Identifying non-conventional supramolecular synthons in the crystalline state

Edward R.T. Tiekink
Research Centre for Crystalline Materials

24th Congress and Assembly of the International Union of Crystallography, Hyderabad, August 21st-28th

Molecular packing

Well known…

Hydrogen bonding
Halogen bonding

"Emerging"

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

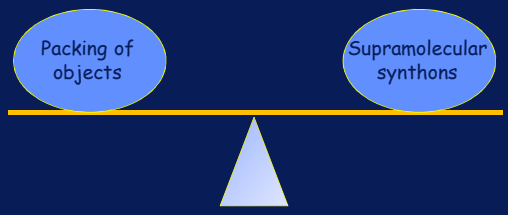
Caveat

Supramolecular synthon approach

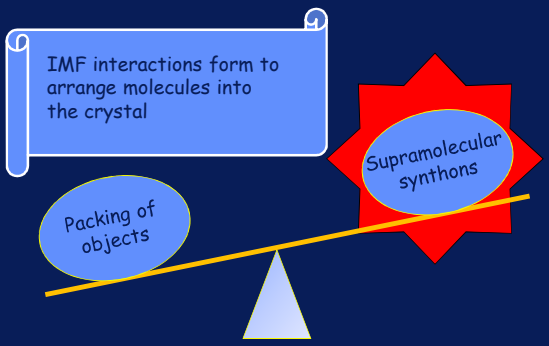
versus

Global crystal packing approach

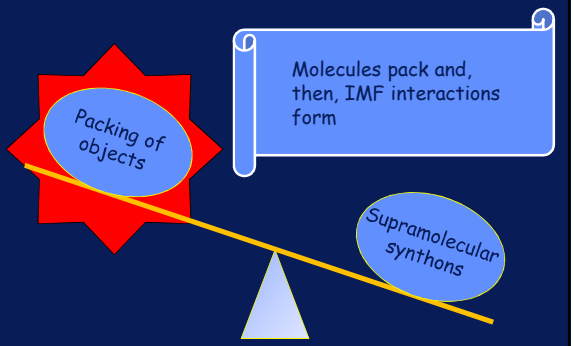
Factors that Control Molecular Packing



Factors that Control Molecular Packing



Factors that Control Molecular Packing



Caveat

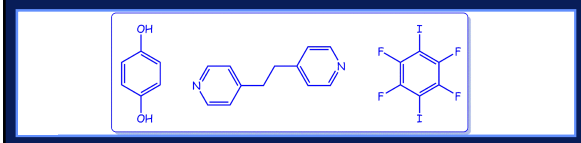
"egg causality dilemma"

Molecular packing

Well known…

Hydrogen bonding
Halogen bonding

Hydrogen Bonding versus Halogen Bonding

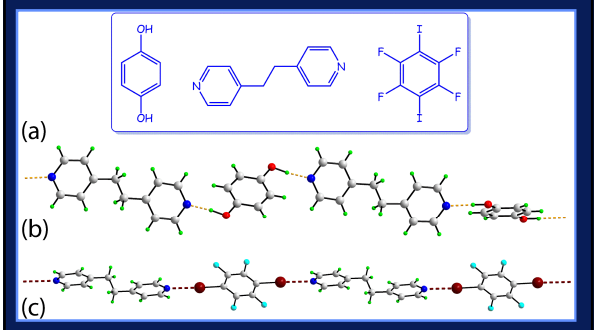


Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly Processes**

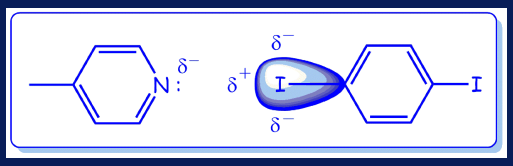
Eleonora Corradi, Stefano V. Meille, Maria T. Messina, Pierangelo Metrangolo,* and Giuseppe Resnati*

 © WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2000 0570-0833/00/3910-1782 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2000**, *39*, No. 10

Hydrogen Bonding versus Halogen Bonding



Hydrogen Bonding vs Halogen Bonding



polar gap, σ-hole

Molecular packing

Well known…

Hydrogen bonding
Halogen bonding

Similar in energy = 5 – 15 kcal/mol

Molecular packing

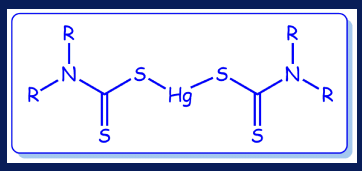
Well known…

Hydrogen bonding
Halogen bonding

"Emerging"

