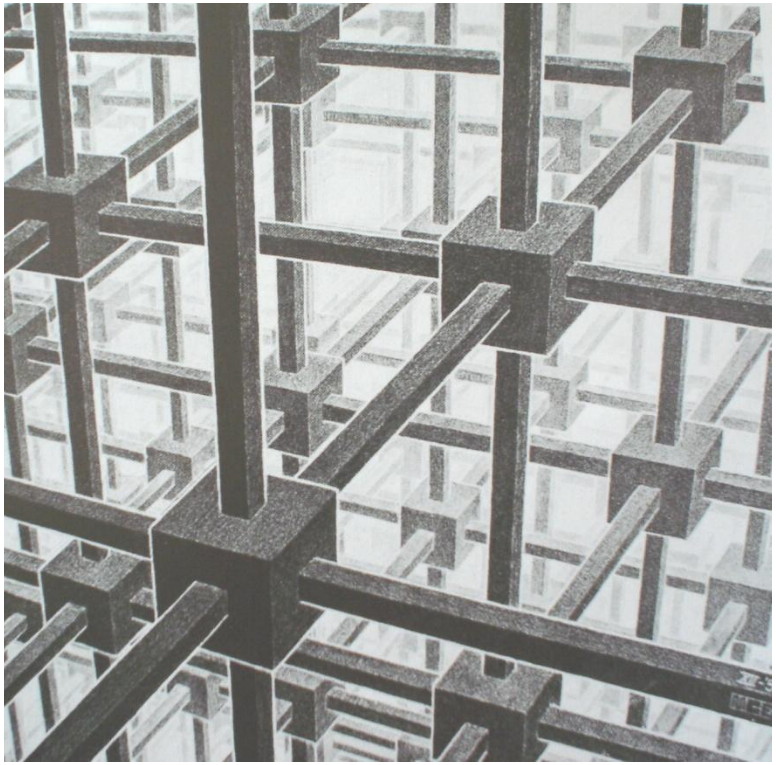
CHIMIE METALOSUPRAMOLECULARA SI MATERIALE MOLECULARE

Marius Andruh
Universitatea din Bucuresti

Metallosupramolecular Chemistry



Escher

Crystal Engineering

Molecular Magnetism
Luminescence
Zeolite-like Materials

LEADING ROLE ACTORS

METAL ION: coordination number and geometry, charge, HSAB behaviour (Coordination algorithm)

Suitable designed (programmed) LIGAND: denticity, shape, size, HSAB behaviour

The metal ions exert a *structural* role
(directing and sustaining the solid-state architecture),
and a *functional* one (carrying magnetic, optical, or redox properties)

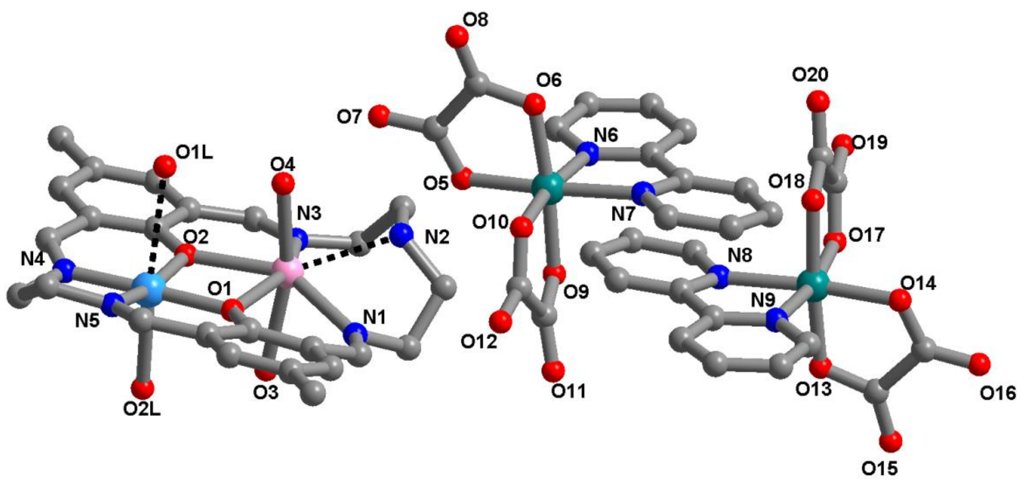
M. Andruh, *Chem. Commun.*, **2007**, 2565 (Feature article).

The long way towards heterotrimetallics

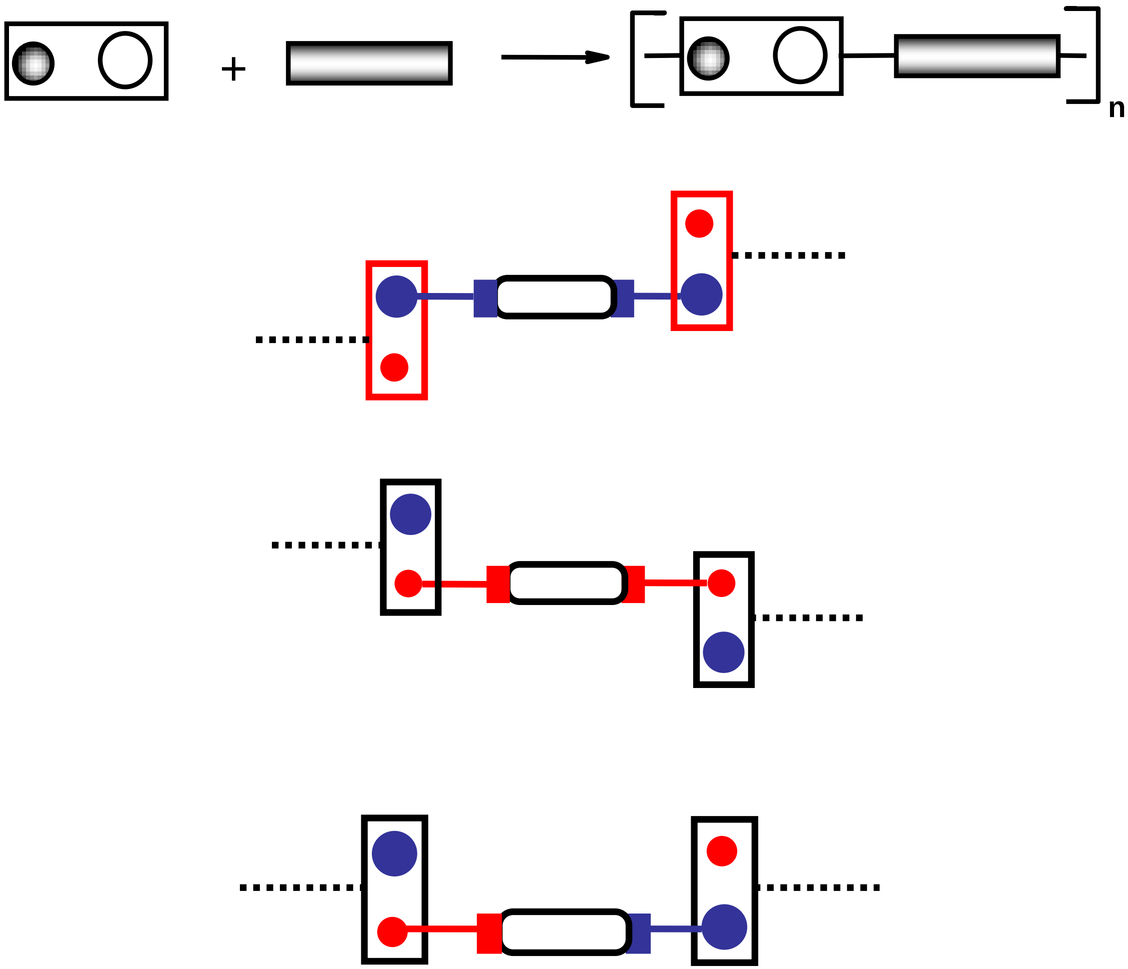
Why heterotrimetallics?

- A challenging synthetic problem
- Novel systems
- Novel network topologies
- More complex magnetic properties
- New properties

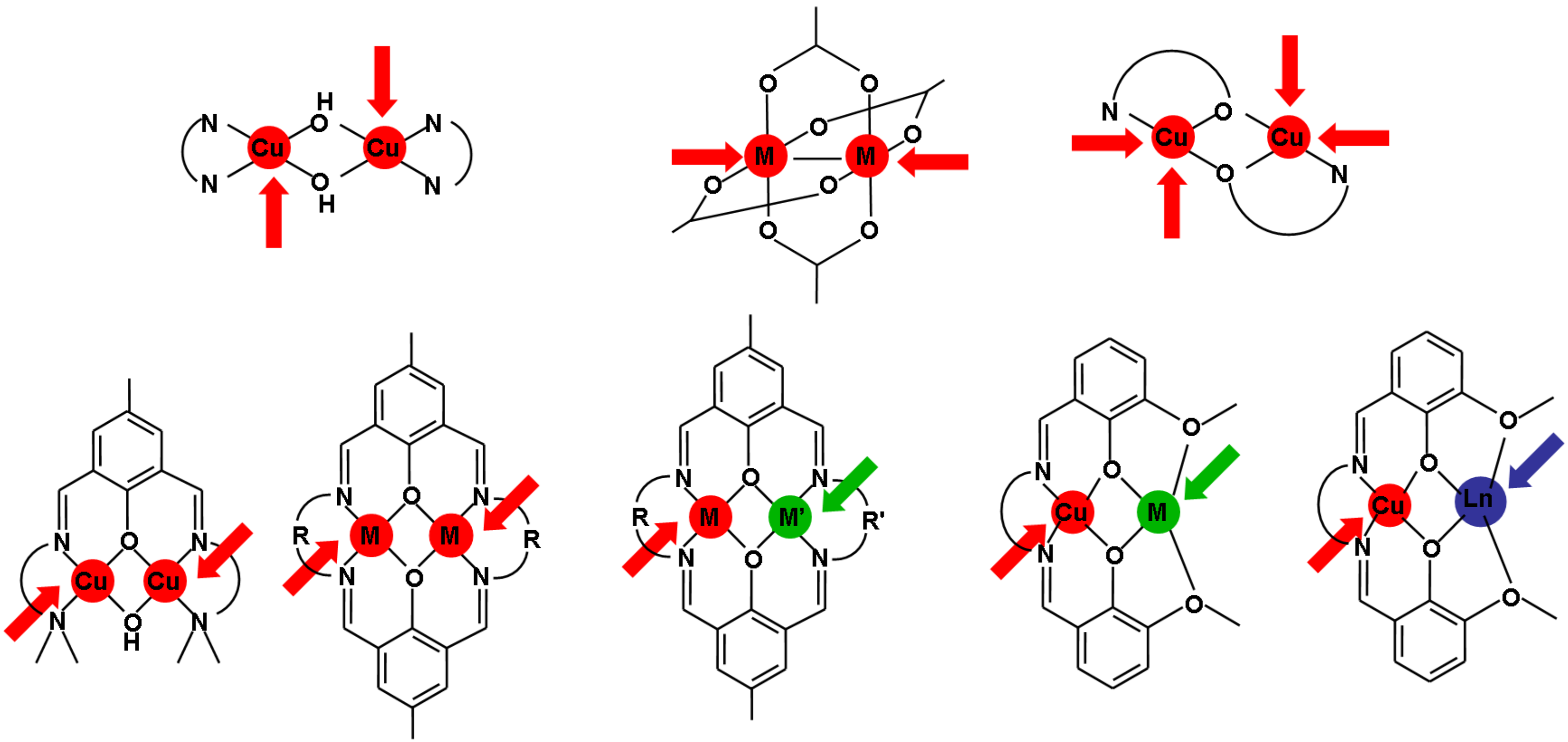
A heterotrimetallic system,
but not a heterotrimetallic complex



Heteronuclear complexes as tectons

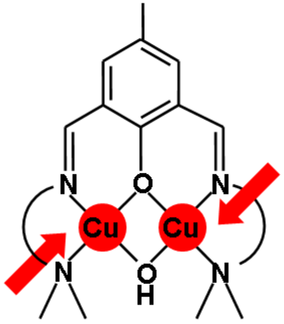


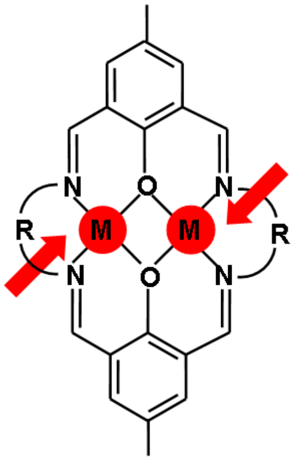
Homo- and Heterobinuclear Complexes as Nodes

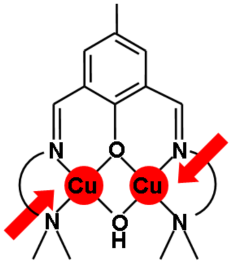


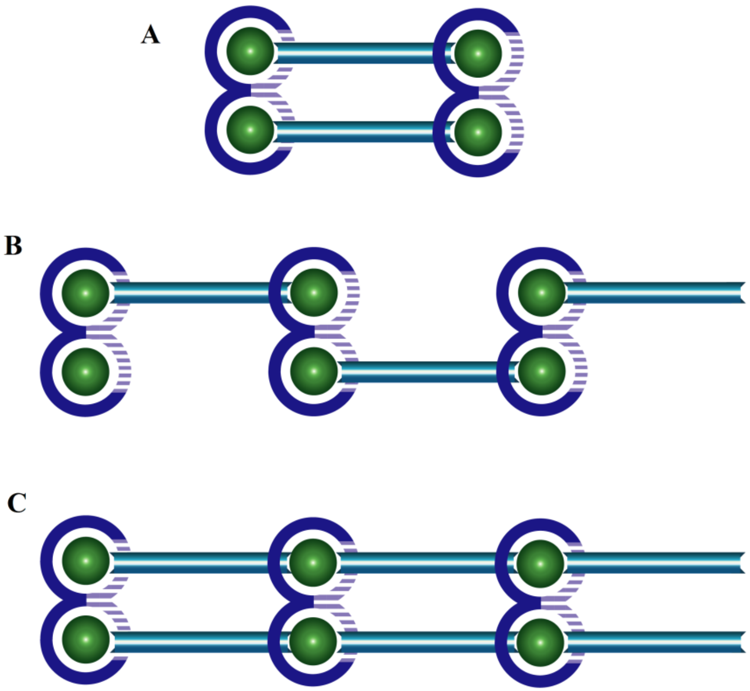
The **heterobinuclear** nodes combine the electronic and the stereochemical peculiarities of the **different** metal ions

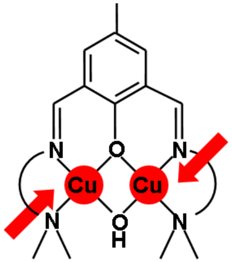
First step: homometallic polynuclear complexes



