

## Resurging interest in secondary bonding

Edward R.T. Tiekink  
Research Centre for Crystalline Materials



## Overview

Non-Covalent Interactions (NCI)

Secondary bonding

Steric control over NCI

Complexation with bipyridyl-bridges

Energy considerations

### Supramolecular Chemistry

DOI: 10.1002/ange.201306501

#### Tetrel-Bonding Interaction: Rediscovered Supramolecular Force

Antonio Bauzá, Tiddo J. Mooibroek, and Antonio Frontera\*

Noncovalent bonding interactions are crucial in many chemical and biological phenomena and they have been intensively investigated for many years.<sup>[1]</sup> The hydrogen bond (AH...D) is probably the most studied and analyzed noncovalent interaction, where A (acceptor) can be basically any atom more electronegative than H and D (donor) can be any entity with the ability to act as an electron donor (lone pair,  $\pi$  system, anion, etc.).<sup>[2]</sup> Among many interactions, those involving

Recently, Taylor et al.<sup>[3]</sup> reported that the synthesis of spirocyclics is significantly improved using  $n$ -butylammonium fluoride (TBAF) as a catalyst. Interestingly, during the reaction work-up a new class of cage compound was obtained showing a fluoride ion perfectly centered within the octaspiroquinone cage (see Figure 1).<sup>[3]</sup> Using NMR data the

Angew. Chem. Int. Ed. 2013, 52, 12377–12381

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## ACCOUNTS

### The Pnictogen Bond: Its Relation to Hydrogen, Halogen, and Other Noncovalent Bonds

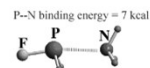
STEVE SCHEINER\*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-2000, United States

RECEIVED ON MAY 4, 2012

#### CONCEPTS

Among a wide range of noncovalent interactions, hydrogen (H) bonds are well known for their specific roles in various chemical and biological phenomena. When describing conventional hydrogen bonding, researchers use the notation AH...D, where A refers to the electron acceptor and D to the donor. However, the AH molecule engaged in an AH...D H-bond can also be placed around



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### Chalcogen Bonding

International Edition: DOI: 10.1002/ange.201309432  
German Edition: DOI: 10.1002/ange.201309432

#### Chalcogen Bonding: An Overview

Lukas Vogel\*, Patrick Wöner\*, and Stefan M. Huber\*

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Angew. Chem. Int. Ed. 2013, 52, 12377–12381

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## Secondary bonding

### Secondary Bonding. Part 1. Crystal and Molecular Structures of $(C_6H_5)_3X$ ( $X = Cl, Br, I$ )

By Nathaniel W. Alcock and Rachel M. Countrymen, Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

The structures of the title compounds have been determined. The three compounds are isomorphous, monoclinic, space group  $C2/c$ ,  $Z = 4$ , with the following cell constants and  $R$  values:

X	a/Å	b/Å	c/Å	$\beta/^\circ$	$V(\text{Å}^3)$	$R\%$
Cl	20.856(2)	5.895(2)	20.043(4)	102.38(4)*	1.201	4.8
Br	21.482(3)	5.892(2)	20.087(5)	101.64(2)*	1.923	5.1
I	22.121(7)	5.877(2)	20.385(9)	100.90(2)*	1.971	4.3

In the dimeric structures  $(Ph)_3X \cdots (Ph)_3X$ , mean bond lengths are  $C-Cl$  2.08,  $C-Br$  2.08,  $C-I$  2.25, and  $C-H$  1.04 Å. The  $C-H$  bonds are each 0.77 Å longer than in the corresponding  $CH_4$  gas, indicating bond orders of about 0.35. The bonding is interpreted in terms of secondary bonds  $(\cdots X) \cdots X$ , holding  $(Ph)_3X^+$  and  $X^-$  units together.