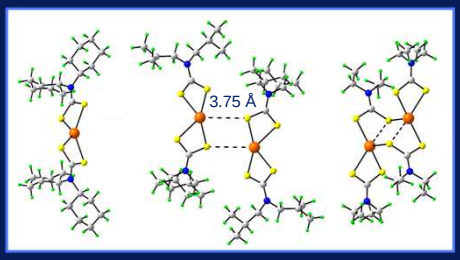
Secondary bonding
M···M interactions
M···H interactions
Interactions involving chelate rings

Steric effects and Secondary Bonding



"$Hg(S_2CNR_2)_2$"

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

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*

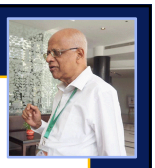
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

DOI: 10.1021/acs.jpca.7b05300
J. Phys. Chem. A 2017, 121, 5661−5668

$TH_{(4-n)}F(n)$ + $:NH_3$

T = C, Si, Ge & Sn

n = 0	0.9 kcal/mol
n = 1*	6 – 9 kcal/mol
SnF_4	25.5 kcal/mol



J. CHEM. SOC. DALTON TRANS. 1993

Database Analysis of Au···Au Interactions†

Swaroop S. Pathaneni and Gautam R. Desiraju*
School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

The geometry of gold–gold interactions in a group of 693 gold-containing crystal structures has been examined using data from the Cambridge Structural Database. These contacts occur in the range 2.50–4.00 Å. Intermolecular Au···Au contacts are formed by compounds of the type AuXY (X, Y = any element) with the X–Au–Au–Y conformation being either staggered or eclipsed. Clusters of the type Au_nZ (where Z is any element including Au) are characterised by a large number of short gold–gold contacts reflecting an approach towards Au^0 in the interior of the cluster.

The existence of attractive gold–gold interactions has been repeatedly confirmed in many recent reports on gold chemistry.[1–3] The energy of the interaction has been estimated to be as high as 7–8 kcal mol^{-1}, comparable to hydrogen bonding. Such interactions have distinctive effects upon structure, properties and stereochemistry[4–6] and have been investigated by experimental and theoretical methods.[7–11] was initiated because no systematic analysis of the trends in gold–gold distances has been reported.[12]

Results and Discussion

A preliminary survey showed the presence of a large number of gold–gold distances in the range 2.50–4.00 Å. As a reference, the

24th Congress and General Assembly
of the International Union of Crystallography
Hyderabad International Convention Centre
21 - 28 August 2017, Hyderabad, India

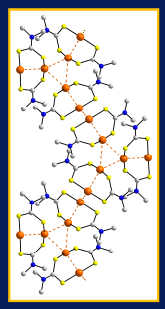
Aurophilic interactions

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

$5d^{10}$ closed shell interactions - relativistic effects



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

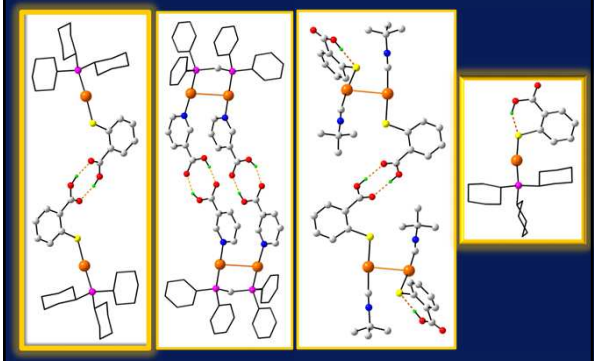
Gold Chemistry

Competition between

i) Au···Au and hydrogen bonding

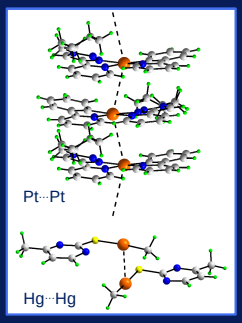
Comparable in energy

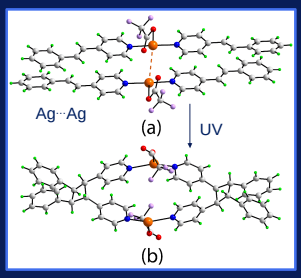
Gold structures with carboxylic acids



Coordination Chemistry Reviews, 275 (2014) 130 – 153

Heterometallophilic (M···M') interactions





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

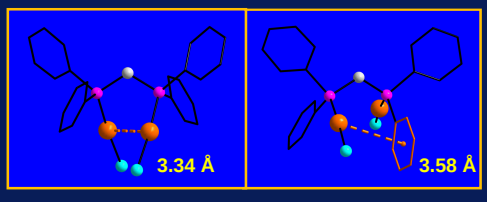
Gold Chemistry

Competition between

i) Au···Au and hydrogen bonding

ii) Au···Au and Au···π(arene)