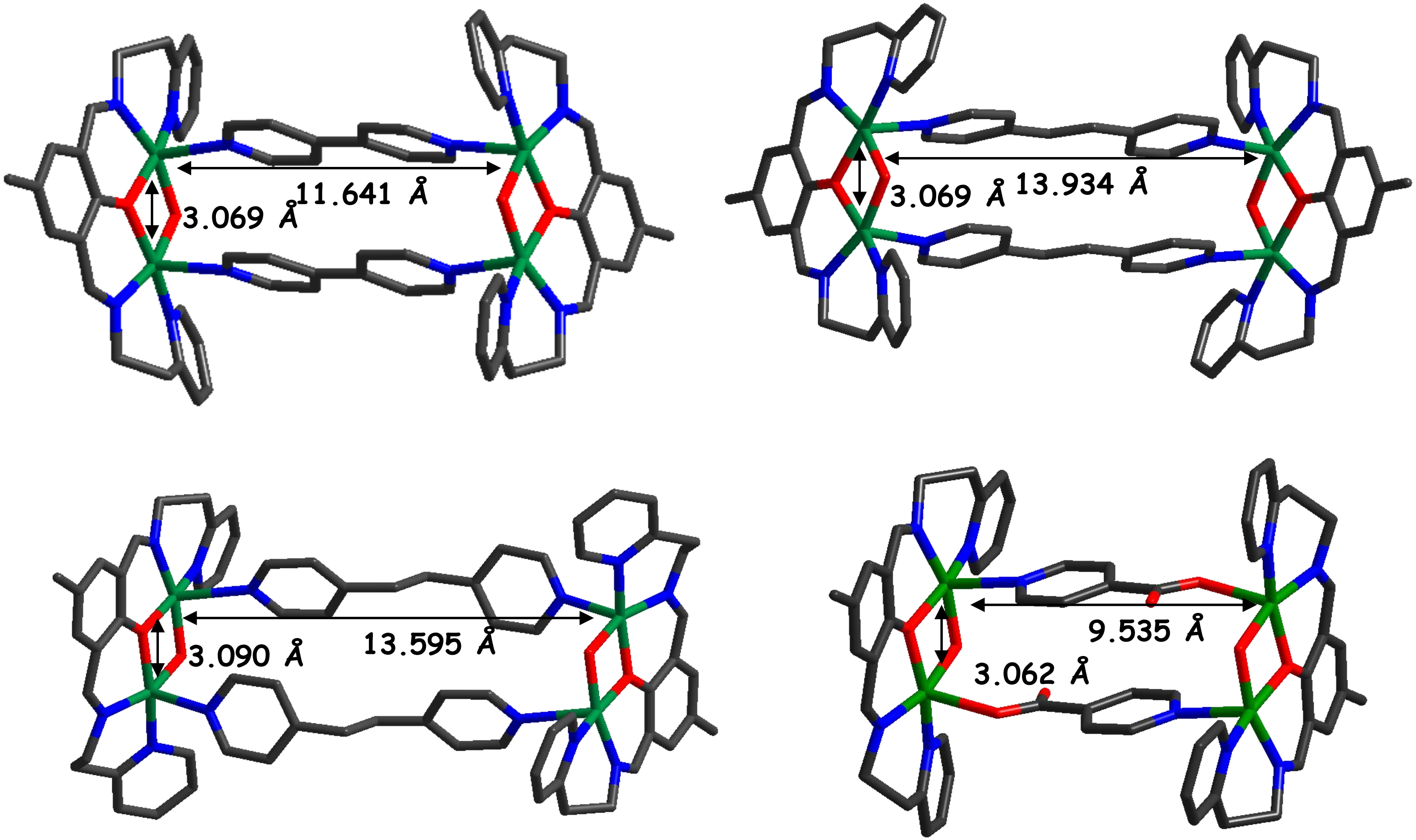



O
N
N
Cu
Cu
N
O
H
N

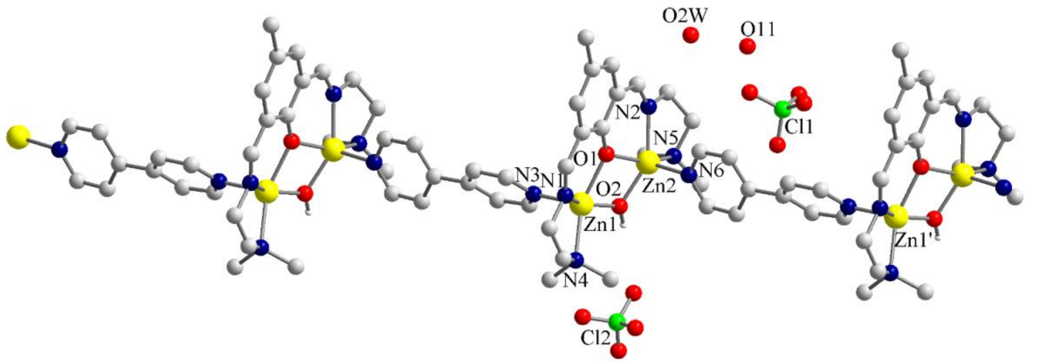

A
B
C

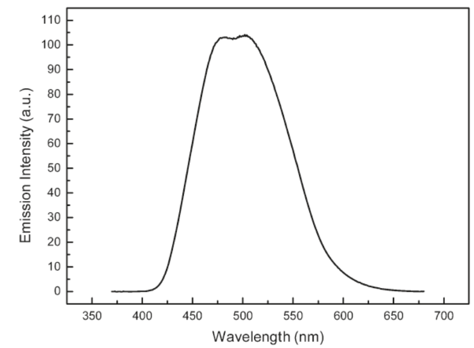


Molecular $[Cu^{II}_4]$ Rectangles

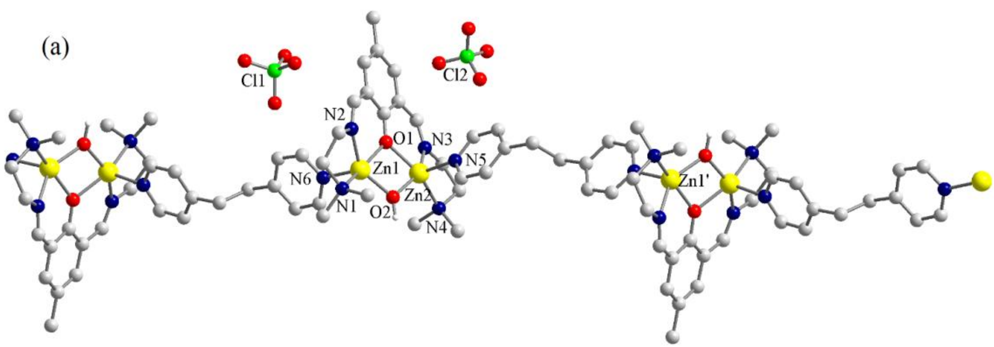


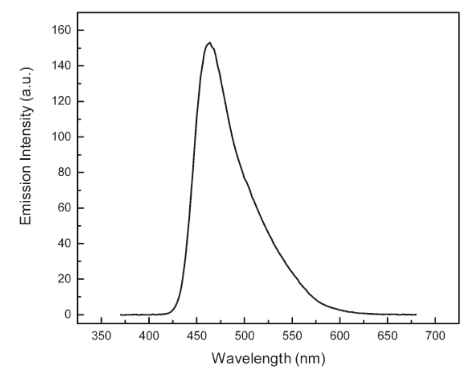
D. Visinescu, G. I. Pascu, M. Andruh, J. Magull, H. W. Roesky, *Inorg. Chim. Acta* **2002**, *340*, 201.



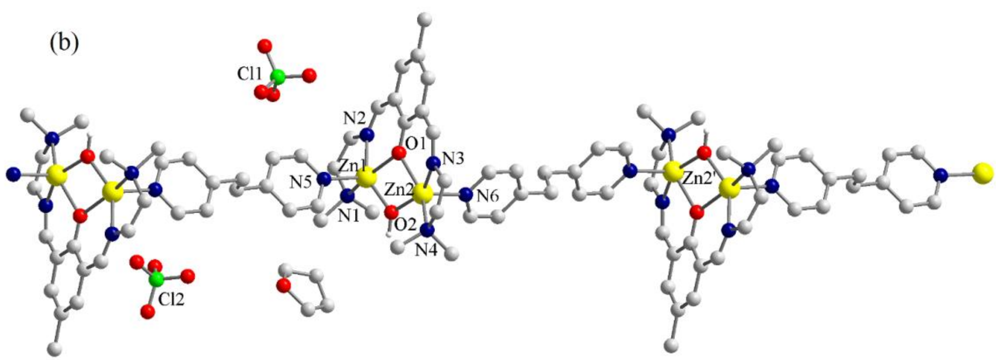


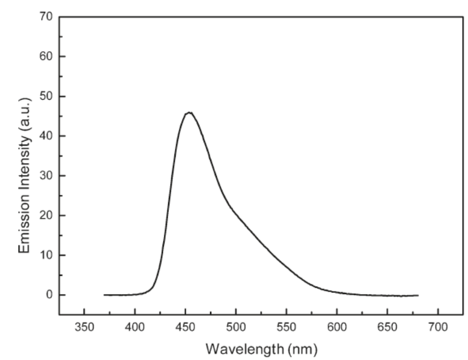
(a)



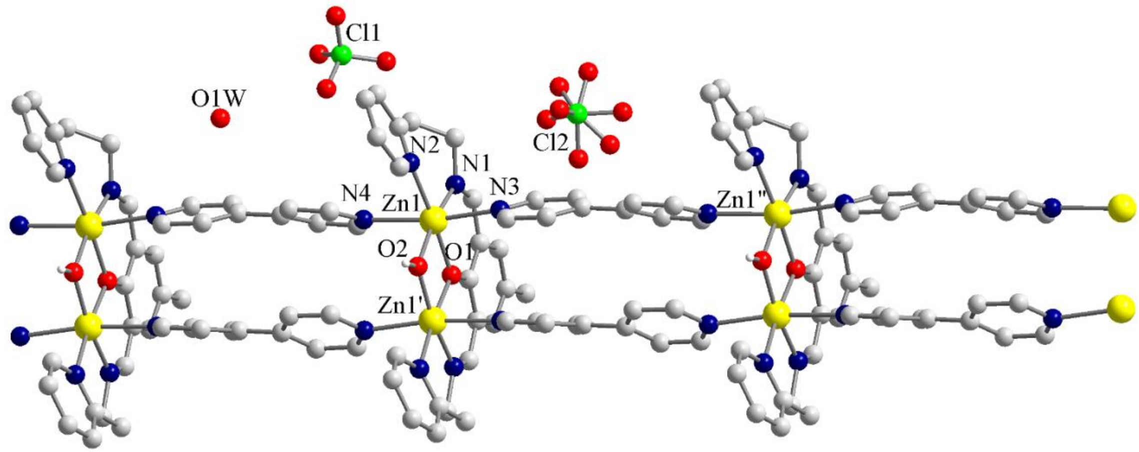


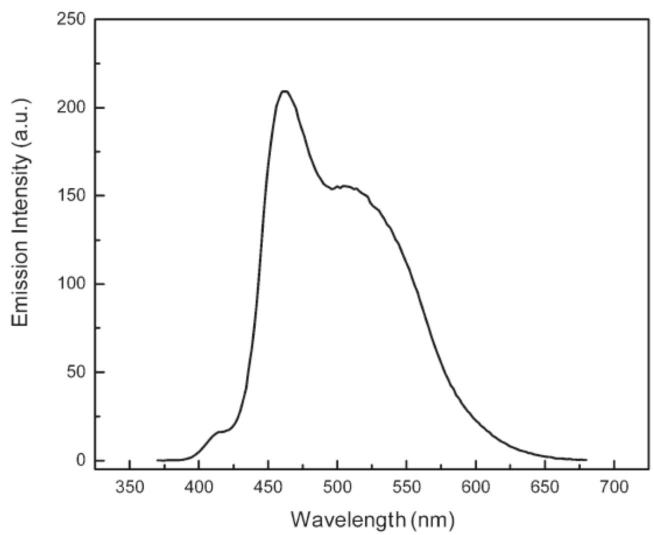
(b)



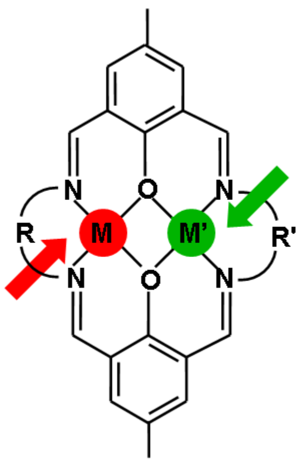


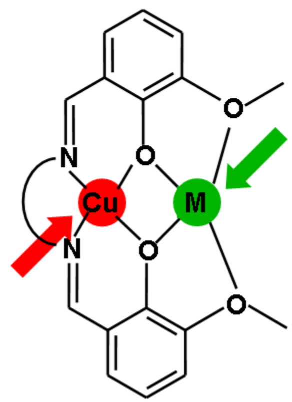
G. Marinescu, G. Marin, A, M, Madalan, A. Vezenu, C. Tiseanu, M. Andruh, *Cryst. Growth & Des.* **2010**, *10*, 2096

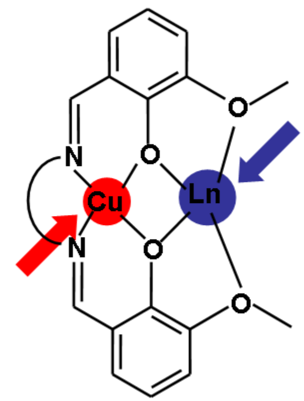

Cl1
O1W
Cl2
N2
N1
N3
N4
Zn1
Zn1''
O2
O1
Zn1'

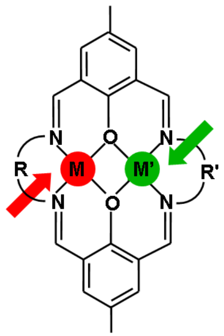

Emission Intensity (a.u.)
Wavelength (nm)
0
50
100
150
200
250
350
400
450
500
550
600
650
700

Second step: heterobimetallics



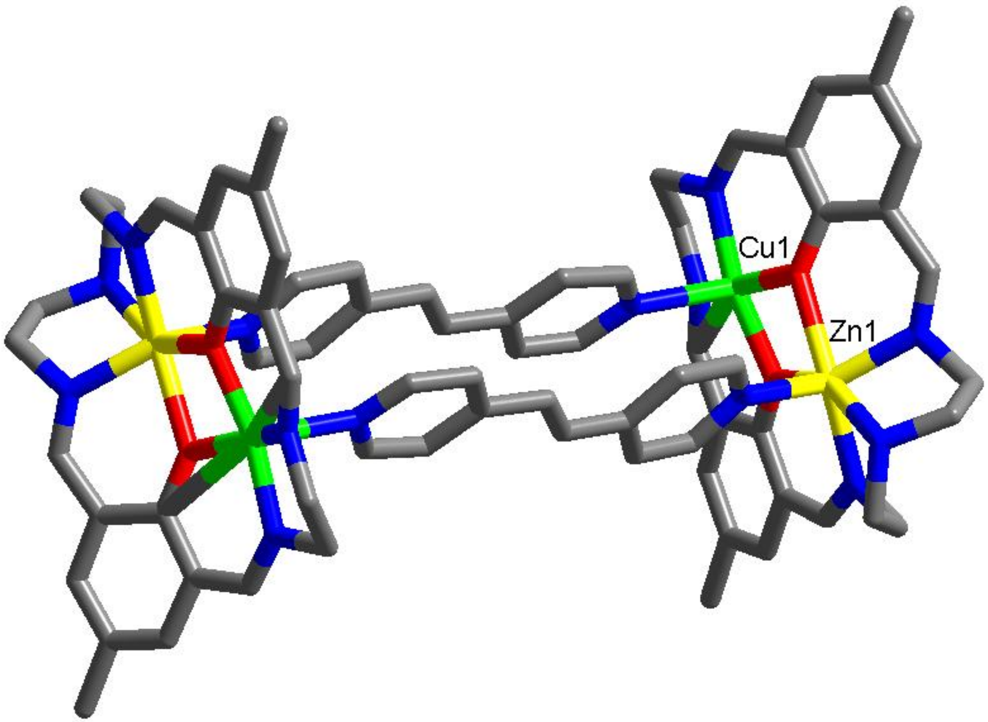




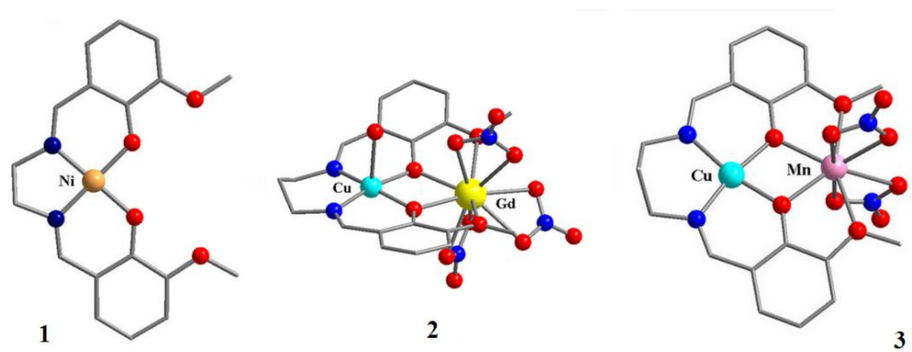


Heterobinuclear tectons

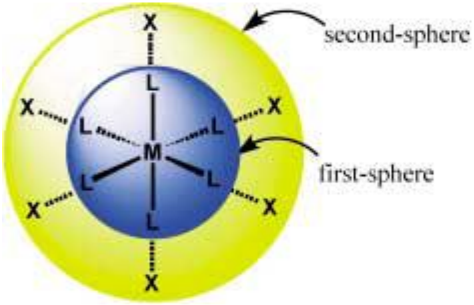
A Heterometallic Rectangle



Useful precursors

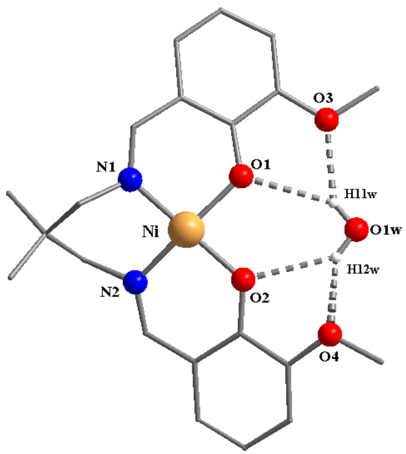


M. Andruh, D. G. Branzea, R. Gheorghe, A. M. Madalan, *CrystEngComm.*, **2009**, *11*, 2571 (Highlight).

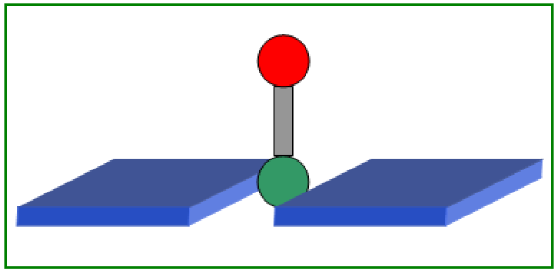


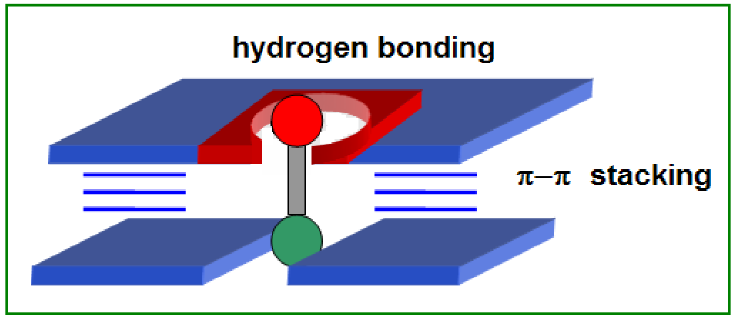
D. A. Beauchamp, S. J. Loeb, *Chem. -Eur. J.*, **2002**, 8, 5084;
S. Ferlay, O. Felix, M. W. Hosseini, J.-M. Planeix, N. Kyritsakas, *Chem. Commun.*, **2002**, 702;
F. M. Raymo, J. F. Stoddart, *Chem. Ber.*, **1996**, *129*, 981.
M. W. Hosseini, *Chem. Commun.*, **2005**, 5825

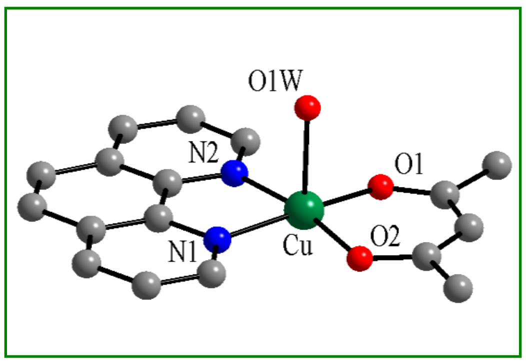
Metal complexes as second coordination sphere ligands
Co-crystallization of two complexes

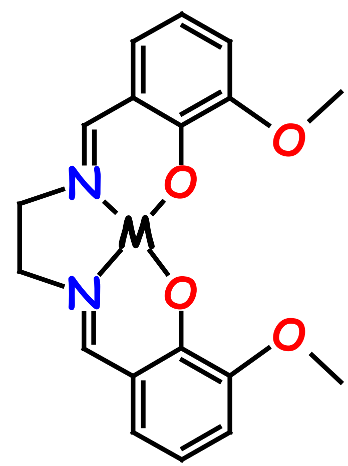


•J.-P. Costes, B. Donnadieu, R. Gheorghe, G. Novitchi, J.-P. Tuchagues, L. Vendier, *Eur. J. Inorg. Chem.* 2008, 5235.



