Long range magnetic cooperativity through extended structural motifs? Introducing intermolecular π-π interactions into [3×3] $Mn(II)_9$ and $Cu(II)_9$ grids.

L.N. Dawe and L.K. Thompson. Department of Chemistry, Memorial University, St. John's, NL, A1B 3X7, Canada

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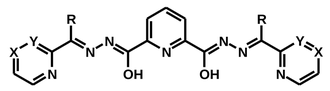
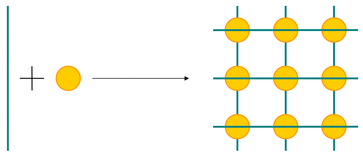
1. Grids by Self-Assembly and π-π Interactions



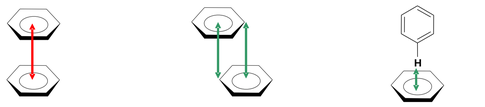
2poap (R=NH_2, X=Y=CH)
2poapz (R=NH_2, X=N, Y=CH)
2pmoap (R=NH_2, X=CH, Y=N)
2pomp(R=CH_3, X=Y=CH)
2popp (R=Ph, X=Y=CH)



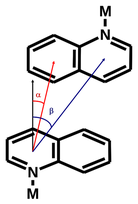
6 L 9 M = Mn(II),Fe(II),Ni(II),Co(II),Cu(II)[1,2]

New ligands have been designed with quinoline-moiety end-groups that increase steric and π-effects.

The Hunter and Sanders rules[3] qualitatively account for charge distribution in a non-polarized π-system:

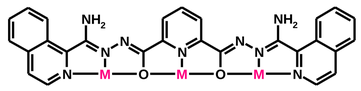


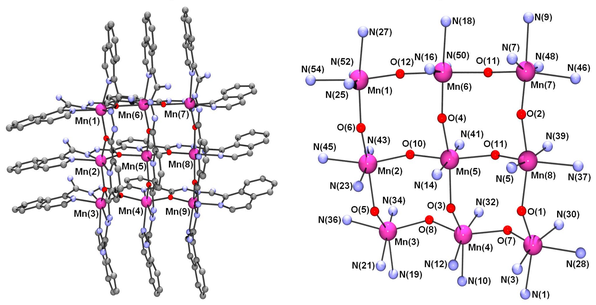
π-π repulsions dominate π-σ attractions dominate π-σ attractions dominate



Most metal-quinoline moiety π-stacking exhibits centroid-centroid distances out to 3.8 Å, with displacement angles (α) of ~20°.[4]

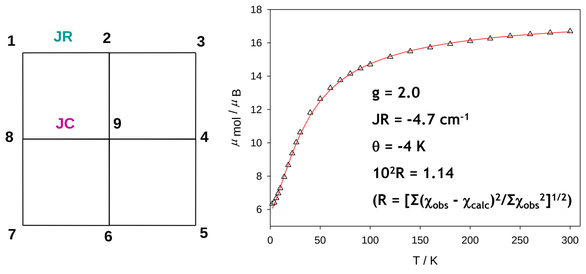
2. An Antiferromagnetic [3x3] $Mn(II)_9$ Grid





Formula: $[(C_{27}H_{19}N_9O_2)_6Mn_9](CF_3SO_3)_3(NO_3)_3{\cdot}3.8H_2O$;
Crystal System: triclinic; Space Group: P-1 (#2); R1 = 0.0889
Unit Cell Parameters: a: 20.514(5) Å, b: 20.643(4) Å, c: 25.948(6) Å
α: 90.917(4)°, β: 108.365(7)°, γ: 90.517(7)°

Mn-Mn (μO-bridged): 3.8450(9) - 3.9607(8) Å, 124.63(14) - 129.72(14)°



$H_{ex} = -JR\{S_1{\bullet}S_2+S_2{\bullet}S_3+S_3{\bullet}S_4+S_4{\bullet}S_5+S_5{\bullet}S_6+S_6{\bullet}S_7+S_7{\bullet}S_8+S_1{\bullet}S_8\} - JC\{S_2{\bullet}S_9+S_4{\bullet}S_9+S_6{\bullet}S_9+S_8{\bullet}S_9\}$

45 electron problem → enormous matrix!