Polymorphs of $(dppm)(AuCl)_2$



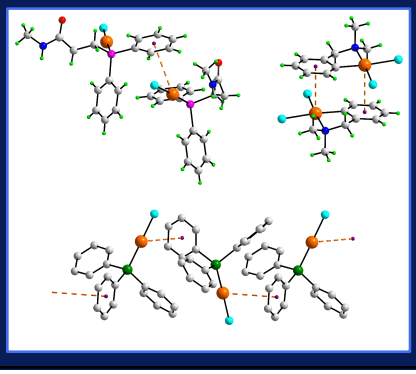
Schmidbaur *et al.* (1977)

Healy (2003)

Intermolecular Au···π(arene) interactions

0-D

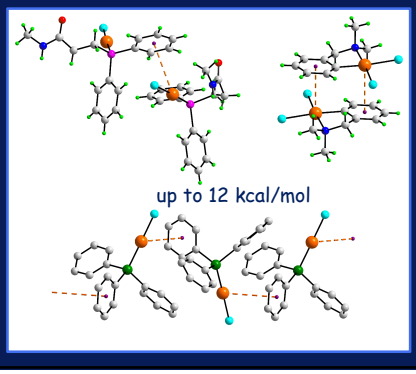
1-D



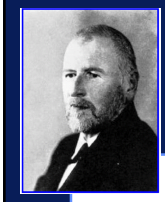
Intermolecular Au···π(arene) interactions

0-D

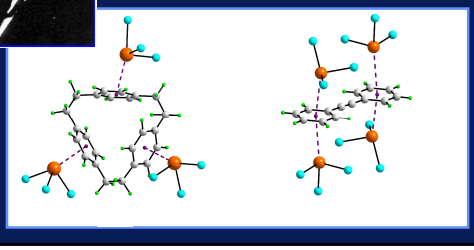
1-D



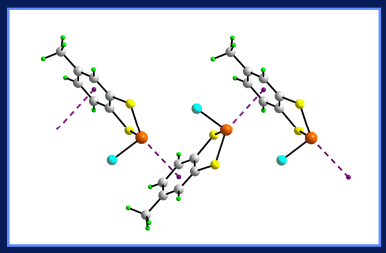
Intermolecular M(lp)···π(arene) interactions



"Menšutkin complexes"



Intermolecular M(lp)···π(arene) interactions



cf. polar gap, σ-hole

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

Energy?

ChemComm

COMMUNICATION

View Article Online

View Journal | View Issue

On the nature of the stabilisation of the E···π pnicogen bond in the $SbCl_3$···toluene complex†

Rabindranath Lo,[a] Petr Švec,[b] Zdeňka Růžičková,[b] Aleš Růžička[b] and Pavel Hobza*[ac]

Cite this: *Chem. Commun.*, 2016, 52, 3500

Received 17th December 2015, Accepted 27th January 2016

DOI: 10.1039/c5cc10363k

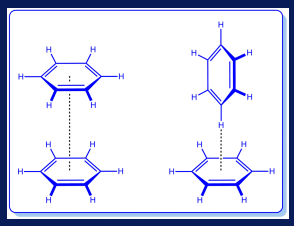
$SbCl_3$ + C_6H_6 7.7 kcal/mol

C_6H_5Me 9.6 kcal/mol

C_6Me_6 15.5 kcal/mol

π-Systems in Supramolecular Chemistry

Classic π-systems/interactions

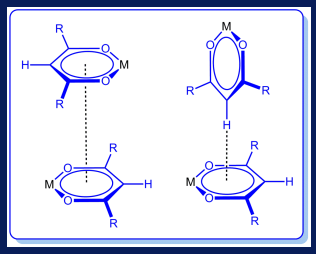


face-to-face edge-to-face

π-Systems in Supramolecular Chemistry

TM Chelate π-systems/interactions

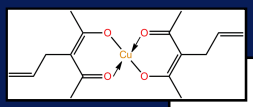
Snezana Zarić

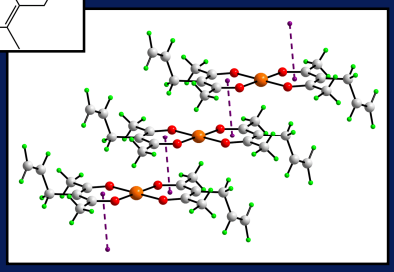


face-to-face edge-to-face

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

TM π(chelate)···π(chelate) interactions





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

π(chelate)···π(chelate) interactions

Coordination Chemistry Reviews 345 (2017) 318–341

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journal homepage: www.elsevier.com/locate/ccr

Review

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

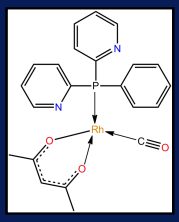
Dušan P. Malenov [a], Goran V. Janjić [b], Vesna B. Medaković [a], Michael B. Hall [c], Snežana D. Zarić [a,d,*]