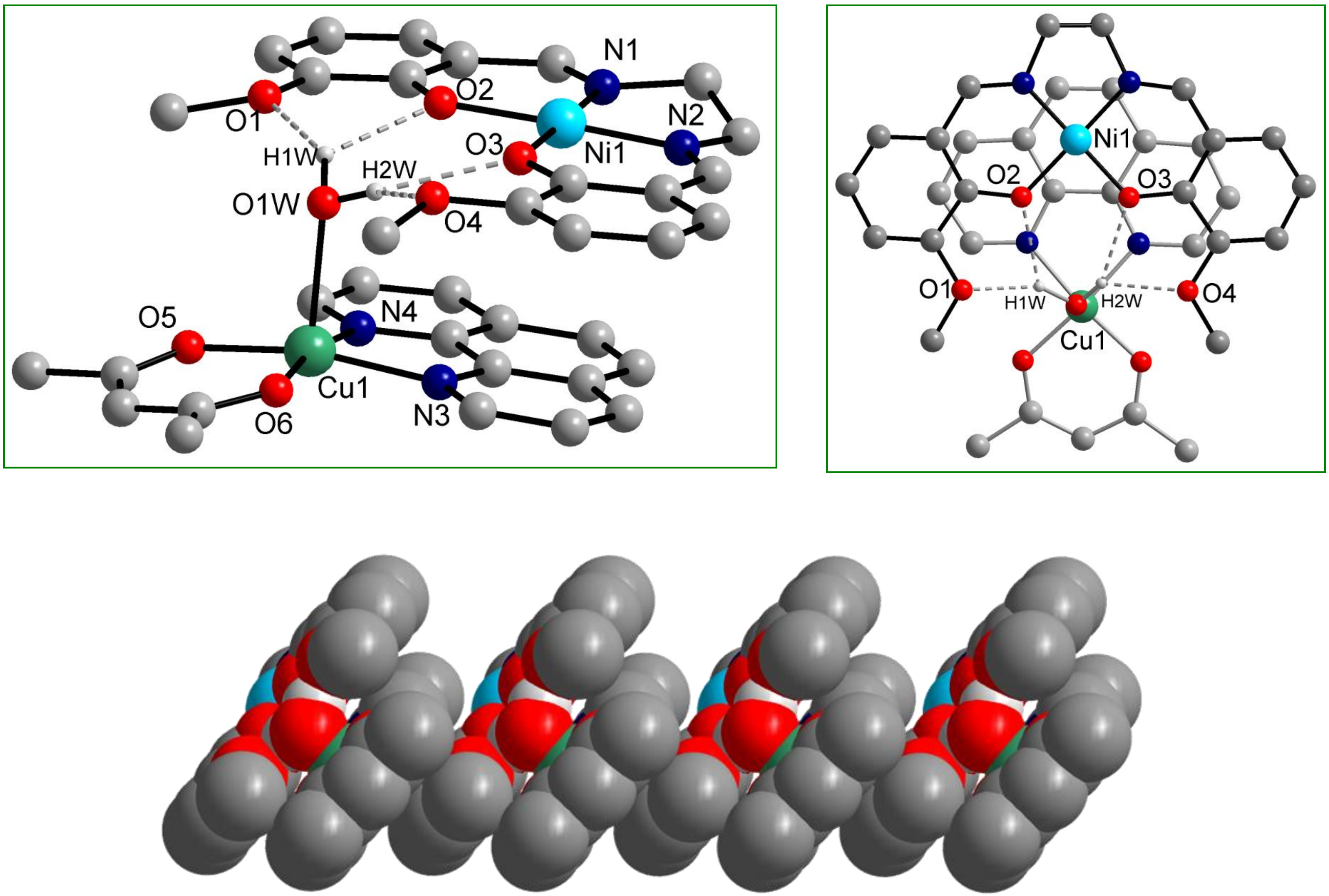




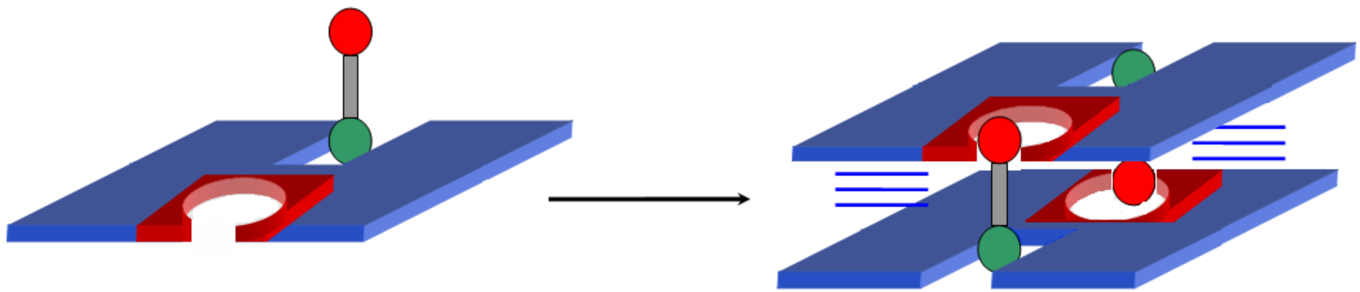


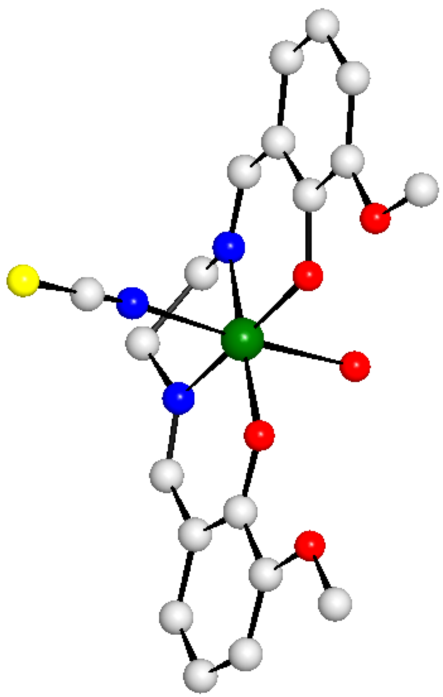
M = **Pd**$^{2+}$, **Ni**$^{2+}$

A.M. Madalan, N. Avarvari, M. Andruh, *New J. Chem.* **2006**, *30*, 521.


N1
O2
O1
N2
O3
Ni1
H1W
H2W
O1W
O4
N4
O5
Cu1
O6
N3
Ni1
O2
O3
O1
H1W
H2W
O4
Cu1

Self-complementary species

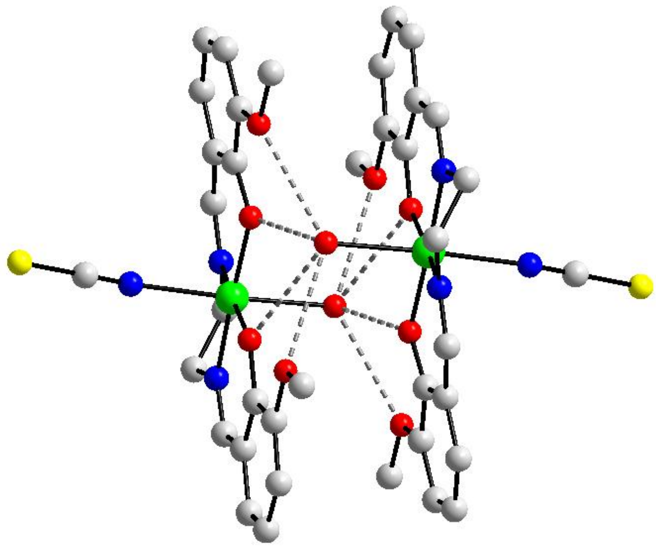


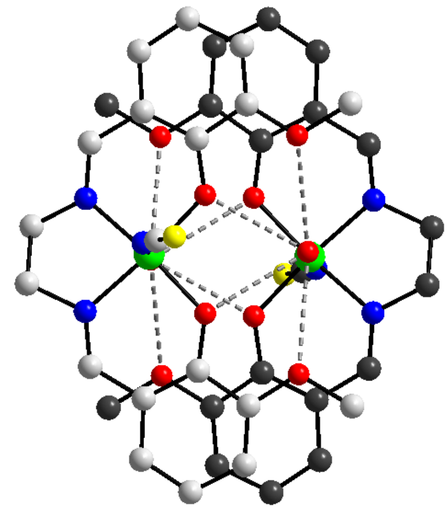


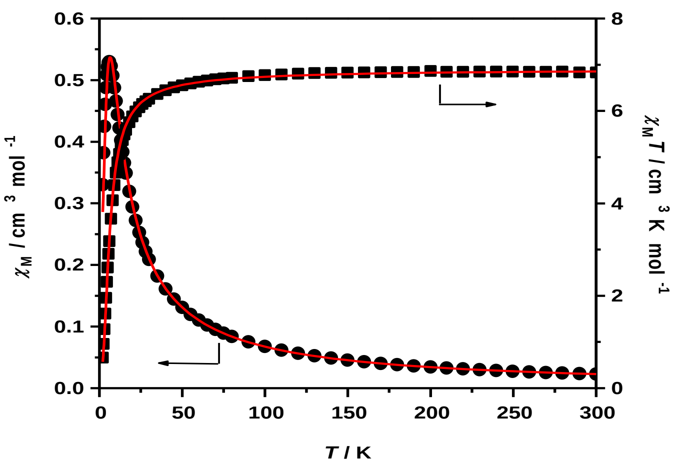
[Mn(III)(valen)(H_2O)(NCS)]

S. Nastase, F. Tuna, C. Maxim, C. A. Muryn, N. Avarvari, R. E. P. Winpenny, M. Andruh, *Cryst. Growth & Des.*, **2007**, *7*, 1825.

Supramolecular dimers

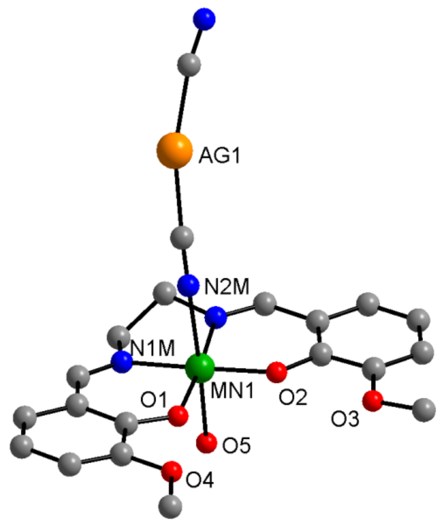




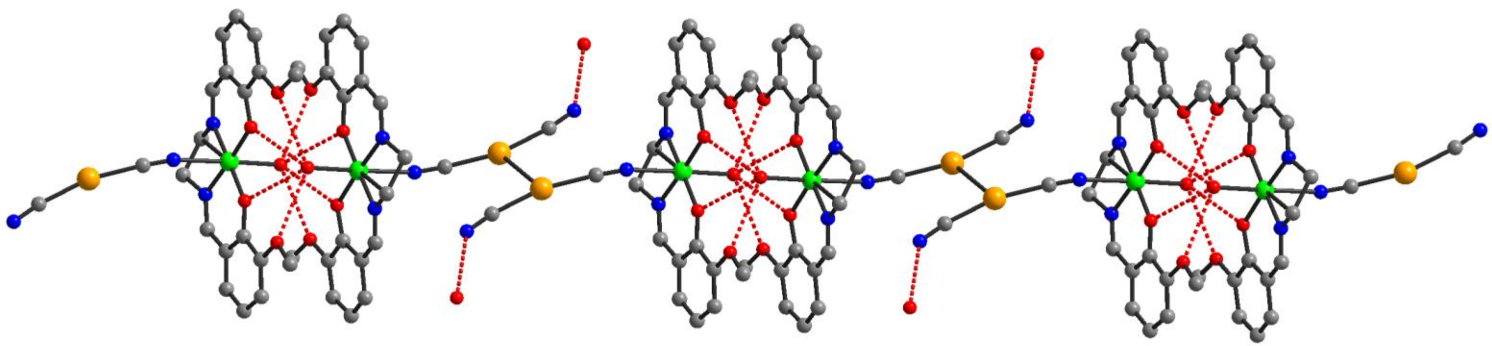


$$H = -J\mathbf{S}_1\mathbf{S}_2 + D_1[\mathbf{S}_{1z}^2 - 1/3\, S_1(S_1 + 1)] + D_2[\mathbf{S}_{1z}^2 - 1/3\, S_2(S_2 + 1)]$$

$J = -0.42\ \mathrm{cm}^{-1}$, $D = -3.1\ \mathrm{cm}^{-1}$



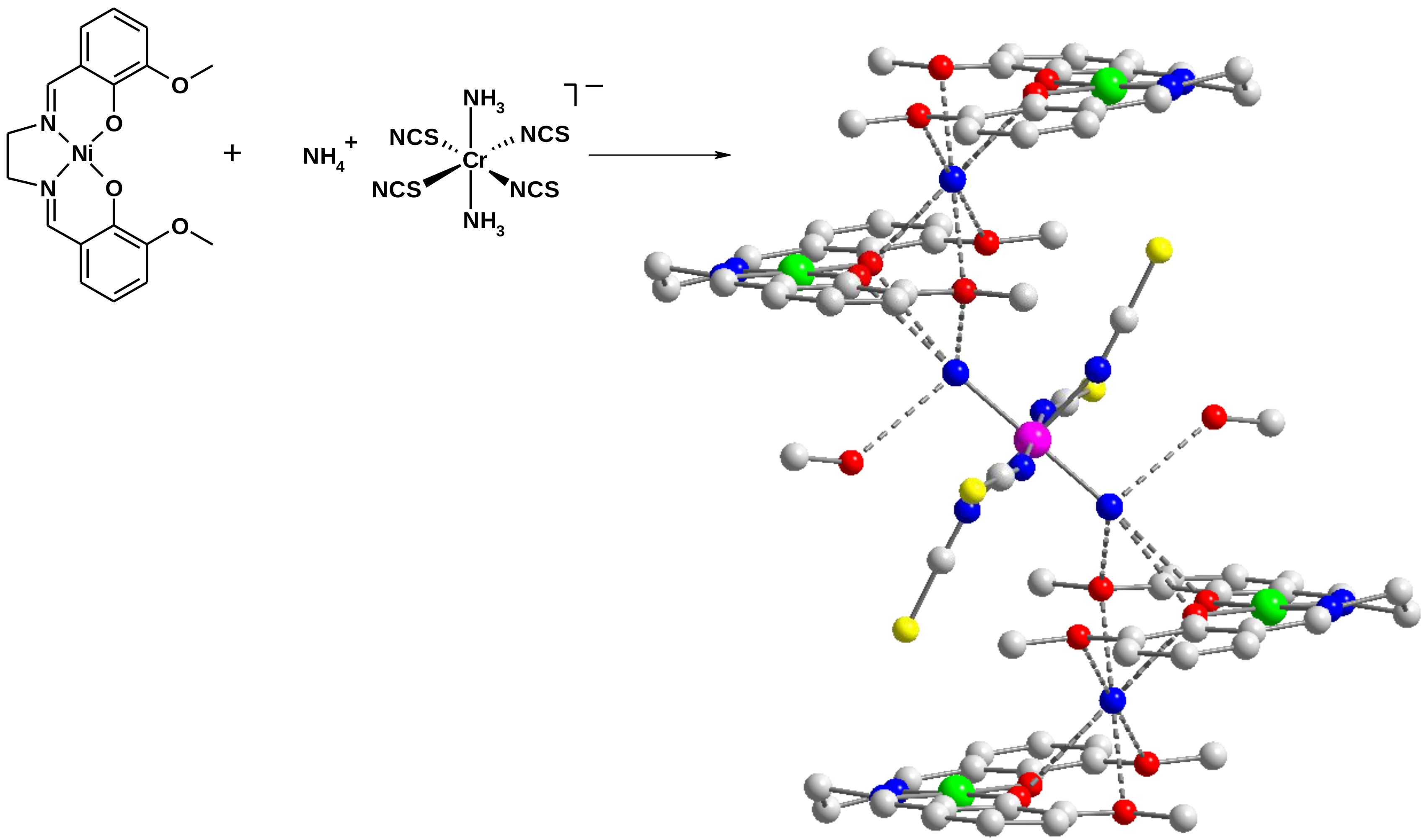
Convolution of H-bond and d^{10}-d^{10} interactions