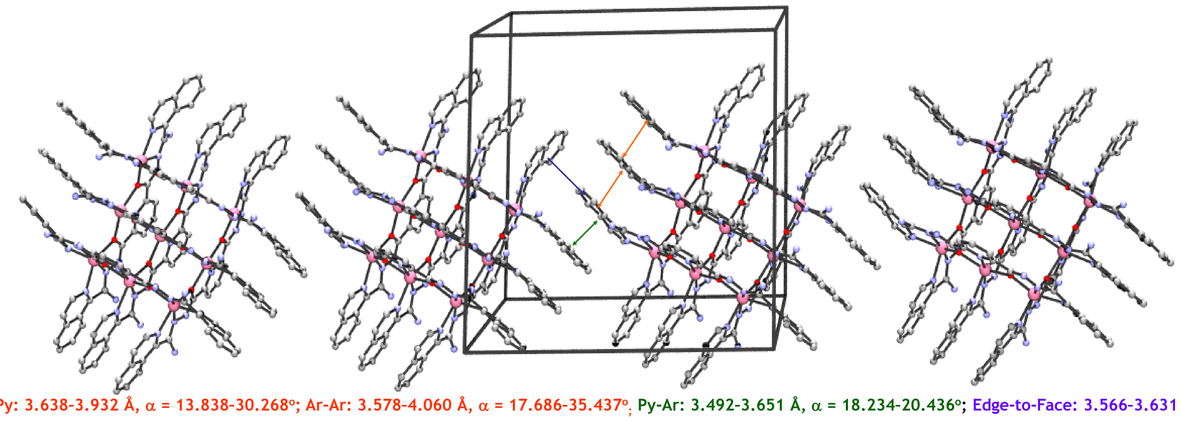
Fischer Model[1,2]: Isolates the eight-membered Mn ring from the central Mn → effectively sets JC = 0

$$\chi_{Mn} = \frac{Ng^2\beta^2 S(S+1)}{3kT}\frac{(1+u)}{(1-u)} \qquad u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$

$$\chi_{mol} = [(8{*}\chi_{Mn} + 1.094{*}g^2)/(T-\theta)]{*}(1-\rho) + (1.094{*}g^2/T){*}\rho + TIP$$

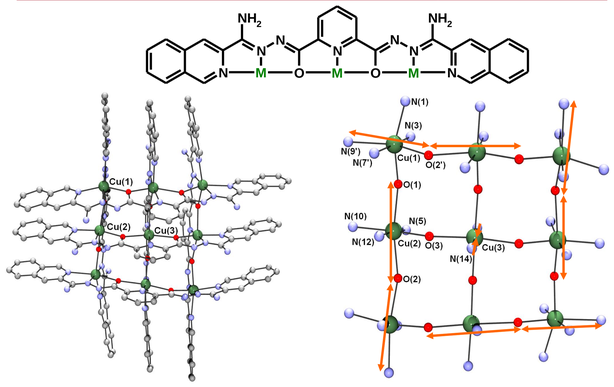
References

1. L. K. Thompson, O. Waldmann, Z. Xu, *Coord. Chem. Rev.*, **2005**, *249*, 2677.
2. L. N. Dawe, et al., *J. Mater. Chem.*, **2006**, *16*, 2645.
3. C.A. Hunter, J.K M. Sanders, *J. Am. Chem. Soc.*, **1990**, *112*, 5525.
4. C. Janiak, *J. Chem. Soc., Dalton Trans.*, **2000**, 3885.
5. L. N. Dawe, T.S.M. Abedin, L.K. Thompson, *Dalton Trans.*, **2008**, 1661.
6. S.K. Dey, T.S.M. Abedin, L.N. Dawe, et al., *Inorg. Chem.*, **2007**, *46*, 7767.



