi(\text{arene})$ interactions

0-D



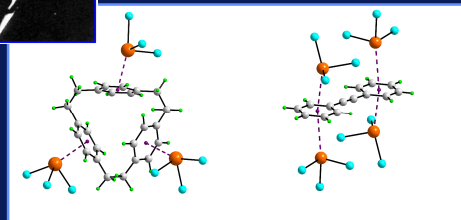
1-D



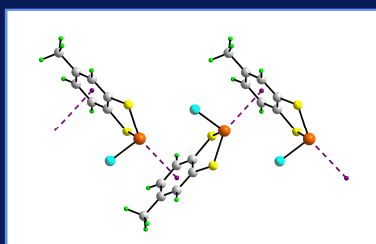
## Intermolecular $\text{M}(\text{lp}) \cdots \pi(\text{arene})$ interactions



"Menšutkin complexes"



## Intermolecular $\text{M}(\text{lp}) \cdots \pi(\text{arene})$ interactions



cf. polar gap,  $\sigma$ -hole

*Inorg. Chim. Acta*, 2008, **361**, 427.

## Energy?

ChemComm

COMMUNICATION

View Article Online  
View Journal | View Issue



Cite this: Chem. Commun., 2015,  
52, 3500.

Received 17th December 2015,  
Accepted 27th January 2016

DOI: 10.1039/C5CC01035B

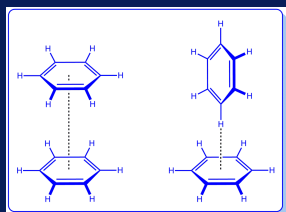
On the nature of the stabilisation of the  $\text{E} \cdots \pi$   
pnictogen bond in the  $\text{SbCl}_3 \cdots \text{toluene}$  complex†

Rabindranath Lo,<sup>a</sup> Petr Švec,<sup>b</sup> Zdeňka Růžicková,<sup>b</sup> Aleš Růžicka<sup>a</sup> and  
Pavel Hobza<sup>a,c</sup>

$\text{SbCl}_3 +$	$\text{C}_6\text{H}_6$	7.7 kcal/mol
	$\text{C}_6\text{H}_5\text{Me}$	9.6 kcal/mol
	$\text{C}_6\text{Me}_6$	15.5 kcal/mol

## $\pi$ -Systems in Supramolecular Chemistry

Classic  $\pi$ -systems/interactions



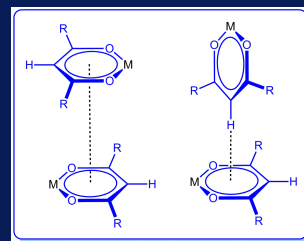
face-to-face edge-to-face

## $\pi$ -Systems in Supramolecular Chemistry

TM Chelate  $\pi$ -systems/interactions



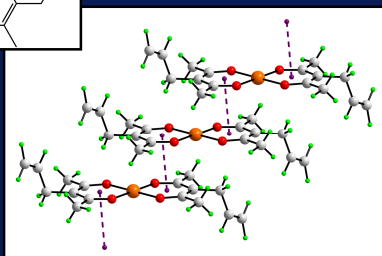
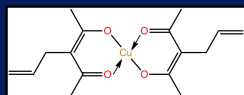
Snezana Zarić



face-to-face edge-to-face

*Cryst. Growth Des.*, 2010, **10**, 3901; *Inorg. Chem.*, 2006, **45**, 4755.

### TM $\pi(\text{chelate})\cdots\pi(\text{chelate})$ interactions



*Acta Cryst. C*, 1983, **39**, 591.