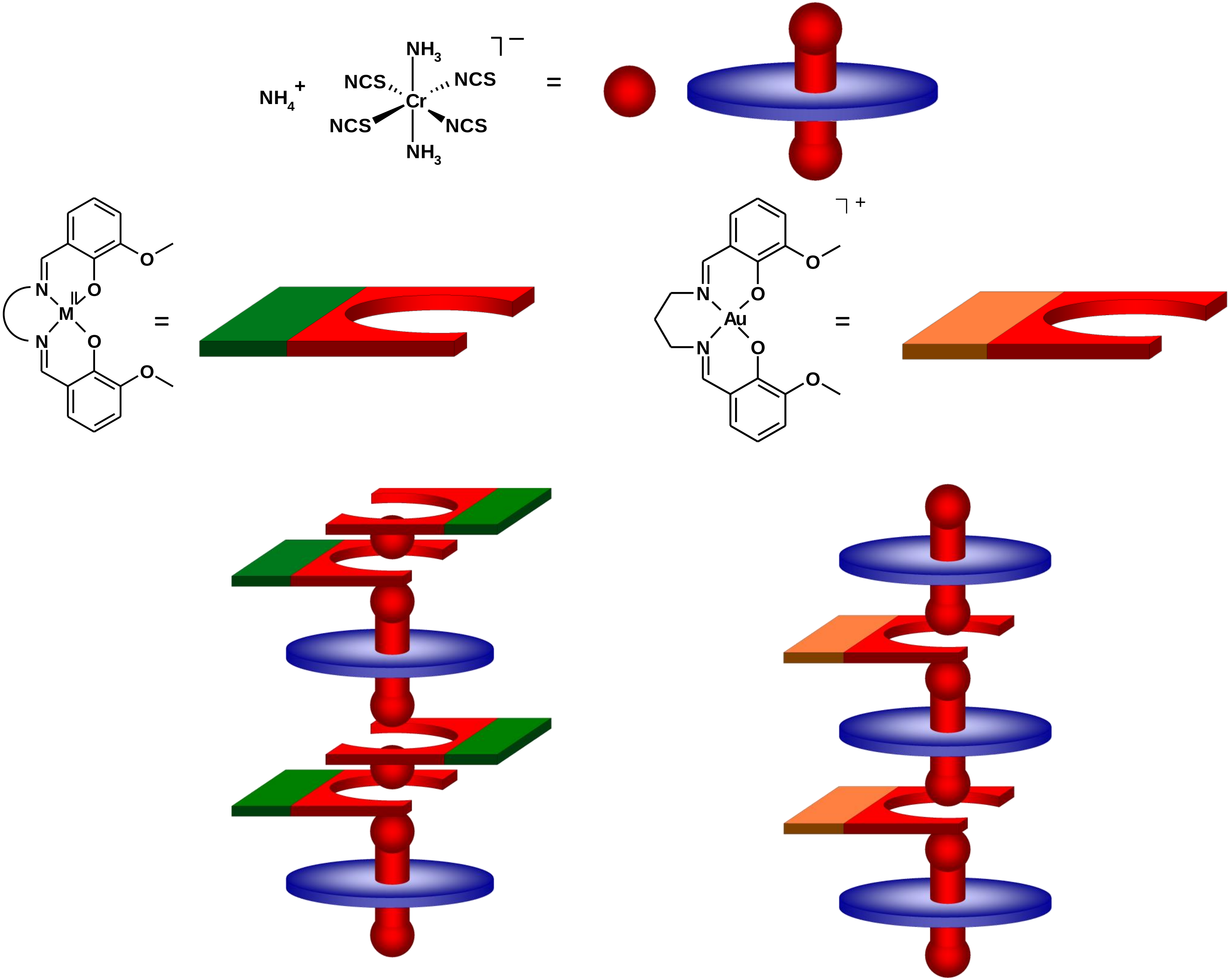
$Ag\cdots Ag$ = 3.092 Å

An interesting H-bond acceptor, the Reinecke salt

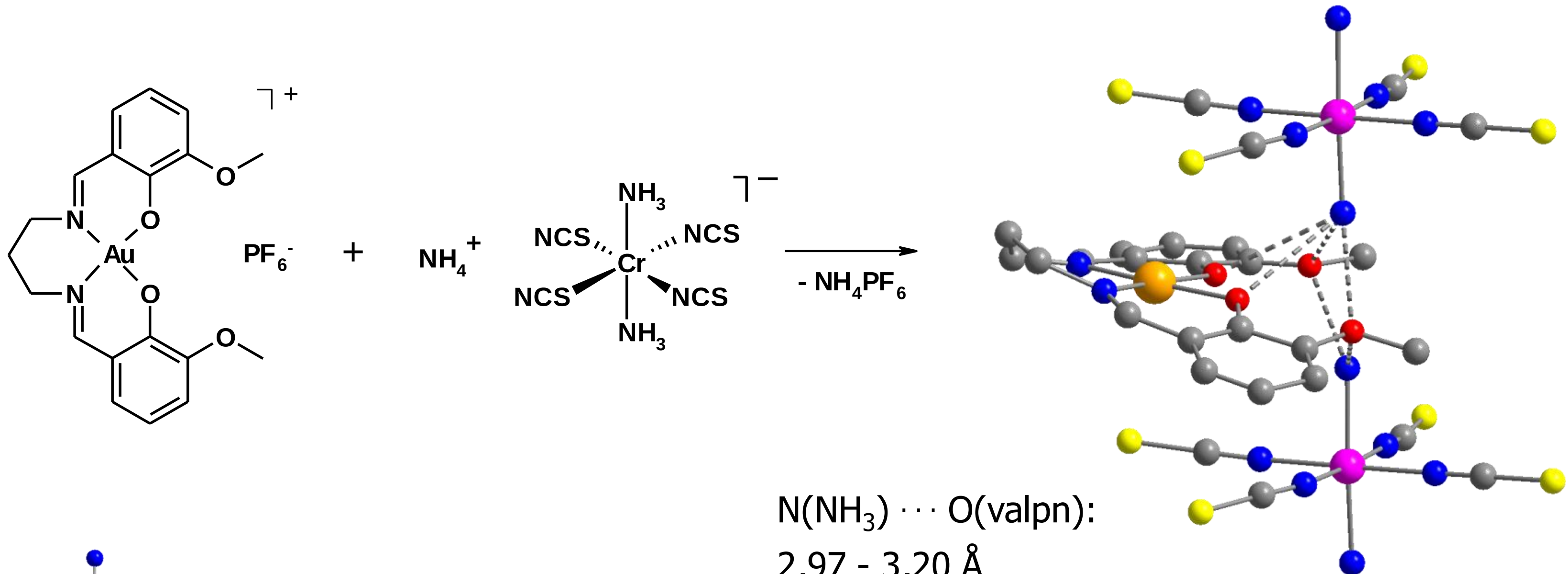
$NH_4[Cr(NCS)_4(NH_3)_2]$



$[Ni(valen)]_2.NH_4[Cr(NCS)_4(NH_3)_2]\cdot CH_3OH$

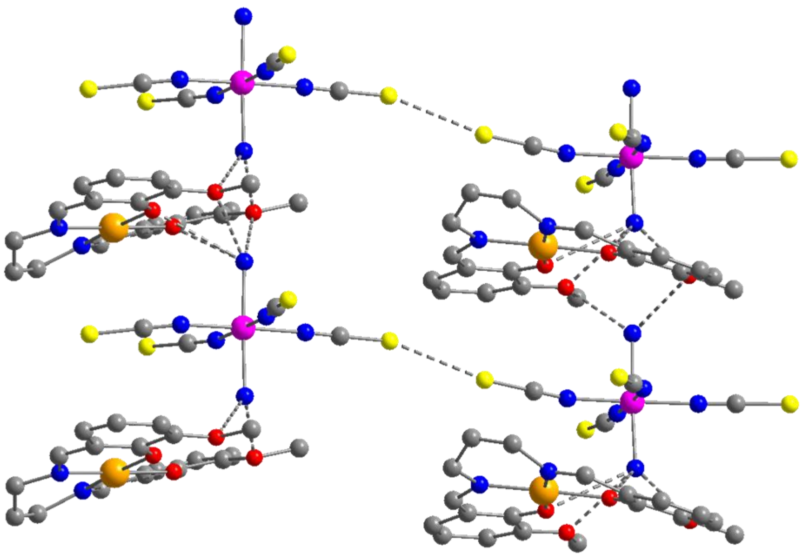


NH_4^+
NH_3
NCS
NCS
Cr
NCS
NCS
NH_3
=
N
O
M
II
N
O
O
O
=
N
O
Au
N
O
O
O
=



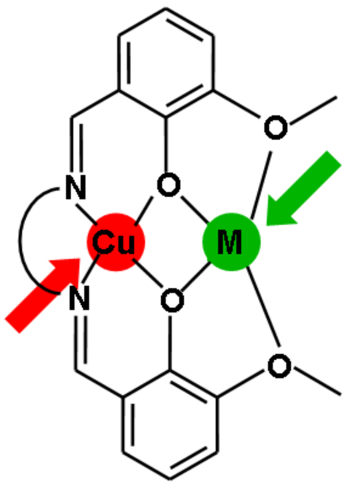
$N(NH_3) \cdots O(valpn)$:
2,97 - 3,20 Å

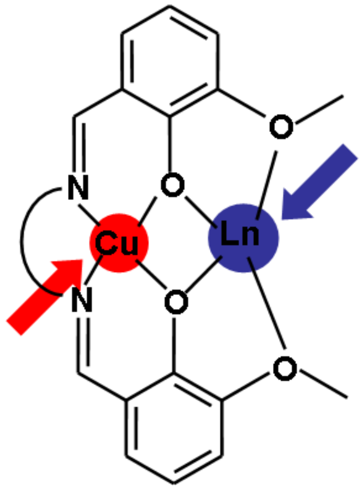
$[Au(valpn)][Cr(NCS)_4(NH_3)_2]$ 11



$S \cdots S$ = 3.55 Å

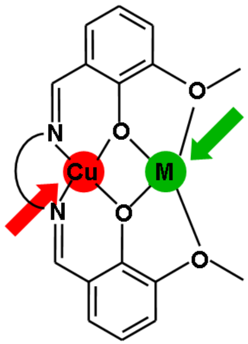
Crystal Engineering based on heterobimetallic tectons



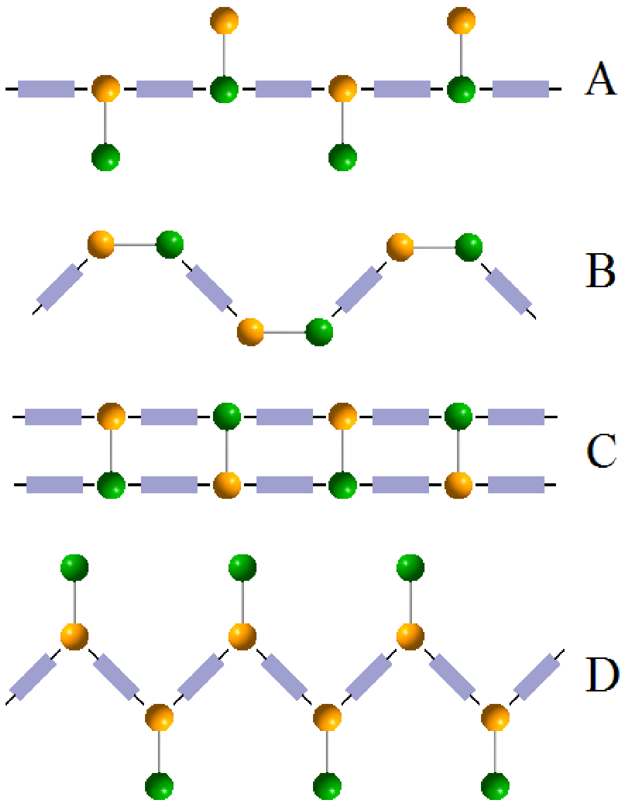


M. Andruh, *Pure Appl. Chem.*, **2005**, *77*, 1685 .

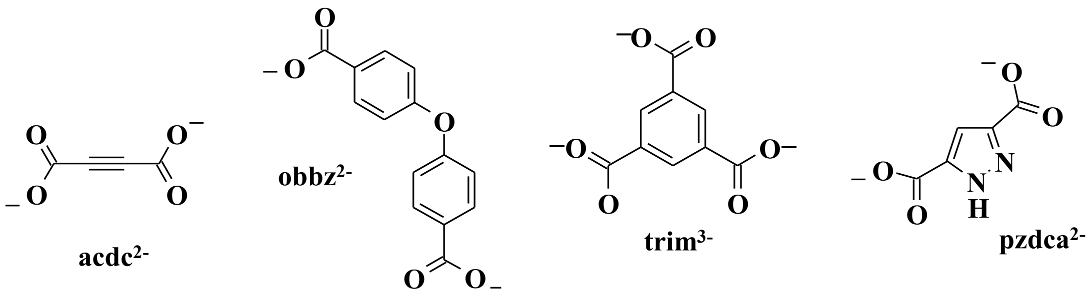
M. Andruh, *Chem. Commun.*, **2007**, 2565.

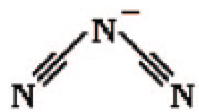


Coordination polymers constructed from 3d-3d' binuclear nodes (Robson's node-and-spacer approach)



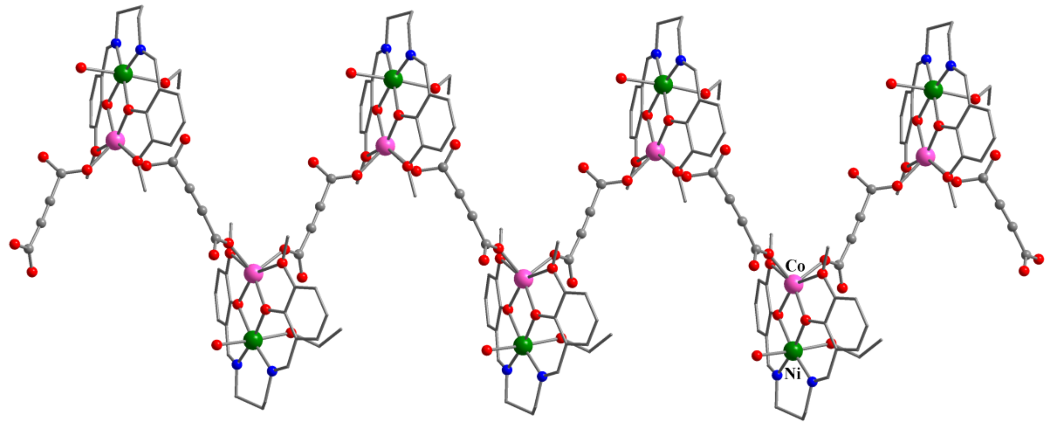
SPACERS



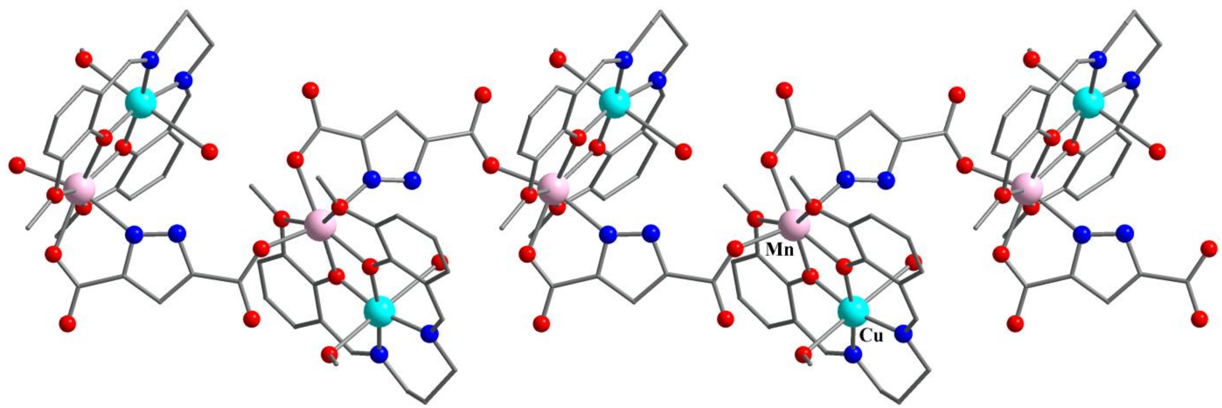


$[Ni(CN)_4]^{2-}$

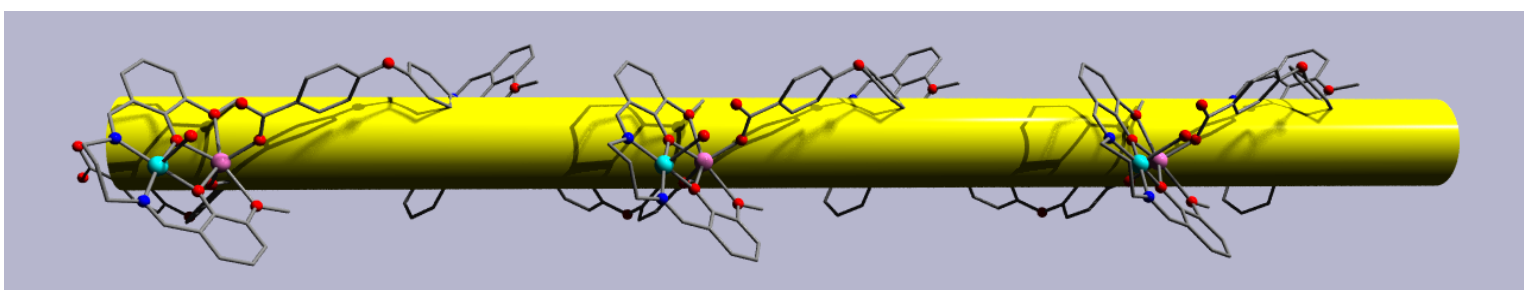
D. G. Branzea, A. Guerri, O. Fabelo, C. Ruiz-Pérez, L.-M. Chamoreau, C. Sangregorio, A. Caneschi, M. Andruh, *Cryst. Growth & Des.*, **2008**, *8*, 941.