Py-Py: 3.638-3.932 Å, α = 13.838-30.268°; Ar-Ar: 3.578-4.060 Å, α = 17.686-35.437°; Py-Ar: 3.492-3.651 Å, α = 18.234-20.436°; Edge-to-Face: 3.566-3.631 Å

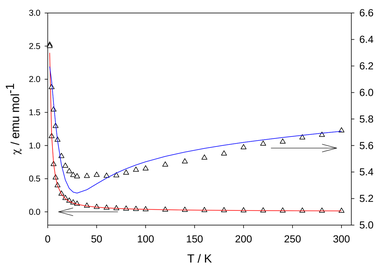
3. A Ferromagnetic [3x3] $Cu(II)_9$ Grid



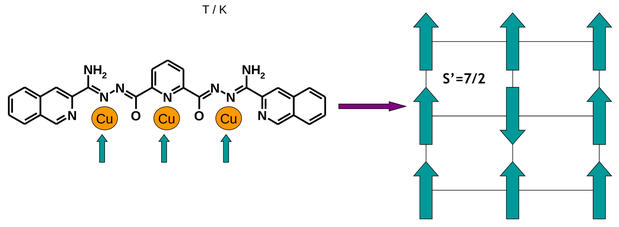
Formula[5]: $[(C_{27}H_{19}N_9O_2)_6Cu_{8.5}](CF_3SO_3)_{1.4}(PF_6)_{3.6}{\cdot}3H_2O$
Crystal System: tetragonal; Space Group: $P4_2/n$ (#86); R1 = 0.1174
Unit Cell Parameters: a = b: 20.580(3) Å; c: 22.970(4) Å

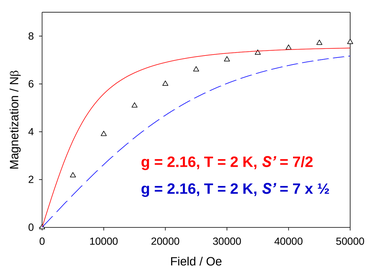
Cu-Cu (μO-bridged): 4.0413(8) - 4.3611(8) Å, 139.28(18) - 144.20(17)°

Jahn-Teller elongation:
Cu-L_{short}: 1.891(5) - 2.067(5) Å, Cu-L_{long}: 2.266(4) - 2.336(5) Å
Jahn-Teller compression:
Cu-L_{short}: 1.908(6) Å, Cu-L_{long}, 2.234(4) Å



g = 2.164
JR = 2.204 cm-1
JC = -27.55 cm-1
TIP = 720 × 10-6 cm3mol-1
ρ = 0.09
θ = -1 cm-1
10²R = 2.54

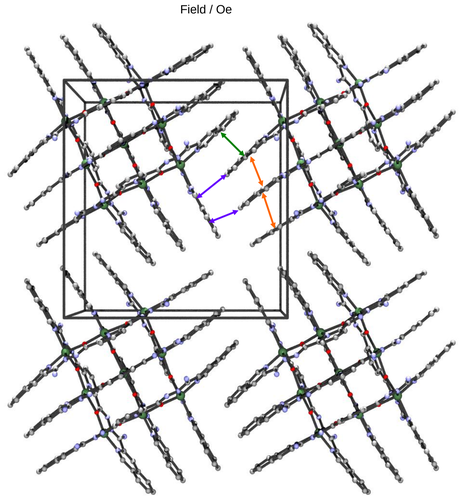




Exchange dominated by JR at low temperature

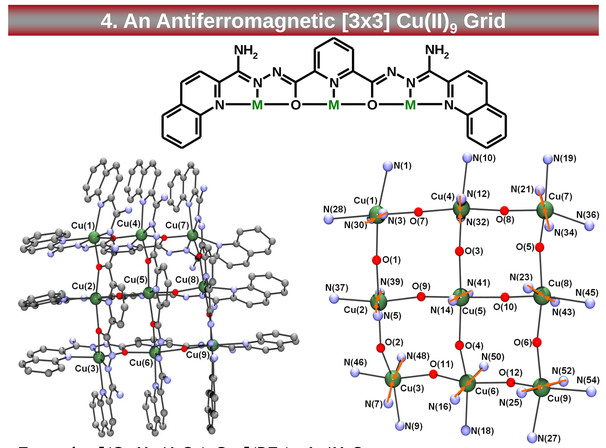
Magnetization simulated from appropriate Brillouin function