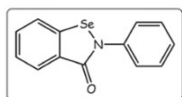
Weak interactions, intermediate in length between single bonds and van der Waals distances, have been shown to be of great importance in the crystal structures of many non-metal compounds, and have been given the name secondary bonds.<sup>1</sup> Characteristically this is a system  $Y-A \cdots X$  in which  $Y-A$  is a normal covalent bond,  $A \cdots X$  a secondary bond, and the angle  $Y-A-X$  is close to  $180^\circ$ . The most plausible explanation for this bonding seems to be (a) two equivalent models: either donation from a lone pair on  $X$  into the  $a^*$  orbital of the  $Y-A$  bond, or as an asymmetric 3-centre system. can be viewed in three ways. First,  $X$  forms one single bond and one dative bond to the two  $A$  atoms; this is the normal view of bridged metal halides, and the two bond lengths are usually equal, and close to the standard covalent distances, as in  $Al_2Br_6$  with terminal  $Al-Br$  of 2.21, and bridging  $Al-Br$  of 2.33 Å.<sup>2</sup> Secondly, they may consist of  $Ph_3X^+$  units, in which  $X$  forms a weak secondary bond to the second  $I$ . Thirdly, they may consist of two  $(Ph)_3X^+ \cdots X^-$  units, in which the two halves are held together only by secondary bonds. The published report on diphenyliodonium chloride

J.C.S. Dalton



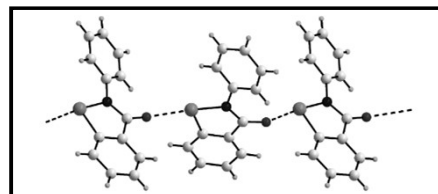
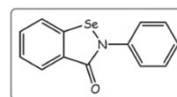
SECONDARY BONDING TO NONMETALLIC ELEMENTS	
N. W. Alcock	
Department of Molecular Sciences, University of Warwick, Coventry, England	
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## Secondary-Bonding (Chalcogen Bonding)



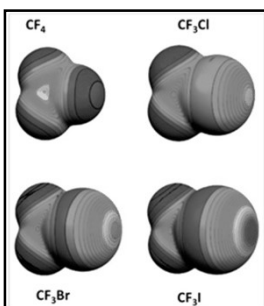
Ebselen®  
anti-inflammatory,  
anti-oxidant and cytoprotective activity

## Secondary-Bonding (Chalcogen Bonding)



Se...O in Ebselen® ~8 kcal/mol

## $\sigma$ -hole



Halogen bonding  
Chalcogen bonding  
Pnicogen bonding  
Tetrel bonding

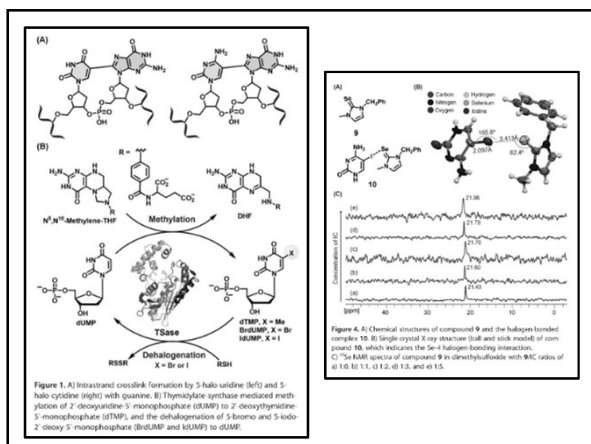
Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P.  
Halogen Bonding: The Sigma-Hole *J. Mol. Model.* **2007**, *13*, 291 – 296

## Not just a solid-state phenomenon

ChemPubSoc Europe DOI: 10.1002/chem.201805112 CHEMISTRY A European Journal Full Paper

|| DNA  
**Dehalogenation of Halogenated Nucleobases and Nucleosides by Organoselenium Compounds**  
Santanu Mondal and Govindasamy Mugesh<sup>1</sup>