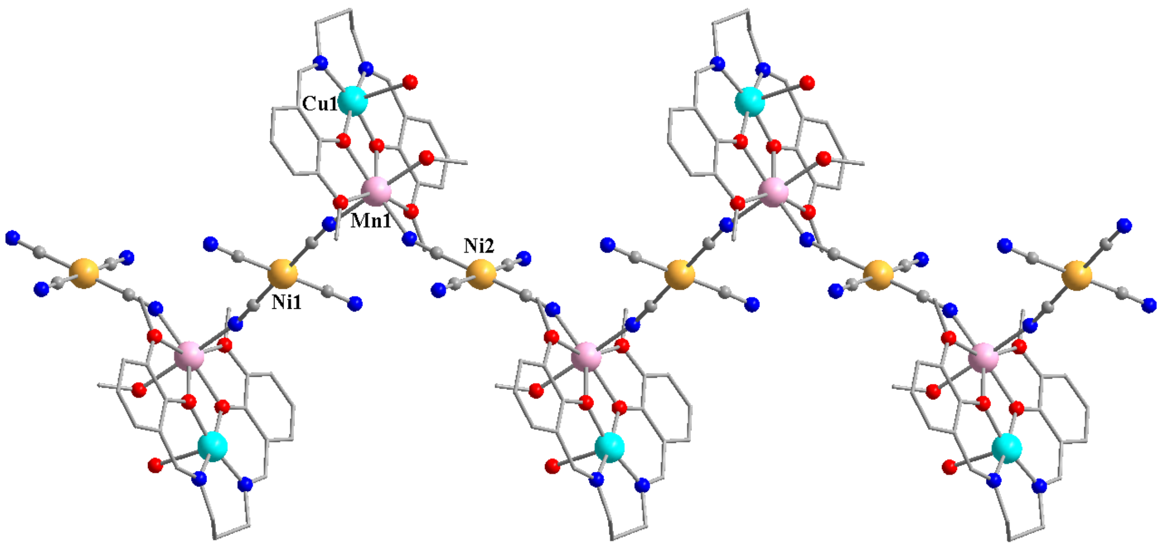
$[L^2NiCo(C_2H_5OH)(H_2O)(acdc)_2]\cdot1.5H_2O$



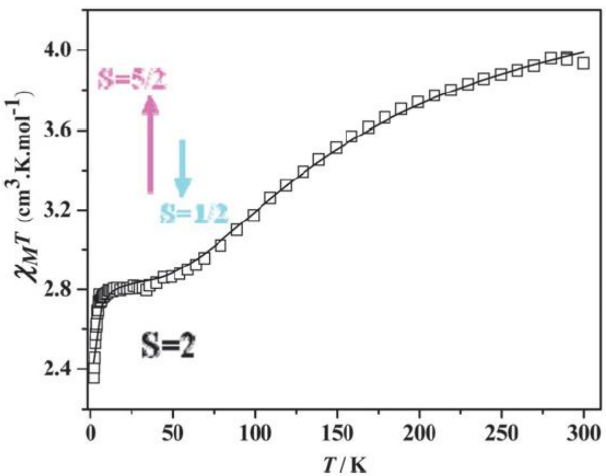
$[L^2CuMn(pzdc)(CH_3OH)(H_2O)]\cdot H_2O$

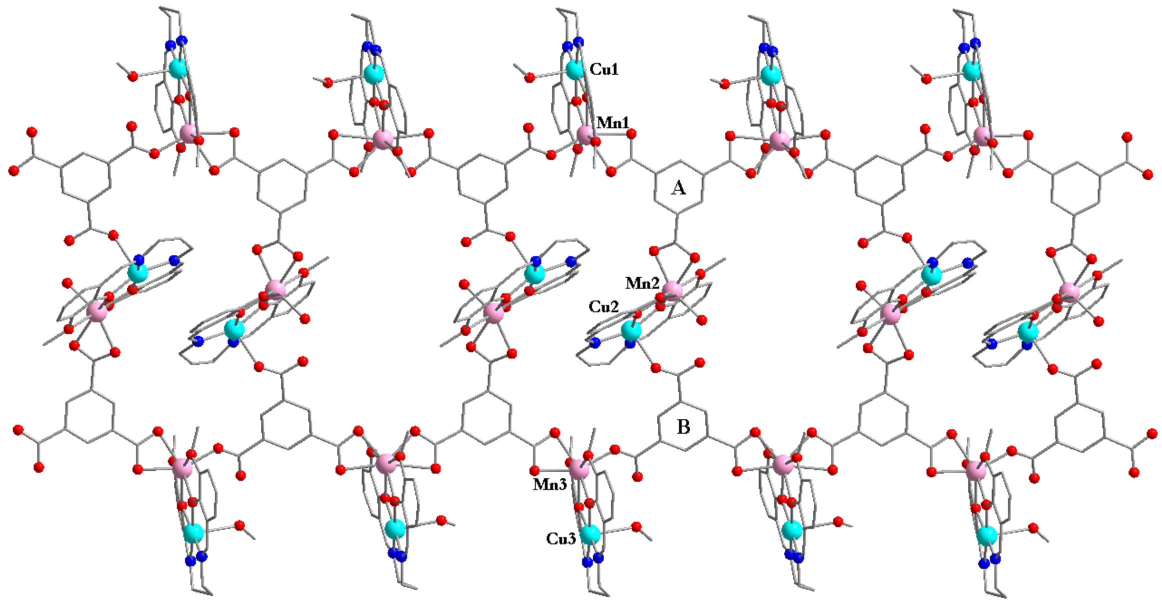


$[L^2CuCo(H_2O)(obbz)]\cdot CH_3CN\cdot C_2H_5OH$

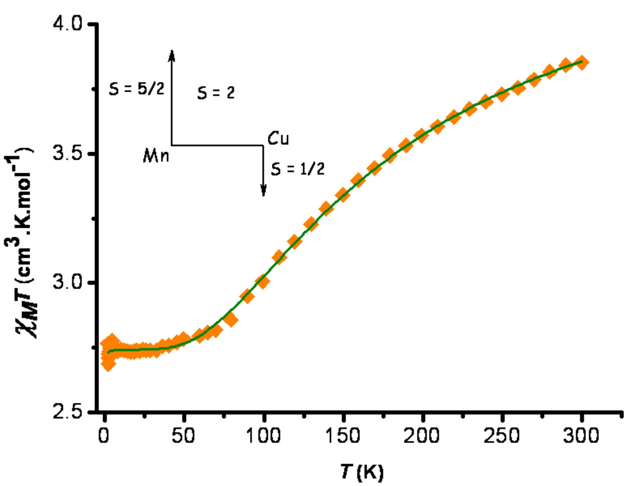


$[L^2CuMn(CH_3OH)(H_2O)(NC)_2Ni(CN)_2]\cdot H_2O\cdot CH_3CN$





$[LCuMn(trim)_{2/3}(CH_3OH)_{2/3}(H_2O)_{1/3}]\cdot 0.66(H_2O)\cdot 0.66(CH_3OH)$

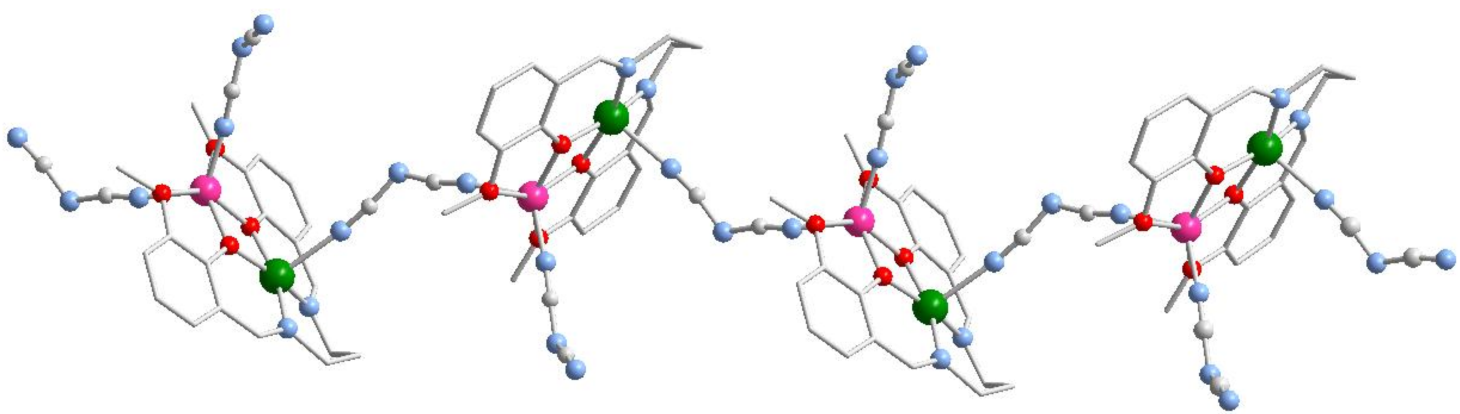


A crystal engineering problem

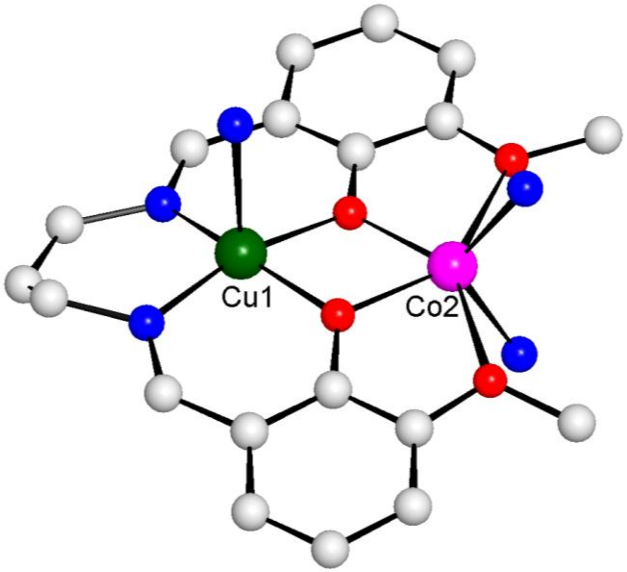
[Cu(II)Co(II)] and [Ni(II)Co(II)] nodes

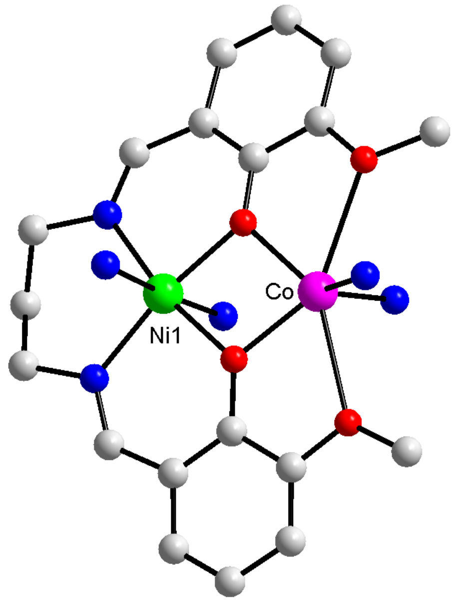
How to increase the dimensionality of the coordination polymers?

The case of the dicyanamido spacer



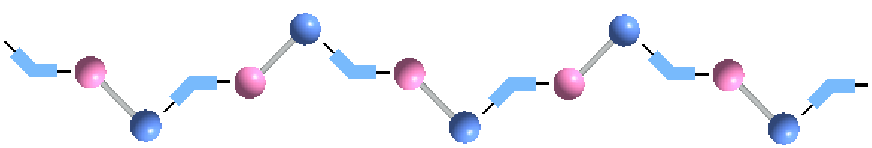
$[\{L^2CuCo\}(dca)_2]$

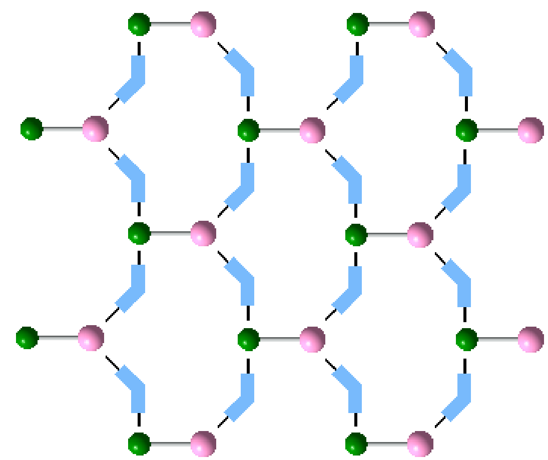


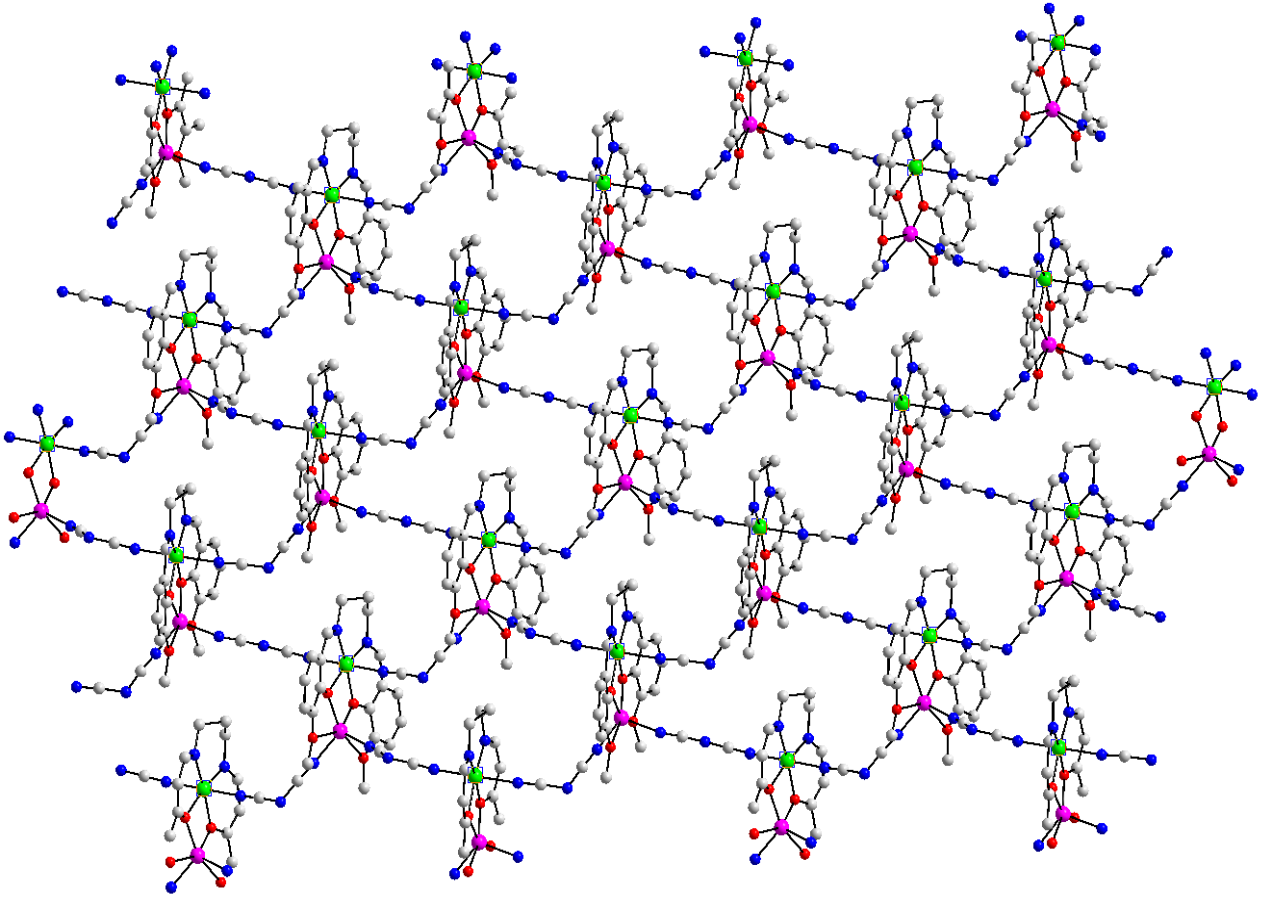


[Cu(II)Co(II)]

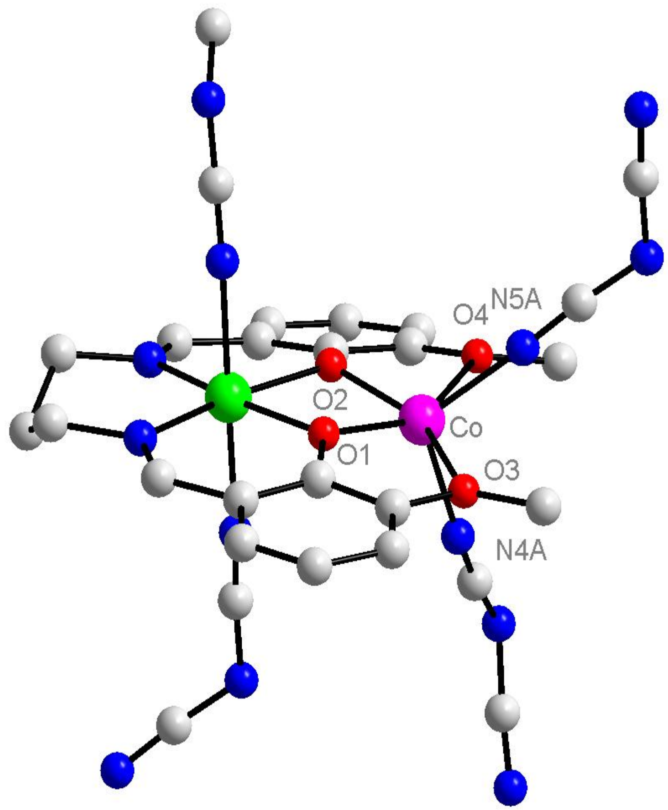
[Ni(II)Co(II)]