Typical of grouped (vs. isolated) Cu(II) centers



Py-Py: 3.818 - 3.961 Å, α = 12.679 - 23.521°
Ar-Ar: 3.675 - 3.857 Å, α = 13.199 - 28.368°
Py-Ar: 3.686 - 3.688 Å, α = 12.02 - 23.262°
Edge-to-Face: 3.089 - 3.563 Å

4. An Antiferromagnetic [3x3] $Cu(II)_9$ Grid



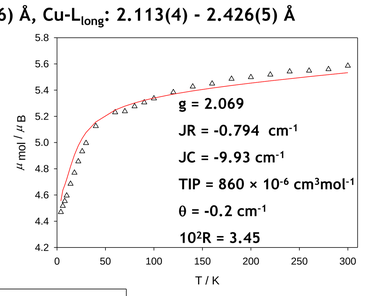
Formula: $[(C_{27}H_{19}N_9O_2)_6Cu_9](BF_4)_6{\cdot}6.4H_2O$
Crystal System: triclinic ; Space Group: P-1 (#2); R1 = 0.0987
Unit Cell Parameters: a = 15.604(3) Å; b: 23.135(4) Å; c: 26.411(5) Å
α = 93.403(4)°; β = 100.014(5)°; γ = 90.626(5)°

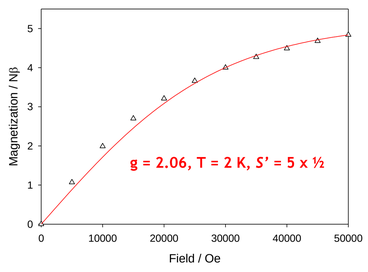
Cu-Cu (μO-bridged): 4.0582(9) - 4.1896(9) Å, 139.8(2) - 144.02(18)°

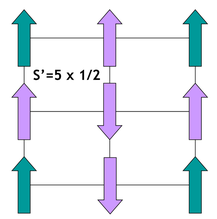
Jahn-Teller compression:
Cu-L_{short}: 1.896(4) - 1.978(6) Å, Cu-L_{long}: 2.113(4) - 2.426(5) Å

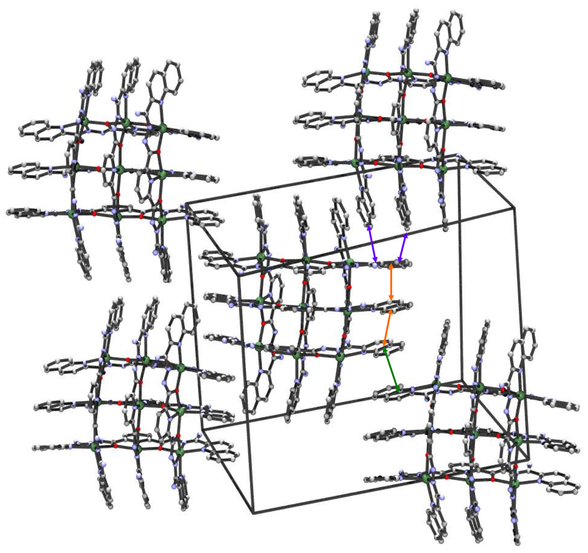
JC dominates at low temperature:

S' = S_{cross} + 4 x S_{Cu}
= 1/2 + 4 x 1/2
= 5 x 1/2



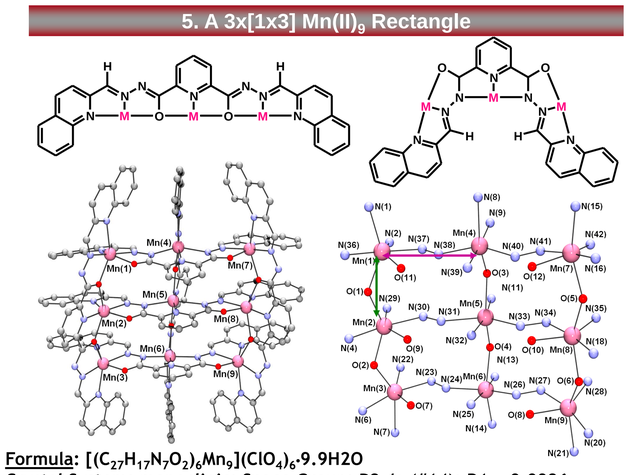






Py-Py: 3.769 - 4.119 Å, α = 13.725 - 28.766°
Ar-Ar: 3.877 - 4.827 Å, α = 8.939 - 27.516°
Py-Ar: 3.704 - 4.032 Å, α = 21.465 - 35.411°
Edge-to-Face: 3.089 - 3.563 Å