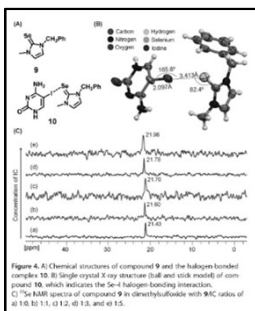
**Abstract:** Halogenated nucleosides, such as 5-iodo-2-deoxyuridine and 5-iodo-2-deoxycytidine, are incorporated into the DNA of replicating cells to facilitate DNA single-strand breaks and intra- or interstrand crosslinks upon UV irradiation. In this work, it is shown that the naphthyl-based organoselenium compounds can mediate the dehalogenation of the halogenated pyrimidine-based nucleosides, such as 5-iodo-2-deoxyuridine and 5-X-2-deoxycytidine (X = Br or I). The rate of deiodination was found to be significantly higher than that of the debromination for both nucleosides. Furthermore, the deiodination of 5-iodocytidines was found to be faster than that of 5-iodouridines. The initial rates of the deiodinations of 5-iodocytosine and 5-iodouracil indicated that the nature of the sugar moiety influences the kinetics of the deiodination. For both the nucleobases and nucleosides, the deiodination and debromination reactions follow a halogen bond-mediated and addition/elimination pathway, respectively.



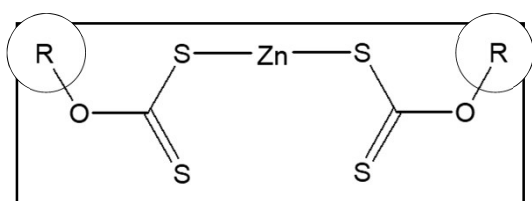
## Zinc thiolates: tuning supramolecular aggregation

Molecular paving with zinc xanthates

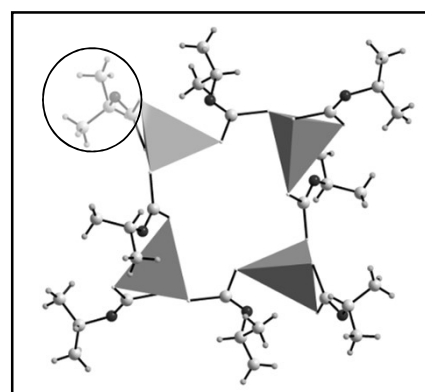
Tailoring luminescence



## Structural diversity in $\text{Zn}(\text{S}_2\text{COR})_2$



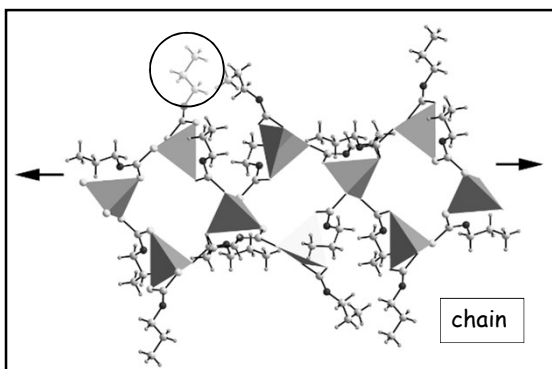
Examine structures for which  $\text{R} = \text{Et}$ ,  $\text{nPr}$  &  $\text{iPr}$