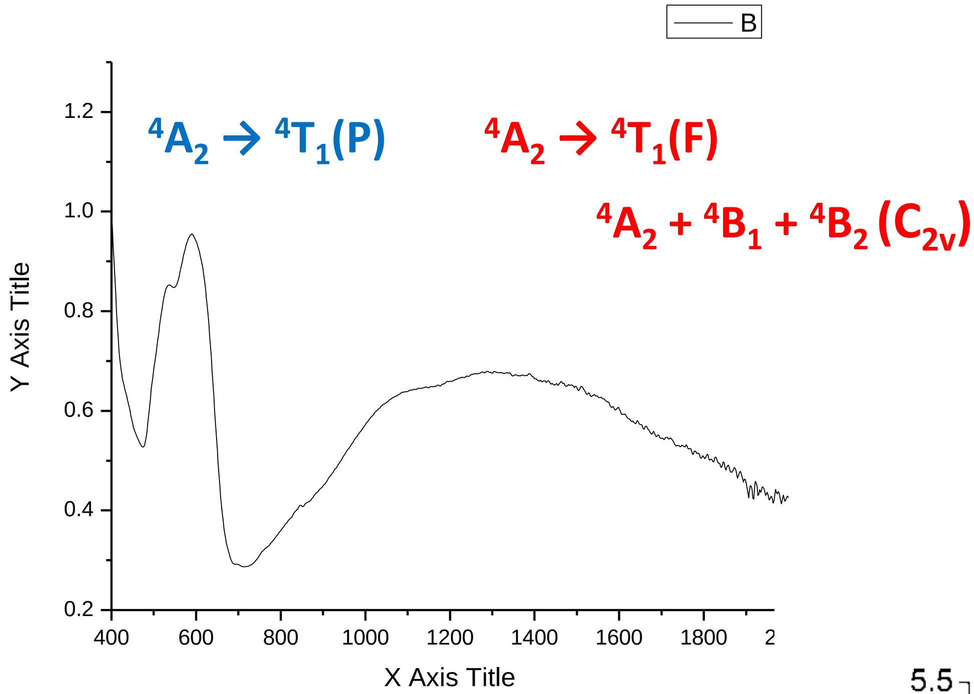


D. G. Branzea, L. Sorace, C. Maxim, M. Andruh, A. Caneschi, *Inorg. Chem.,* **2008**, *47*, 6590.

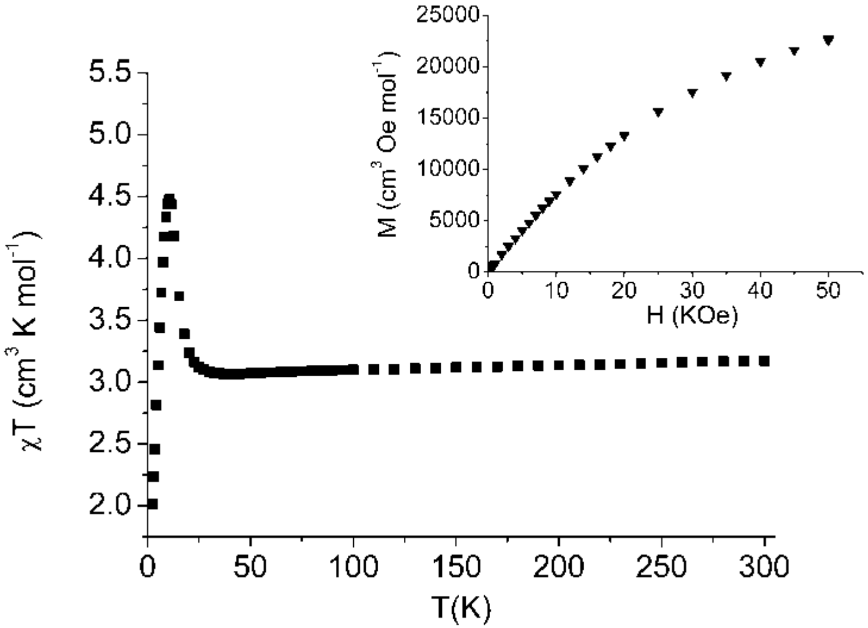


Ambiguous stereochemistry for the cobalt (II) ion:

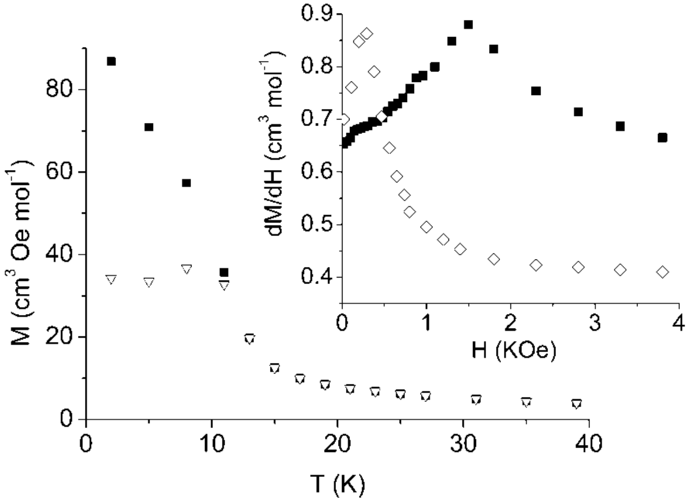
Co – O1 = 1.993 Co – O2 = 1.991; Co – N4A = 2.004; Co – N5a = 1.980
Co – O3 = 2.584; Co – O4 – 2.570 Å



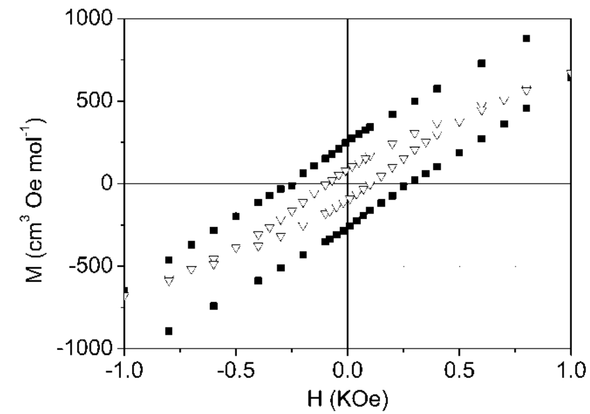
B
$^4A_2 \rightarrow {}^4T_1(P)$
$^4A_2 \rightarrow {}^4T_1(F)$
$^4A_2 + {}^4B_1 + {}^4B_2\ (C_{2v})$
Y Axis Title
X Axis Title



χT (cm³ K mol⁻¹)
T(K)
M (cm³ Oe mol⁻¹)
H (KOe)

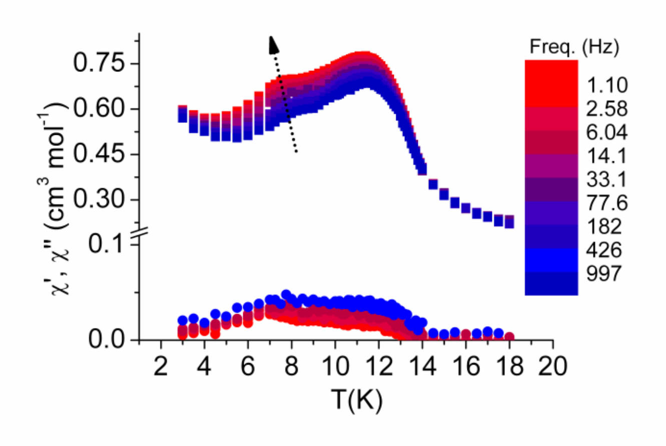


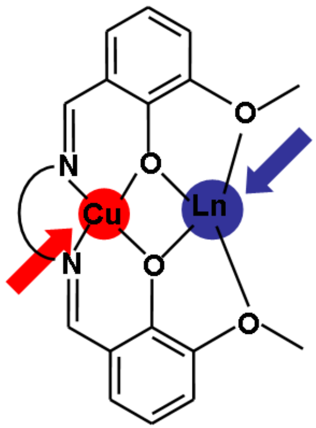
Zero field cooled (empty triangles) and field cooled (full squares) magnetization curves in a field of 50 Oe.

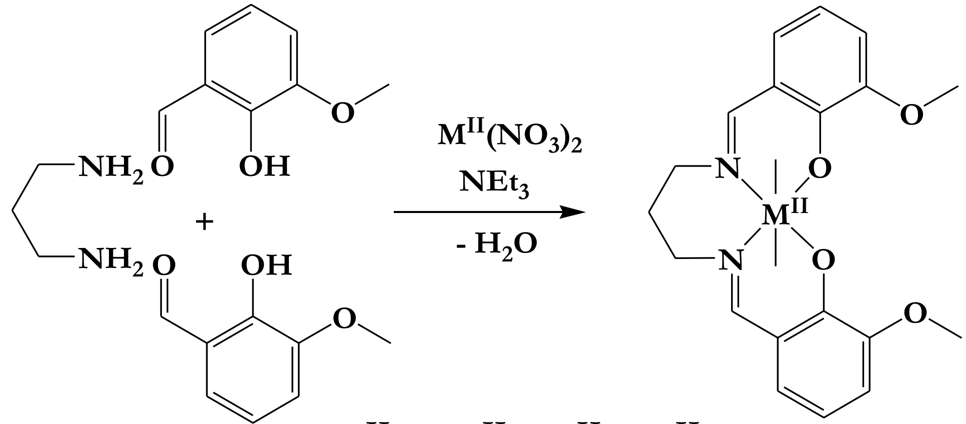


Magnetic hysteresis cycles at 1.9 K (full squares) and 5 K (empty triangles)

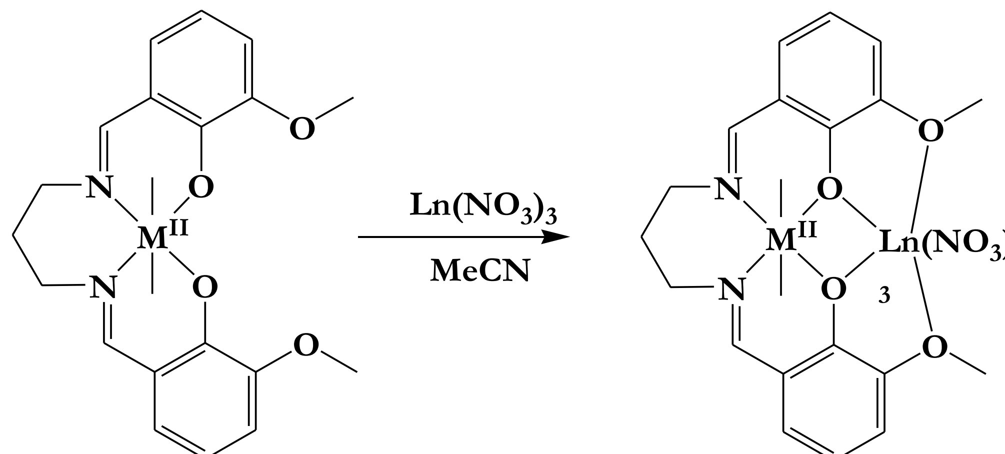
***Hc*= 100 Oe; *Mr*= 90 cm³ Oe mol⁻¹at 5 K;**
***Hc*= 250 Oe; *Mr*= 250 cm³ Oe mol⁻¹ at 1.9 K**





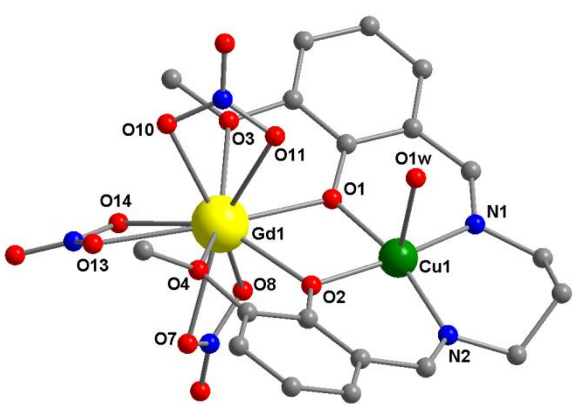


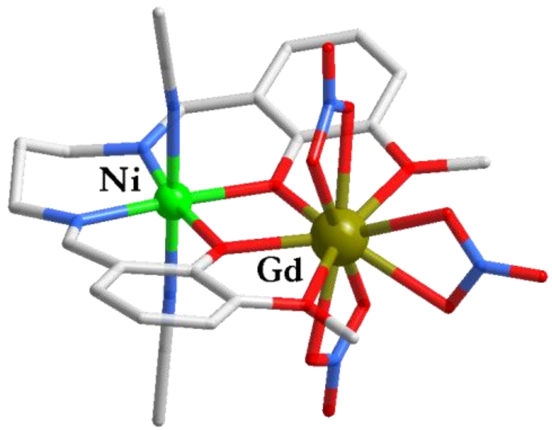
M^{II}= Cu^{II}, Ni^{II}, Zn^{II}

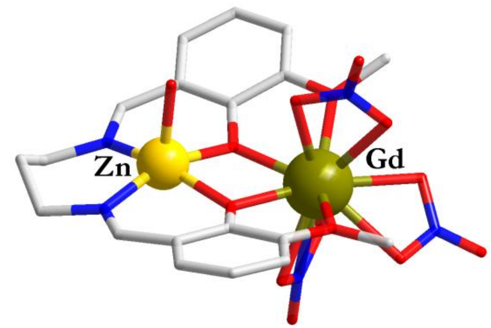


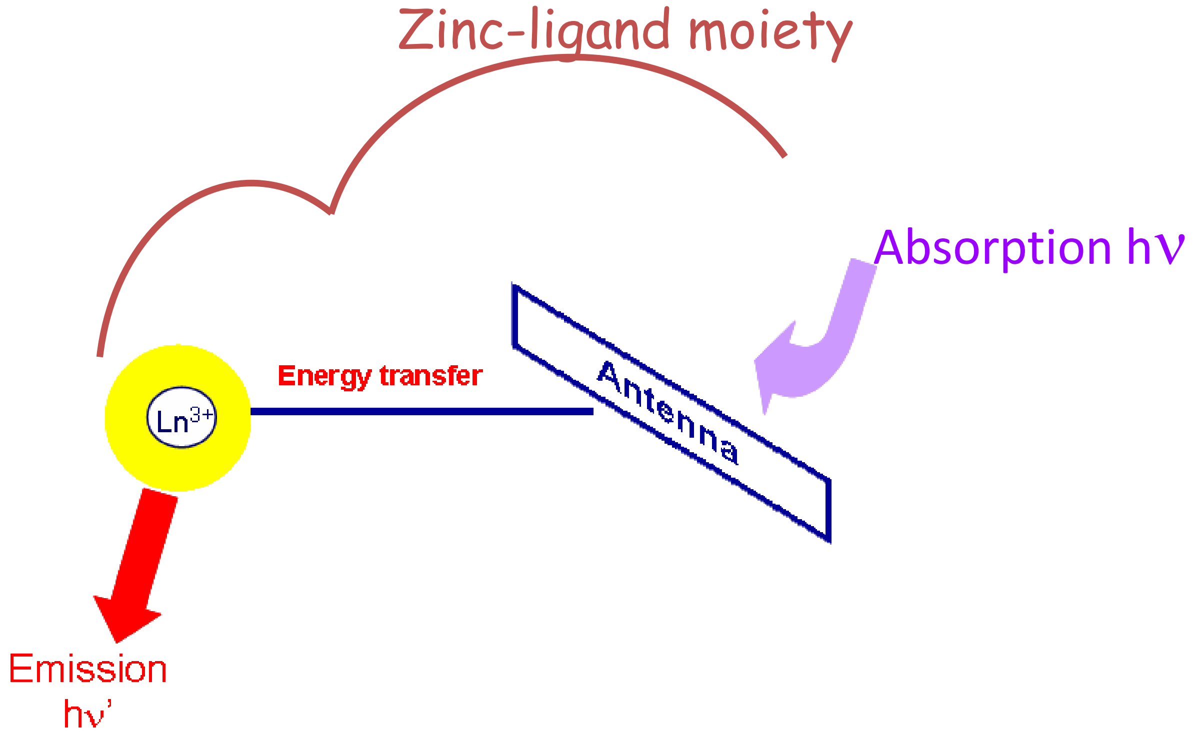
M^{II} = Cu^{II}, Ni^{II}, Zn^{II}

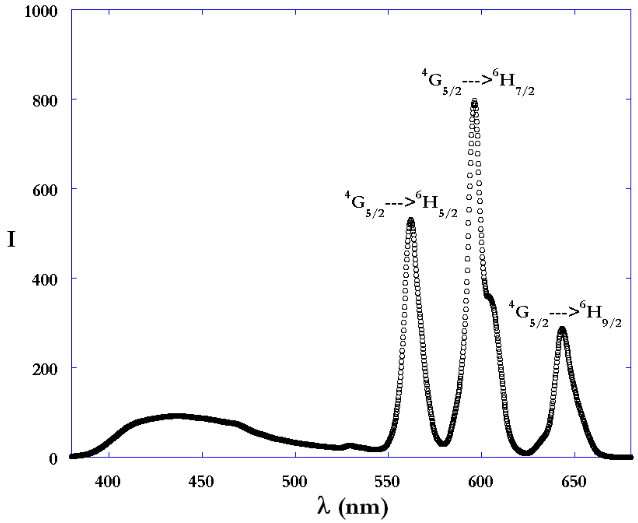
Complementary chemistries generated by [CuLn], [NiLn], and [ZnLn] nodes