5. A 3x[1x3] $Mn(II)_9$ Rectangle

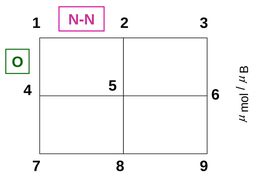


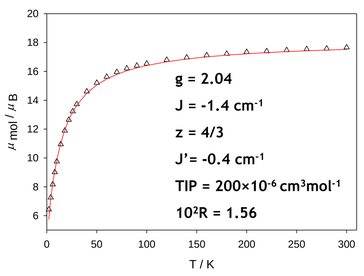
Formula: $[(C_{27}H_{17}N_7O_2)_6Mn_9](ClO_4)_6{\cdot}9.9H2O$
Crystal System: monoclinic; Space Group: $P2_1/n$ (#14); R1 = 0.0936
Unit Cell Parameters: a: 20.908(4) Å; b: 27.102(4) Å; c: 32.492(5) Å;
β : 98.239(4)°
Mn-Mn (μO-bridged): 4.1417(10) - 4.1819(12) Å, 132.33(15) - 134.37(18)°
Mn-Mn (μNN-bridged): 5.2159(10) - 5.6163(9) Å, τ = 160.6 - 179.1°

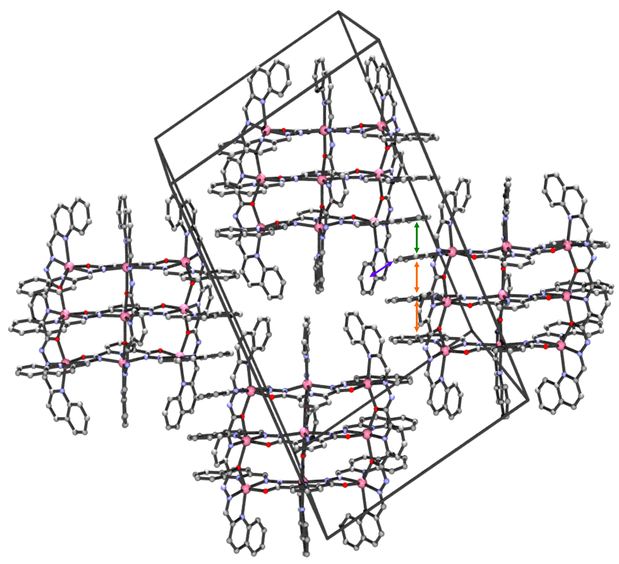
Rectangular grid treated as three $[M_3\text{-}(\mu\text{-}O)_2]$ subunits with a molecular field correction to account for the μ-NN bridges.[6]

$$H_{ex} = -J\{S_1{\bullet}S_4 + S_4{\bullet}S_7\}$$

$$\chi_{mol} = \frac{N\beta^2 g^2}{3k(T - zJ'\chi_{trimer})}\frac{\sum S'(S'+1)(2S'+1)e^{-E(s')/kT}}{\sum(2S'+1)e^{-E(S')/kT}}(1-\rho) + \frac{N\beta^2 g^2 S(S+1)\rho}{3kT} + TIP$$







Py-Py: 3.612 - 3.709 Å, α = 7.802 - 20.935°
Ar-Ar: 3.530 - 3.715 Å, α = 13.542 - 23.398°
Ar-Ar: 3.569 - 3.582 Å, α = 14.781 - 24.848°
Edge-to-Face: 3.08 - 3.69 Å

6. Conclusions

Face-to-face and edge-to-face π-π interactions organized $M(II)_9$ complexes into chains, 2D layers and 3D arrays.

A novel [3x3] antiferromagnetic $Cu(II)_9$ grid and 3x[1x3] $Mn(II)_9$ rectangle were synthesized and characterized.

Long-range magnetic ordering was not observed.

Acknowledgements

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NSERC CRSNG School of Graduate Studies ACA American Crystallographic Association