SUNWAY UNIVERSITY

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ACCC6
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COPPER(I) COMPLEXES: INTRAMOLECULAR AND INTERMOLECULAR ARENE-C–H···π(QUASI-CHELATE RING) INTERACTIONS

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Nurturing the Seeds of Wisdom

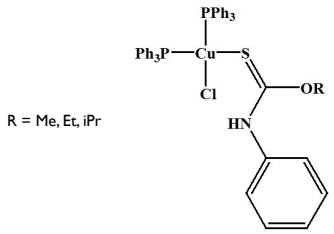
SUPRAMOLECULAR SYNTHONS

- Hydrogen bonding
- Coordinate bonding
- Halogen bonding

INTERACTIONS INVOLVING π SYSTEMS

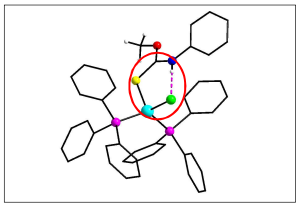
- π···π interactions
- Mixed π (arene)···π (chelate) interactions
- π (chelate)···π (chelate) interactions

$(Ph_3P)_2Cu[ROC(=S)N(H)Ph]Cl$

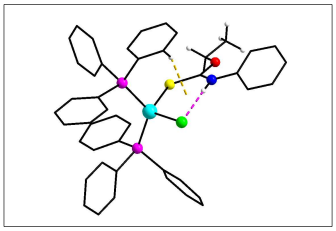


R = Me, Et, iPr

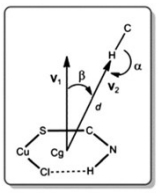
QUASI CHELATE RING – CuCl…HNCS



INTRAMOLECULAR: C-H…π(QUASI-CHELATE RING)



C-H…π (QUASI-CHELATE RING)



The distance (d) : ≤ 3.6 Å
from the ring centroid (Cg) to the H atom

The C–H ··· Cg angle (α) : 110 < α <180

The angle between the normal of the least squares plane through the six atoms and the C–H vector (β) : ≤ 15°
(quasi-chelate ring was not restricted to be planar)

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INTERMOLECULAR: C-H…π(QUASI-CHELATE RING)

- A search of the Cambridge Structural Database (CSD):
- 16 out of 94 structures featuring intramolecular arene-C-H…π(quasi-chelate ring) – approximately 17%

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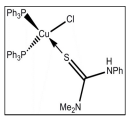
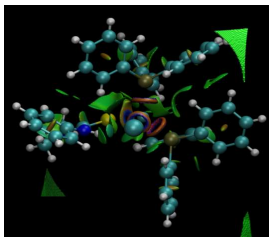
INTRAMOLECULAR: C-H…π(QUASI-CHELATE RING)



Chemical structure of the molecule subjected to DFT-D calculations (BP86-D/def2-TZVP)



Gradient isosurface

Ca. 3.5 kcal mol^{-1}

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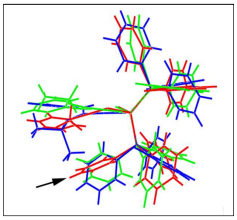
INTRAMOLECULAR: C-H…π(QUASI-CHELATE RING)

- Red – Me
- Green – Et
- Blue – iPr



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INTERMOLECULAR: C-H…π(QUASI-CHELATE RING)

Supramolecular association based on second tier interactions – IMPORTANT when hydrogen bonding is absent!

Quasi chelate ring: functions as a π system

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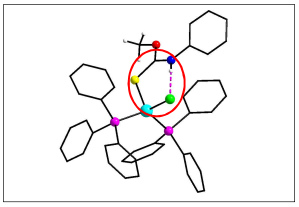
INTERMOLECULAR: C-H…π(QUASI-CHELATE RING)

- CuCl…HNCS



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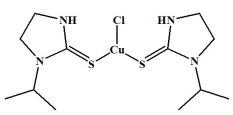
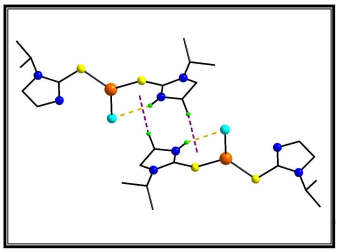
INTERMOLECULAR: C-H…π(QUASI-CHELATE RING)

- A search of the Cambridge Structural Database (CSD):
- 17 out of 94 structures featuring intermolecular arene-C-H…π(quasi-chelate ring)
- 15 out of 17 operate independently of other obvious supramolecular synthon

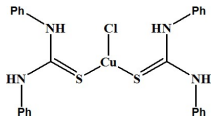
INTERMOLECULAR: 0-D



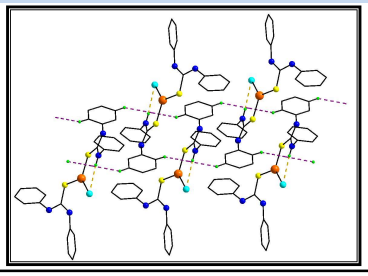
* One donor and one acceptor C–H…π(quasi chelate) interactions



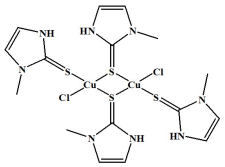
INTERMOLECULAR: 1-D



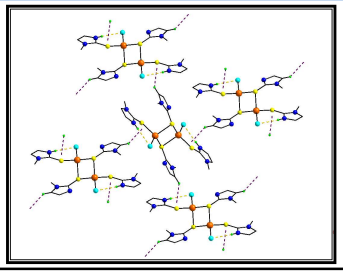
*Two donor and two acceptor C–H…π(quasi chelate) interactions



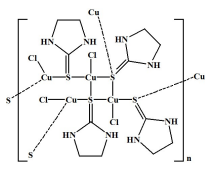
INTERMOLECULAR: 2-D



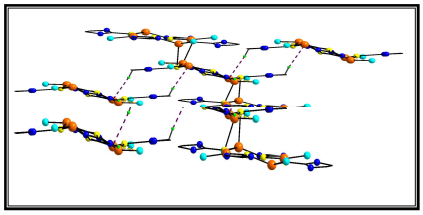
*Two donor and two acceptor C–H…π(quasi chelate) interactions



INTERMOLECULAR: 3-D



*Two donor and two acceptor C–H…π(quasi chelate) interactions



CONCLUSION

- C–H…π(quasi chelate) interactions impart stabilisation to copper(I) structures where quasi six-membered chelate rings of {CuCl…HNCS} are identified.

ACKNOWLEDGEMENT

- Professor Dr Edward R. T. Tiekink
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  Professor Dr Marco A. B. Ferreira
- Sunway University for the financial support

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ACCC7

Kuala Lumpur, Malaysia in 2019

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Places of Attractions

Cultural Heritage

Foods

Thank you for your attention…