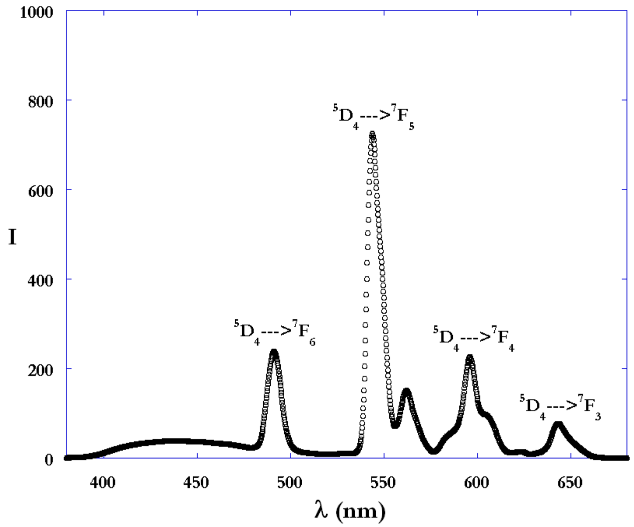


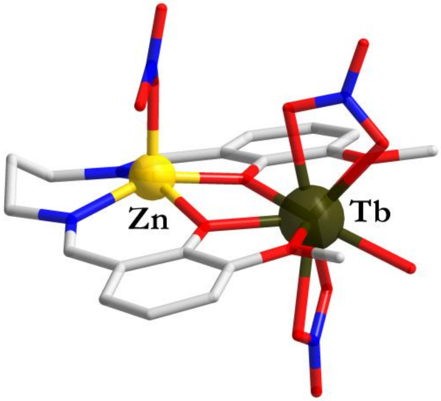



Zinc-ligand moiety
Absorption hν
Energy transfer
Ln3+
Antenna
Emission
hν'



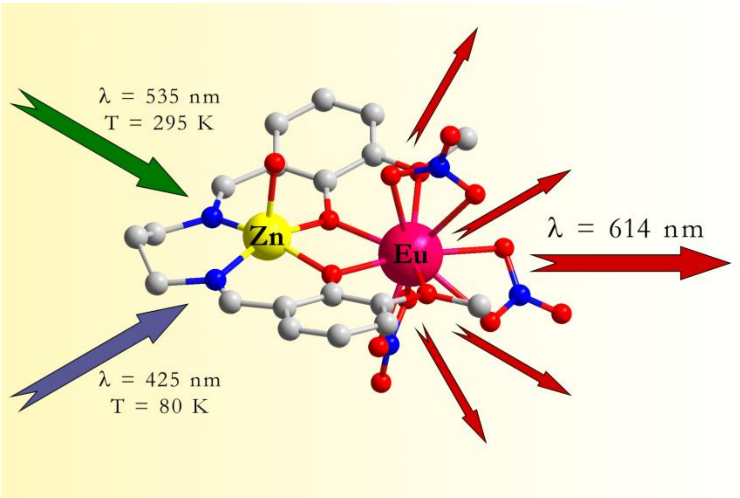
[Zn(valpn)Sm]

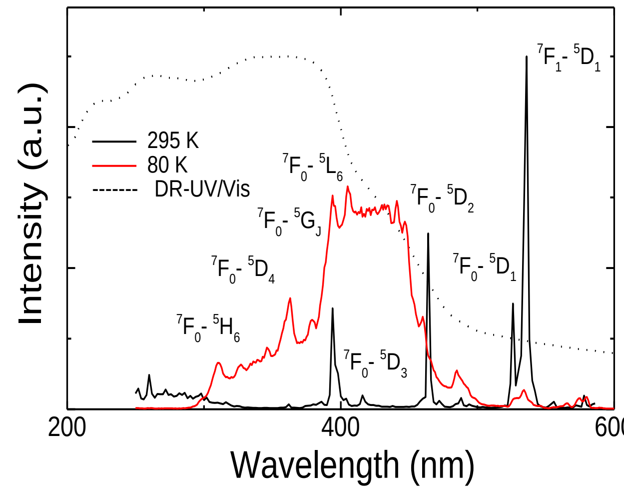




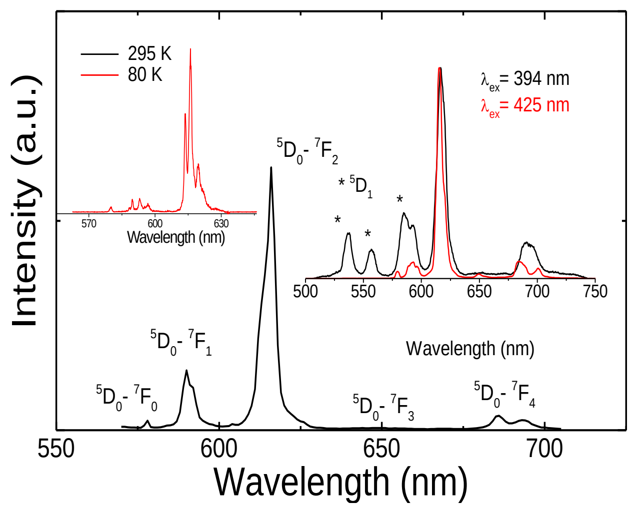
[Zn(valpn)Tb]

Temperature switching of LMCT role: From quenching to sensitivation of europium emission in the Zn^{II}-Eu^{III} Binuclear Complex

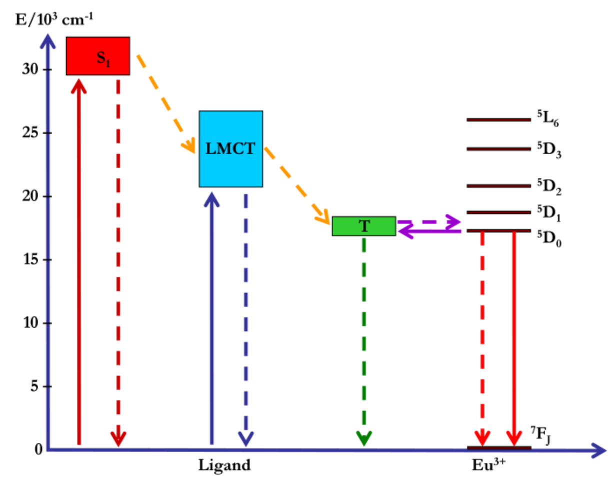




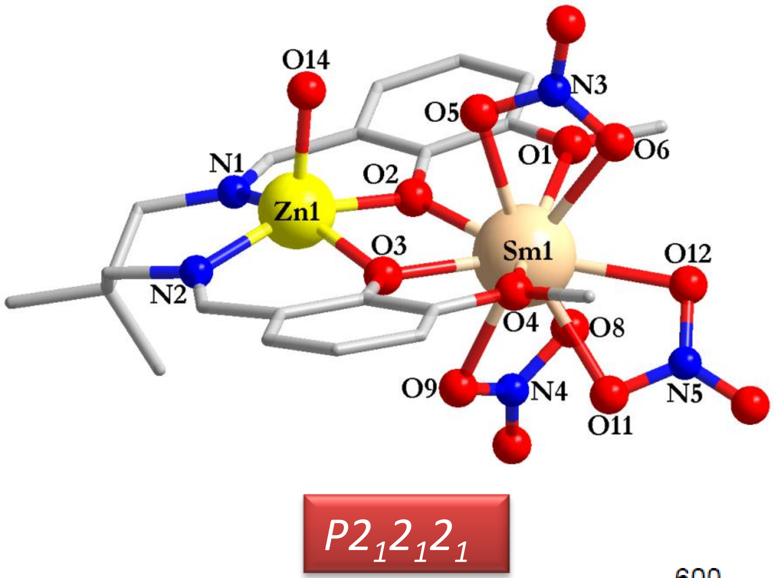
PL excitation spectra of $[Zn(valpn)Eu(NO_3)_3(H_2O)]$ measured at 295 and 80 K



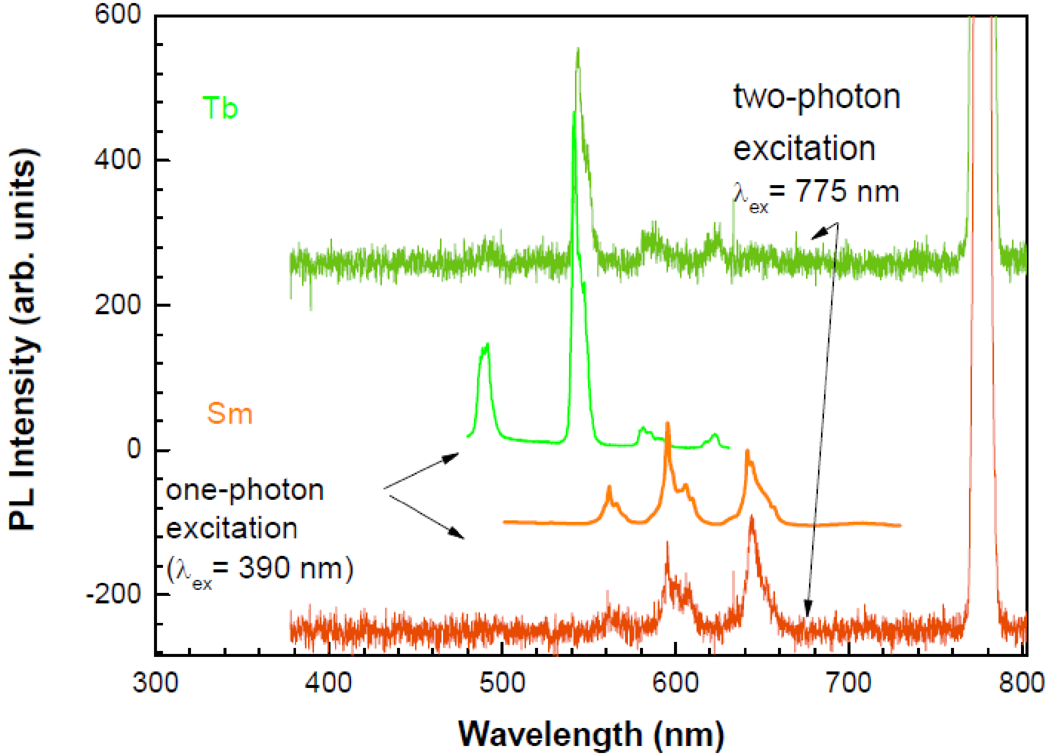
PL emission spectra of $[Zn(valpn)Eu(NO_3)_3(H_2O)]$ measured at: λ_{ex}= 535 nm (295 K); 394 and 425 nm



T. D. Pasatoiu, A. M. Madalan, M. U. Kumke, C. Tiseanu
M. Andruh, *Inorg. Chem.*, 2010, **49**, 2310



Two-photon induced emission in heterobimetallic Zn^{II}-Sm^{III} and Zn^{II}-Tb^{III} complexes

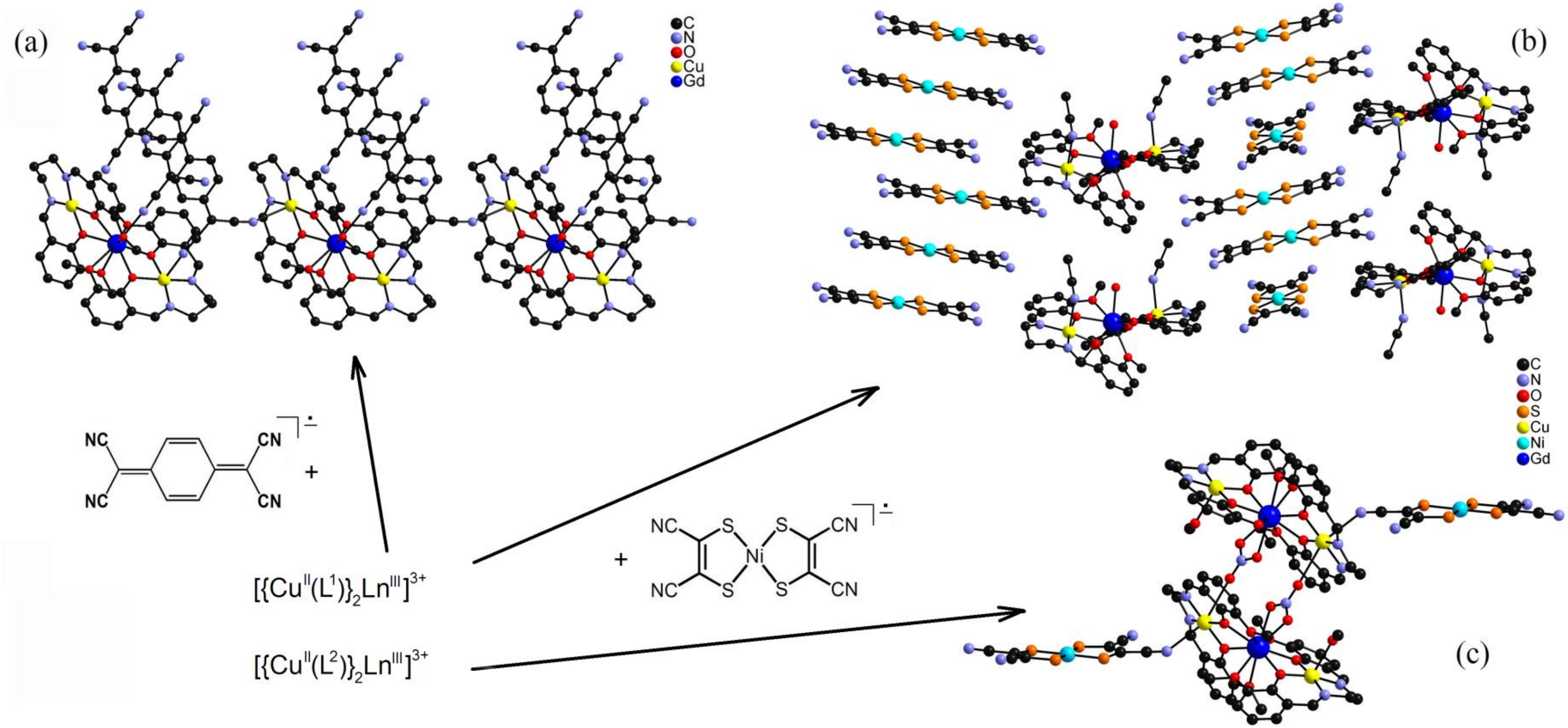


Third step: heterotrimetallics

HETEROSPIN COMPLEXES

2p-3d-4f
3p-3d-4f
3d-3d'-4f
3d-4d-4f
3d-5d-4f

2p-3d-4f



3p-3d-4f

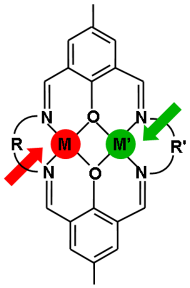
A.M. Madalan, N. Avarvari, M. Fourmigué, R. Clérac, L. F. Chibotaru, S. Clima, M. Andruh, *Inorg. Chem.* **2008**, *47*, 950;
A. M. Madalan, H. W. Roesky, M. Andruh, M. Noltemeyer, N. Stanica *Chem. Commun.* **2002**, 1638.

A rational synthetic route leading to heterotrimetallic complexes

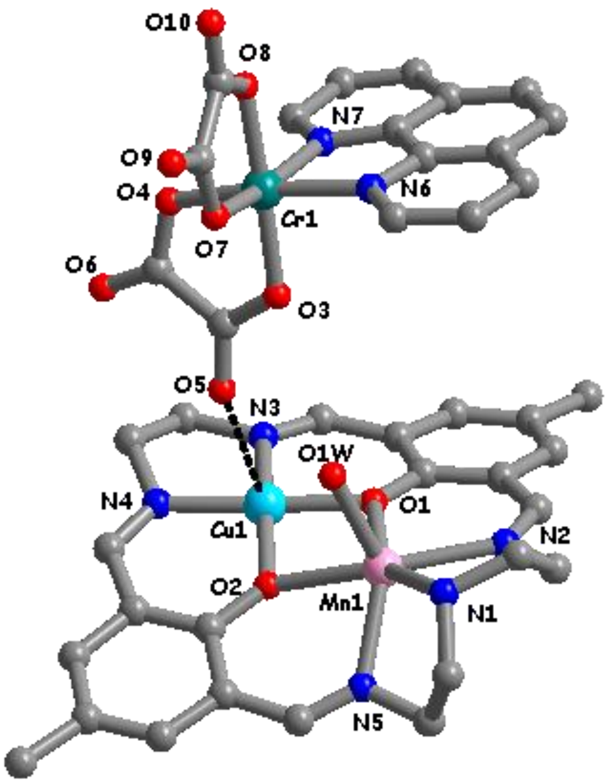
- Binuclear complexes + metalloligands

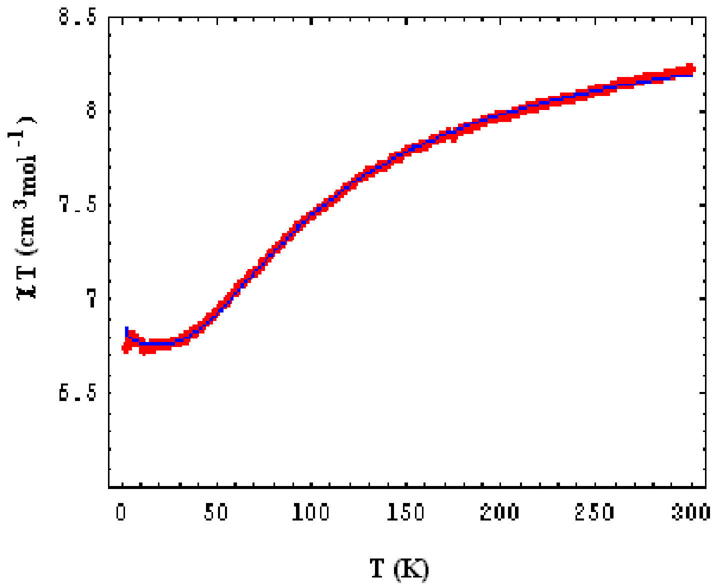
Useful metalloligands

- $[M(CN)_6]^{n-}$
- $[M(CN)_8]^{n-}$
- $[M(C_2O_4)_3]^{3-}$
- $[Cr(AA)(C_2O_4)_2]^-$ (AA = bipy; phen)
- $[Cr(NCS)_4L_2]^-$