### $\pi(\text{chelate})\cdots\pi(\text{chelate})$ interactions

Coordination Chemistry Reviews 540 (2011) 118–161

Contents lists available at ScienceDirect

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journal homepage: [www.elsevier.com/locate/ccr](http://www.elsevier.com/locate/ccr)

Review

Noncovalent bonding: Stacking interactions of chelate rings of transition metal complexes

Dušan P. Malenović<sup>a</sup>, Goran V. Janjić<sup>b</sup>, Vesna B. Medaković<sup>a</sup>, Michael B. Hall<sup>c</sup>, Snežana D. Zarić<sup>a,d,\*</sup>

<sup>a</sup>Department of Chemistry, University of Belgrade, Studentski trg 12–16, 11000 Belgrade, Serbia

<sup>b</sup>Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Bulevar 12, 11001 Belgrade, Serbia

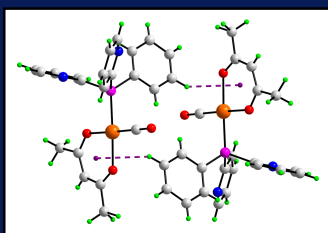
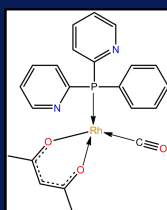
<sup>c</sup>Department of Chemistry, Texas A&M University, College Station, TX 77843–3255, USA

<sup>d</sup>Department of Chemistry, Sremski Karlovci University at Osijek, P. O. Box 21893, Osijek, Croatia

$\pi(\text{chelate})\cdots\pi(\text{arene}) \sim 6 \text{ kcal/mol}$

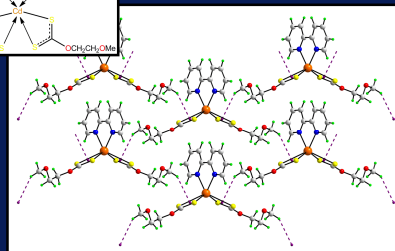
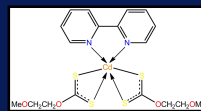
$\pi(\text{chelate})\cdots\pi(\text{chelate}) \sim 9 \text{ kcal/mol}$

### TM arene- $\text{H}\cdots\pi(\text{chelate})$ interactions



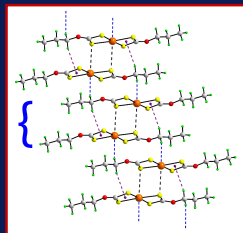
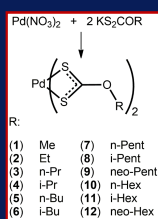
*Bull. Pol. Acad. Sci. Chem.*, 1994, **42**, 205.

### Main group arene- $\text{H}\cdots\pi(\text{chelate})$ interactions

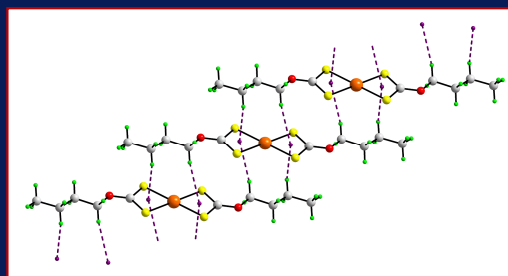


*Z. Kristallogr.*, 2002, **218**, 747.

### C—H $\cdots\pi(\text{chelate})$ interactions:



### C—H $\cdots\pi(\text{chelate})$ interactions:



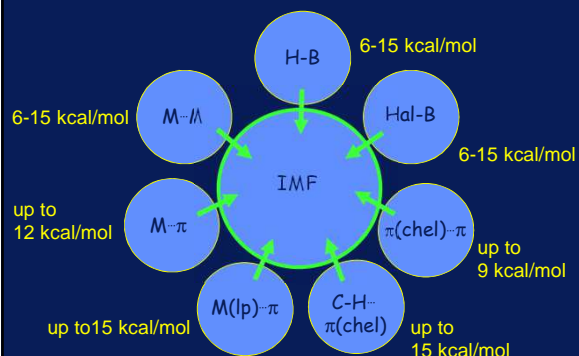


## Intermolecular interactions involving chelate rings



$\text{Pd} \cdots \text{S}$  16 kcal/mol  
 $\text{C-H} \cdots \pi(\text{chelate})$  15 kcal/mol

## Overview



## Conclusions

More than  $(\text{HB})^2$

Energies of "emerging" interactions similar

## Sunway University



SUNWAY EDUCATION GROUP  
 Sunway University  
 Sunway Education Group

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



7<sup>th</sup> Asian Conference on Coordination Chemistry (ACCC7)  
 22-26 July 2019 / Kuala Lumpur, Malaysia  
 (Organised by Institut Kimia Malaysia)



SEACCE 2018

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