$\text{R} = \text{iPr}$

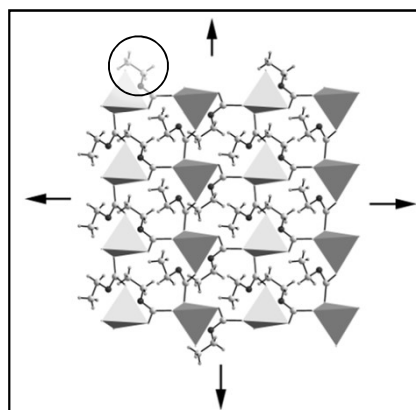
isolated tetramer

$\text{R} = \text{nPr}$

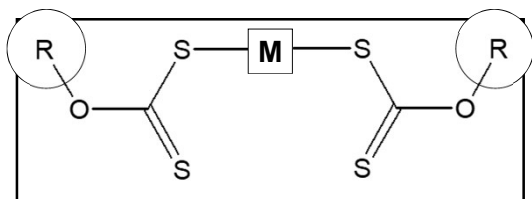


$\text{R} = \text{Et}$

layer

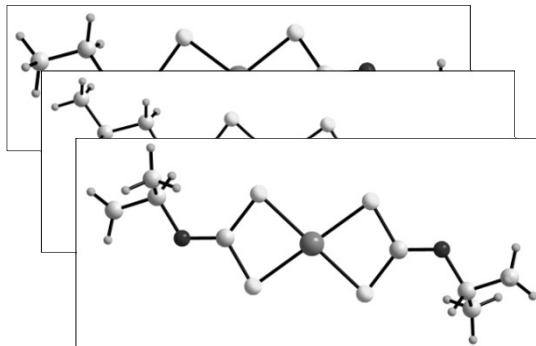


### Structural diversity in $M(S_2COR)_2$

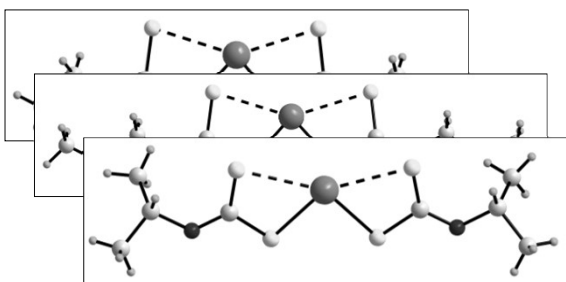


Examine other structures for which  
M = Ni(II) & Te(II); R = Et, nPr & iPr

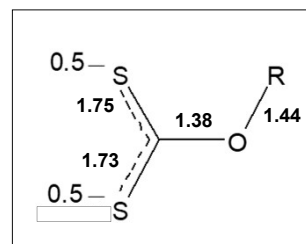
### $Ni(S_2COR)_2$ for R = Et, nPr & iPr