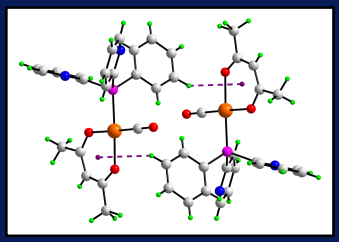
[a] Department of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia
[b] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11001 Belgrade, Serbia
[c] Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA
[d] Department of Chemistry, Texas A&M University at Qatar, P. O. Box 23874, Doha, Qatar

π(chelate)···π(arene) ~ 6 kcal/mol

π(chelate)···π(chelate) ~ 9 kcal/mol

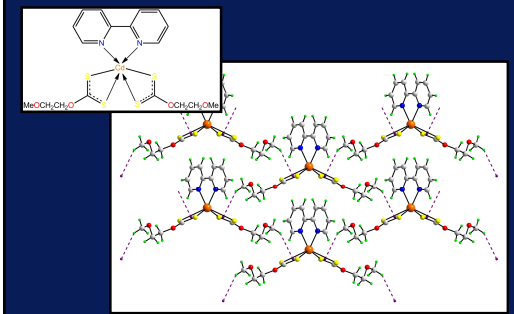
TM arene-H···π(chelate) interactions





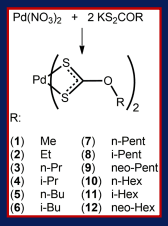
Bull. Pol. Acad. Sci. Chem., 1994, **42**, 205.

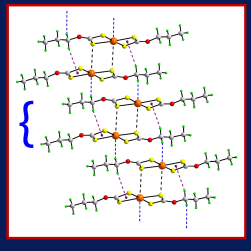
Main group arene-H···π(chelate) interactions



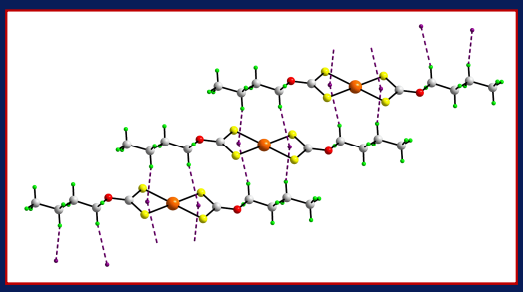
Z. Kristallogr., 2002, **218**, 747.

C—H···π(chelate) interactions:

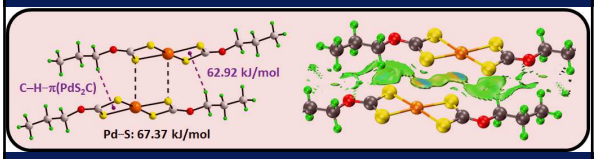




C—H···π(chelate) interactions:

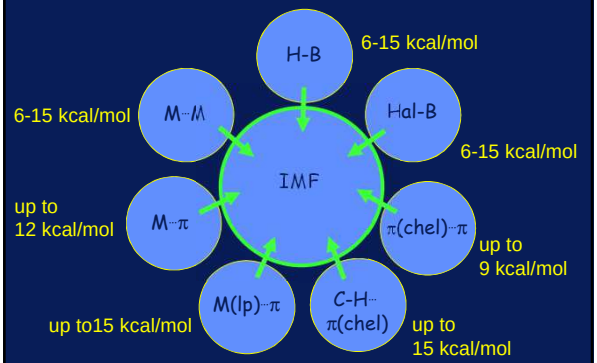


Intermolecular interactions involving chelate rings



Pd···S	16 kcal/mol
C–H···π(chelate)	15 kcal/mol

Overview



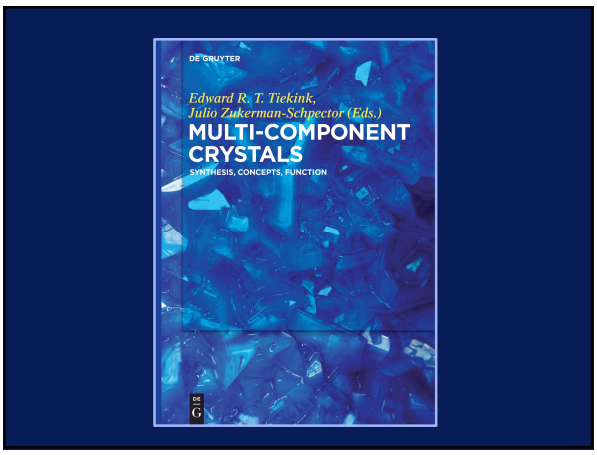
Conclusions

More than hydrogen-bonding (halogen-bonding)

Energies of "emerging" interactions similar

Sunway University

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


DE GRUYTER
Edward R. T. Tiekink,
Julio Zukerman-Schpector (Eds.)
MULTI-COMPONENT CRYSTALS
SYNTHESIS, CONCEPTS, FUNCTION