### $Te(S_2COR)_2$ for R = Et, nPr & iPr

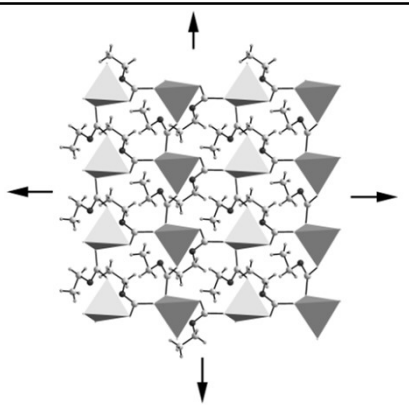


### Ab initio molecular orbital calculations on $-S_2COR$

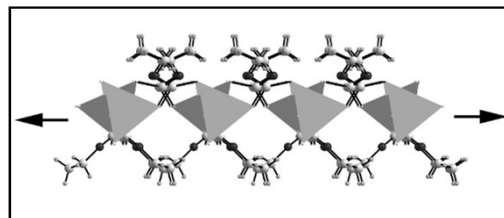


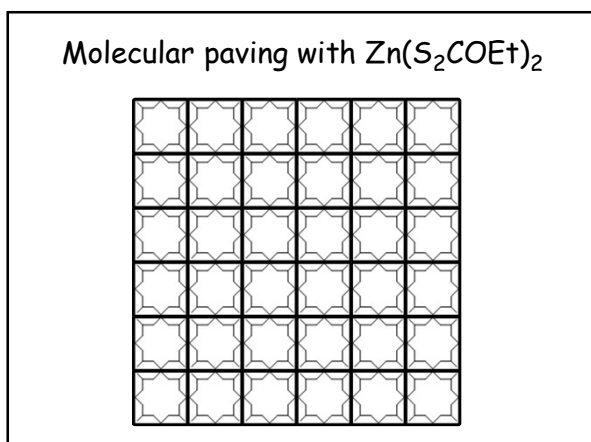
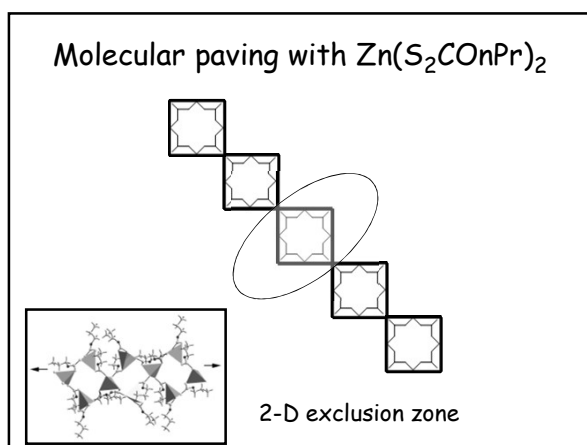
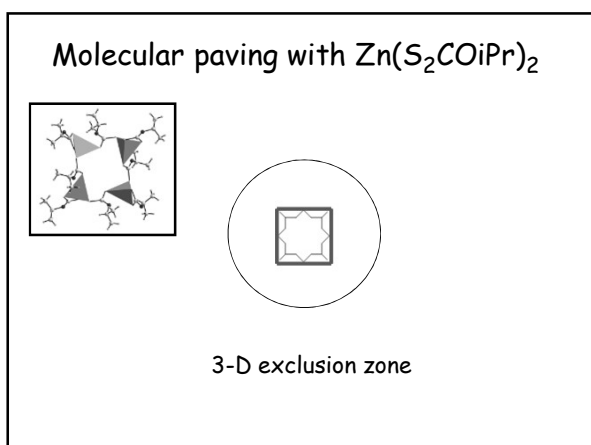
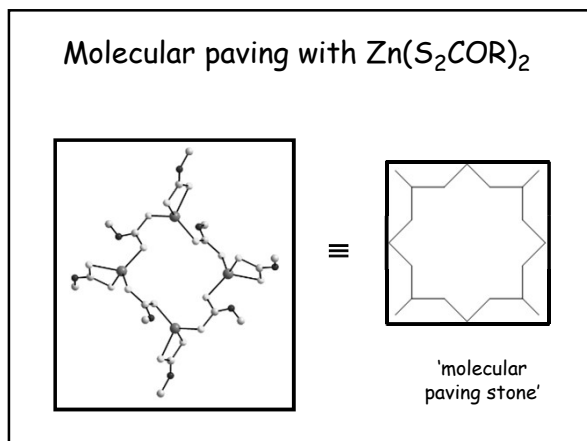
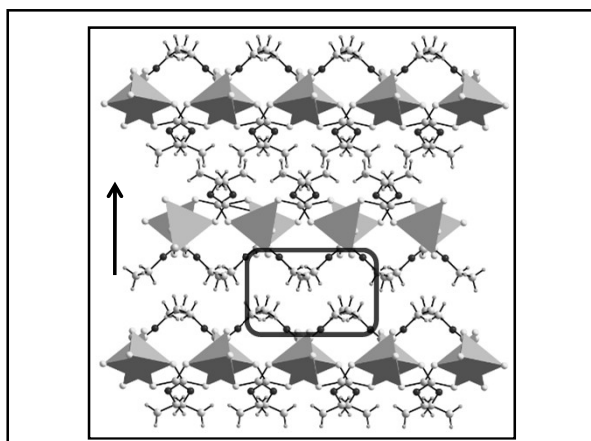
R = Et

layer



### Molecular paving with $Zn(S_2COEt)_2$





### Alcohol-O-H...O(alcohol) Hydrogen Bonding

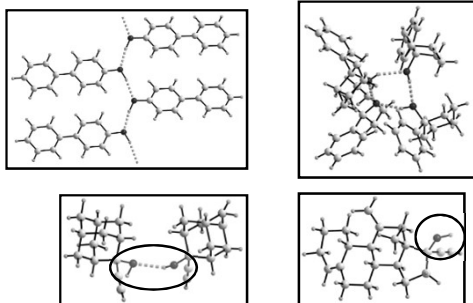
*Chem. Mater.* 1994, 6, 1307-1312 1307

#### Anomalous Space-Group Frequencies for Monoalcohols $\text{C}_n\text{H}_m\text{OH}^1$

Carolyn Pratt Brock\* and Laura L. Duncan  
*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055*  
 Received February 2, 1994. Revised Manuscript Received March 14, 1994\*

Consideration of the spatial requirements of OH...O bonds suggests that the frequencies of high-symmetry space groups, which are more likely than low-symmetry groups to be chiral or noncentrosymmetric, should be disproportionately high for structures of monoalcohols  $\text{C}_n\text{H}_m\text{OH}$ . Structures having more than one molecule in the asymmetric unit should also occur much more frequently for monoalcohols than for molecular crystals in general. These predictions have been confirmed using crystallographic information retrieved from the Cambridge Structural Database. Data for monoamines  $\text{C}_n\text{H}_m\text{NH}_2$  are much more limited, but these molecules appear to follow the same crystallization patterns.

## Alcohol-O-H...O(alcohol) Hydrogen Bonding



Steric bulk moderates hydrogen bonding

"All good proton donors and acceptors are used in hydrogen bonding" (M. C. Etter, *Acc. Chem. Res.*, 1990, 23, 120-126). This is Margaret Etter's first rule, part of pioneering work which has proven both insightful and accurate over the intervening 20 years since its publication. In this work we question whether a good donor or acceptor can be identified solely from a chemical perspective, e.g. given only a chemical diagram. Results indicate that 2.5% of the organic structures in the Cambridge Structural Database which contain what would be considered a strong donor and an acceptor do not hydrogen bond. We have revealed in 2/3 of the cases, donors or acceptors with reduced accessible surface are responsible *i.e.* due to steric crowding by neighbouring atoms. We have further identified significant

DOI: 10.1039/0000000000

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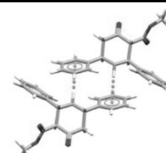
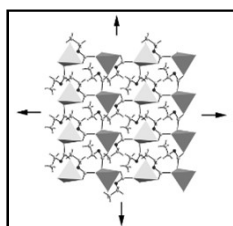
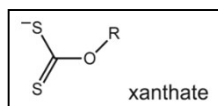


Fig. 4 Crystal packing diagram from the structure of methyl 4-oxo-*r*-2,6-diphenylpiperidine-3-carboxylate (CSD refcode: BIHZFY)<sup>18</sup> showing, in particular, the D-H... $\pi$  intermolecular interactions (shown as green dotted lines). No conventional hydrogen-bonding contacts were observed in this structure based on default Mercury definitions despite the possibility for these.<sup>18</sup>

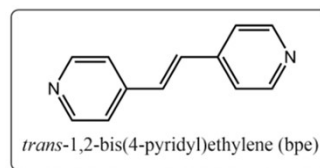
## Coordination polymers of zinc-triad elements

Solid-state polymers cf. solution

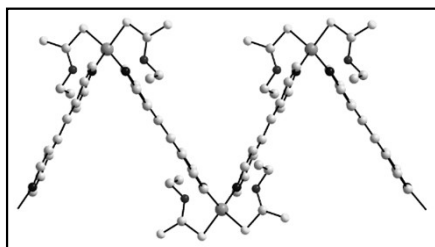
$\text{Zn}(\text{S}_2\text{COR})_2$  + bridging ligands



## Zinc(1,1-dithiolate)<sub>2</sub> + bpe

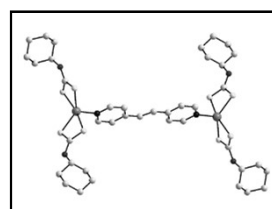


## Zinc(xanthate)<sub>2</sub> + bpe



R = Et

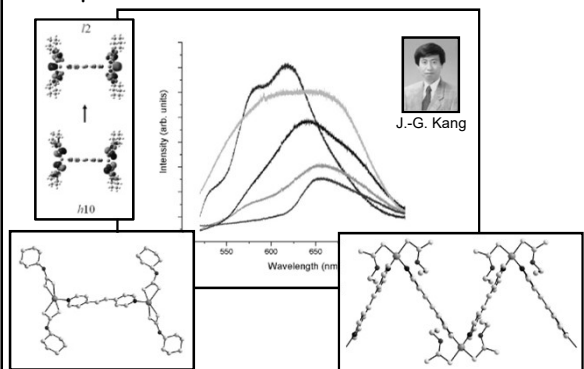
## Zinc(xanthate)<sub>2</sub> + bpe



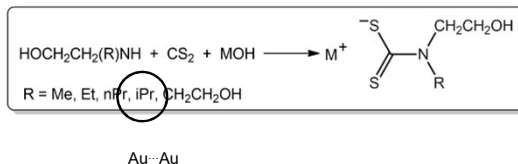
R = Cy

**Steric bulk!**

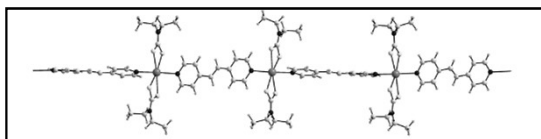
### Implications for solid-state luminescence



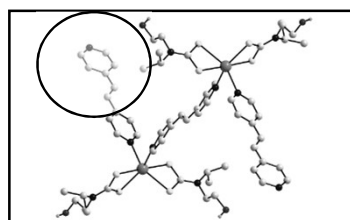
### Introducing hydrogen-bond functionality into dithiocarbamate ligands



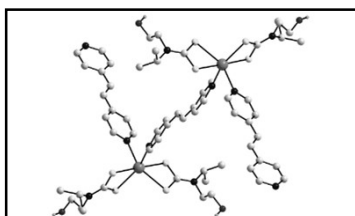
### Cadmium dithiocarbamates: $\{\text{Cd}[\text{S}_2\text{CNEt}_2]_2(\mu_2\text{-bpe})\}_n$



### Cadmium dithiocarbamates: $\{\text{Cd}[\text{S}_2\text{CN}(\text{iPr})\text{CH}_2\text{CH}_2\text{OH}]_2\}_n + \text{bpe}$



### Cadmium dithiocarbamates: $\{\text{Cd}[\text{S}_2\text{CN}(\text{iPr})\text{CH}_2\text{CH}_2\text{OH}]_2\}_n + \text{bpe}$



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

### Family of Intermolecular Interactions

Table 2  
Selected bond lengths and angles of sodium diaquaferenate-water (1/1).

Bond type	Bond length (Å)	Angle type	Angle (°)
Na—O2W <sup>i</sup>	2.3553 (18)	O2W—Na—O1W <sup>i</sup>	103.43 (7)
Na—O1W	2.3675 (19)	O2W—Na—O2W <sup>i</sup>	83.76 (7)
Na—O2W	2.3898 (19)	O1W—Na—O2W <sup>i</sup>	99.36 (7)
Na—O1	2.4129 (18)	O2W—Na—O1 <sup>i</sup>	117.64 (6)
Na—O1W <sup>ii</sup>	2.4559 (19)	O1W—Na—O1	138.62 (7)
Na <sup>i</sup> —Na <sup>i</sup>	3.533 (2)	O2W—Na—O1	90.33 (6)
Na <sup>i</sup> —Na <sup>ii</sup>	3.646 (2)	O2W <sup>i</sup> —Na—O1W <sup>ii</sup>	96.53 (7)
O1—C1	1.267 (2)	O1W—Na—O1W <sup>ii</sup>	81.81 (6)
O2—C1	1.257 (2)	O2W—Na—O1W <sup>ii</sup>	178.71 (6)
N1—C3	1.380 (3)	O1—Na—O1W <sup>ii</sup>	88.42 (6)
N1—C8	1.403 (3)	Na—O1W—Na <sup>ii</sup>	98.19 (6)
C1—C2	1.497 (2)	Na—O2W—Na <sup>i</sup>	96.24 (4)
		C1—O1—Na	124.68 (11)
		O2—C1—O1	122.33 (16)
		C3—N1—C8	126.98 (17)

Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) 1 - x, 2 - y, 2 - z.

Figure 1  
The polymeric structure of sodium diaquaferenamate-water (1/1). Displacement ellipsoids are shown at the 30% probability level. Symmetry codes: (i)  $1-x, 2-y, 1-z$ ; (ii)  $1-x, 2-y, 2-z$ .

up to 9 kcal/mol

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