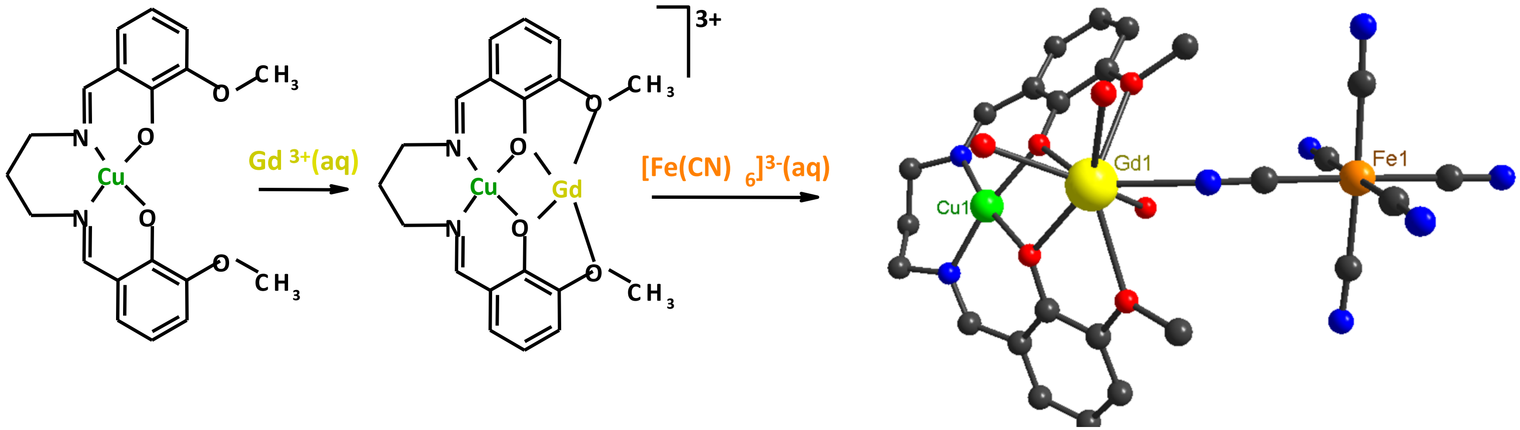


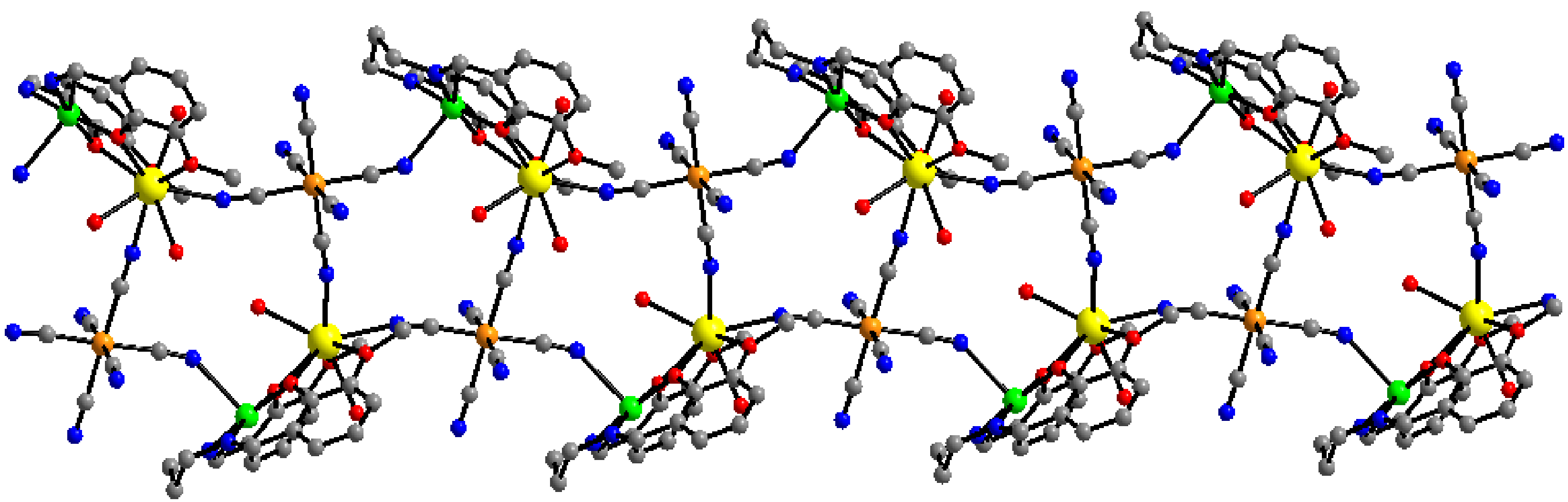
A heterotrimetallic complex





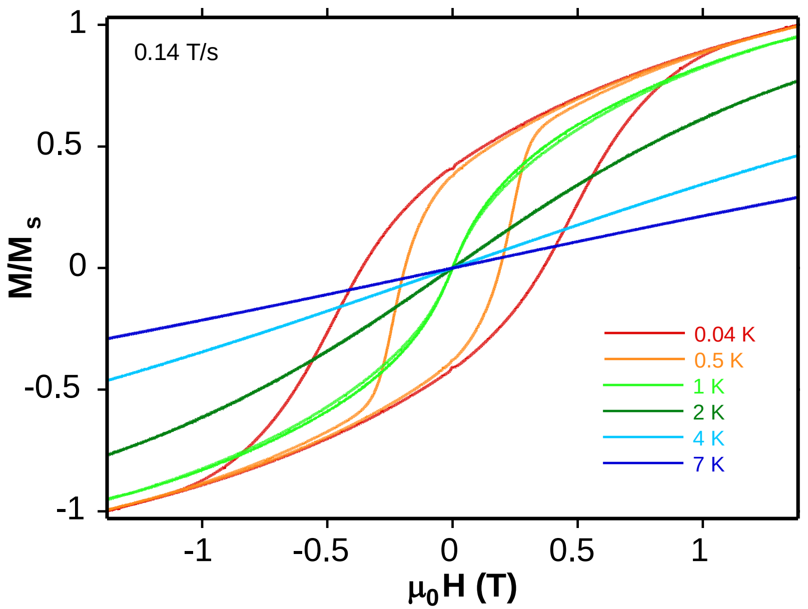
$J_{MnCu} = -39\ cm^{-1}$

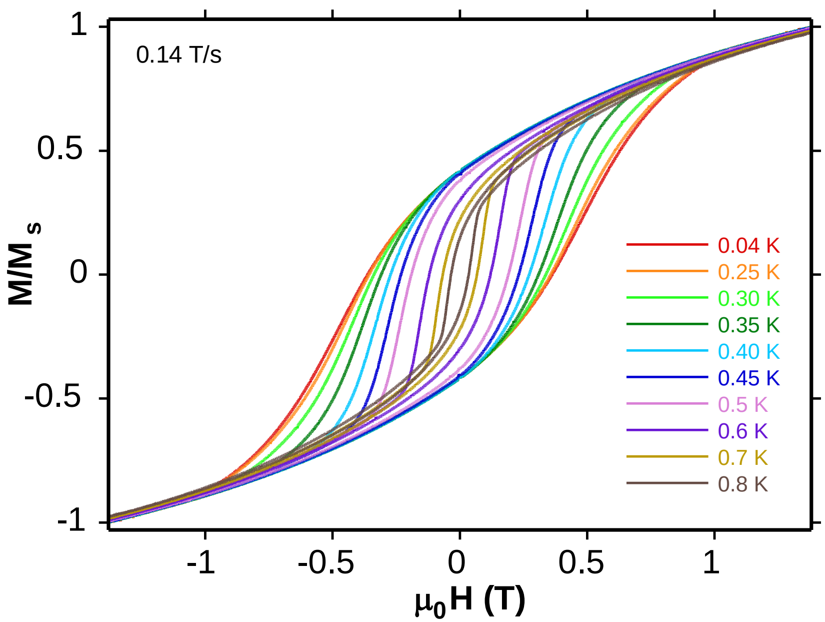




R. Gheorghe, M. Andruh, J.-P. Costes, B. Donnadieu, *Chem. Commun.*, **2003**, 2778
R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu, S. Shova, *Chem. – Eur. J.*, **2006**, 12, 187.

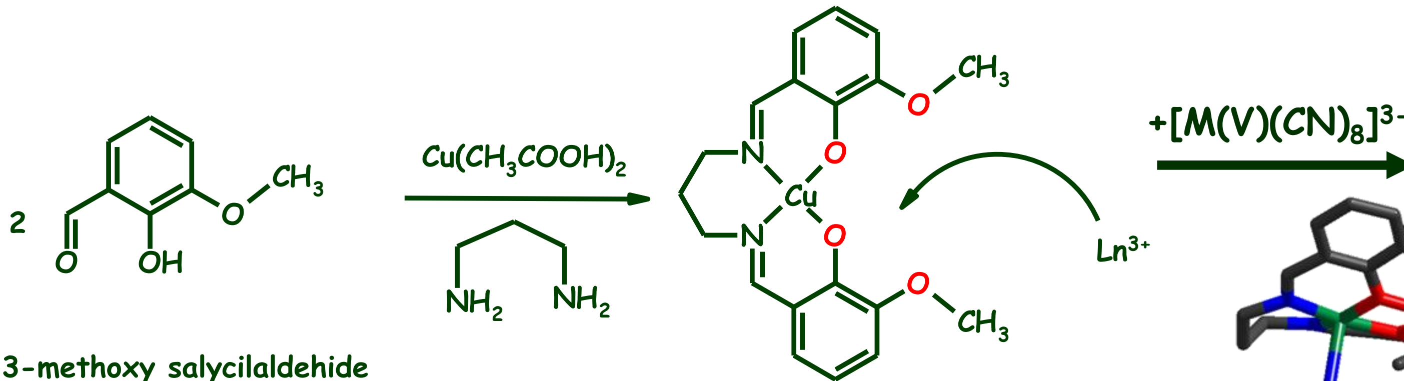
[Cu(II)Tb(III)Fe(III)] – a Single Chain Magnet

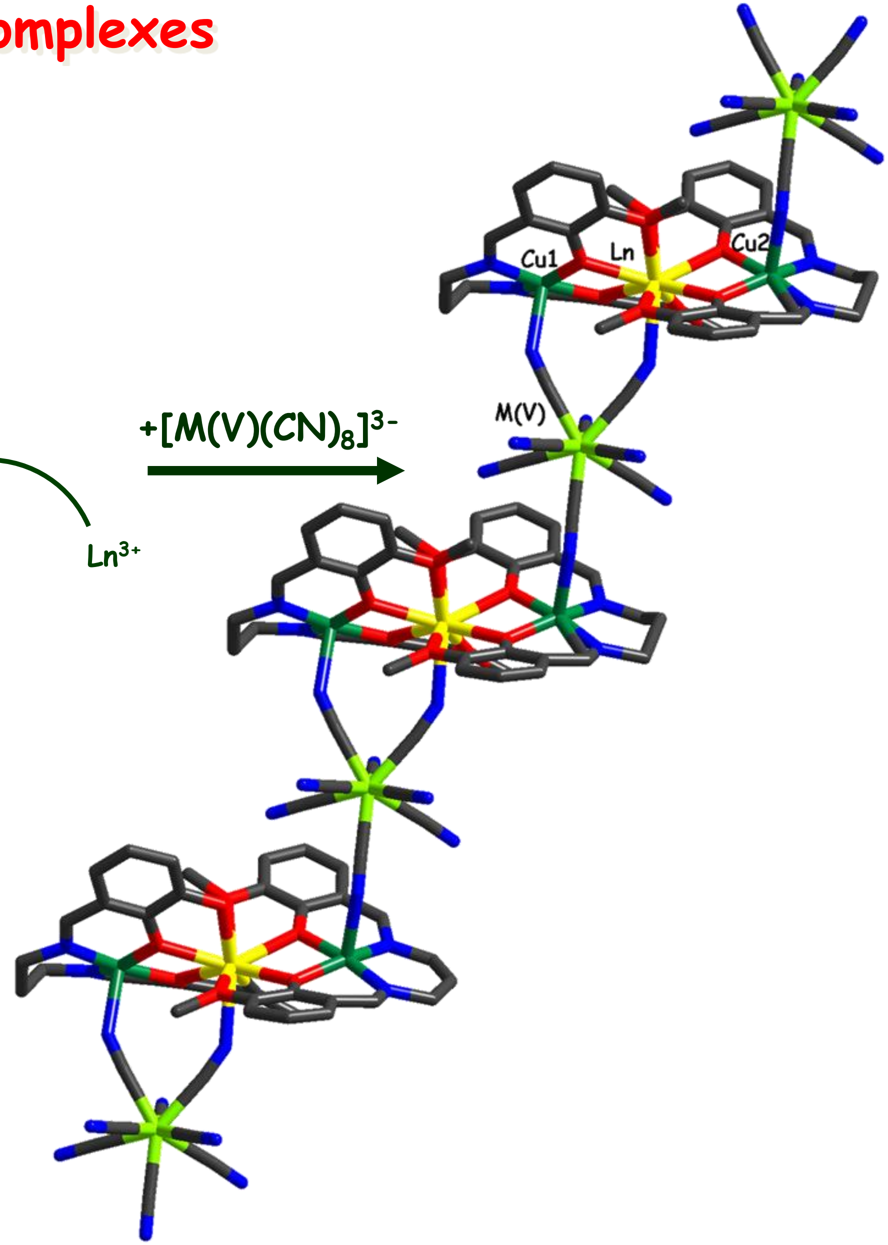




R. Gheorghe, A. M. Madalan, J.-P. Costes, W. Wernsdorfer, M. Andruh, *Dalton Trans.*, **2010**, *39*, 4734.

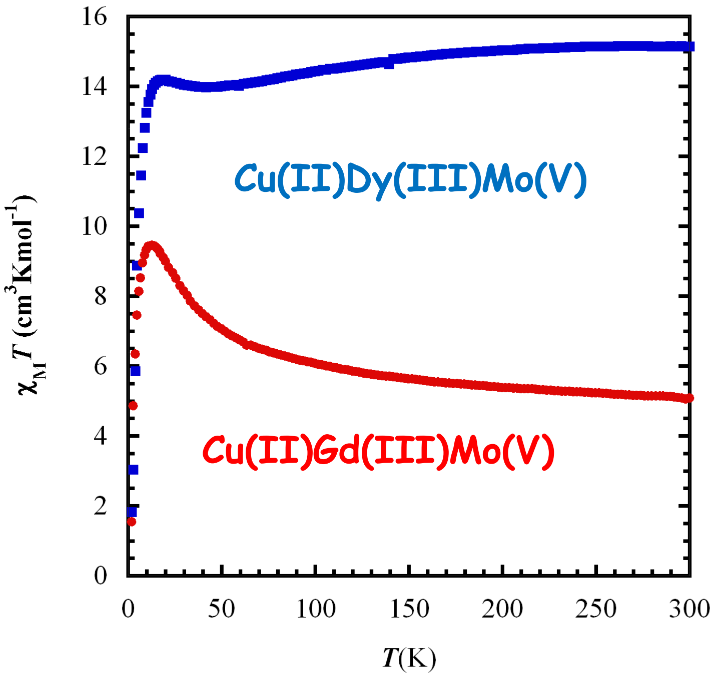
3d-4f-4d(5d) heterotrimetallic complexes

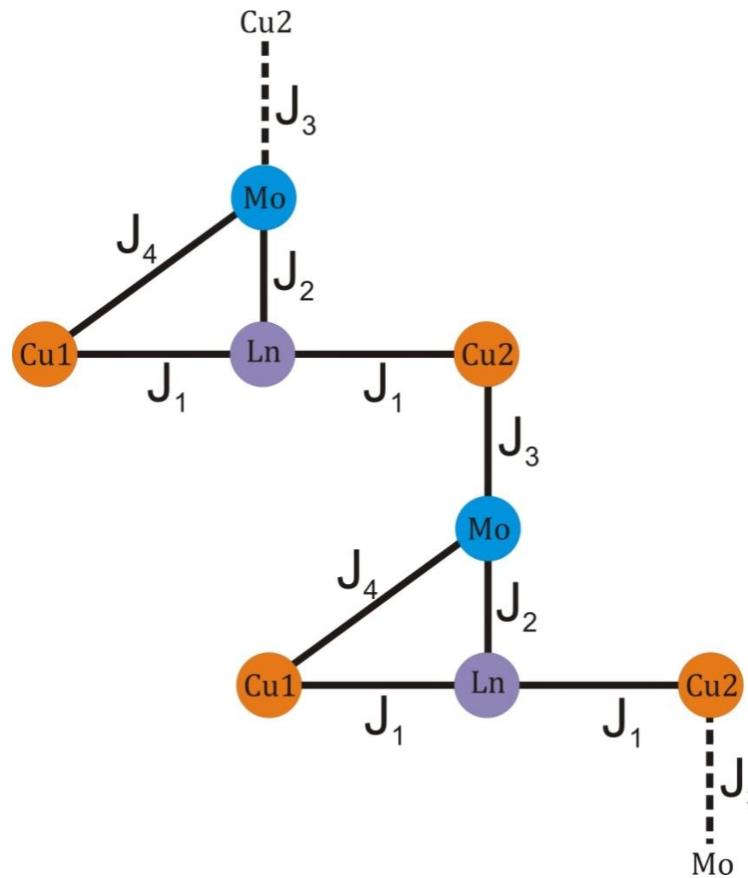




M(V) = Mo(V), W(V)

D. Visinescu, A. M. Madalan, M. Andruh, C. Duhayon, J.-P. Sutter, L. Ungur, W. Van den Heuvel, L. F. Chibotaru, *Chem.-Eur. J.*, **2009**, *15*, 11808.

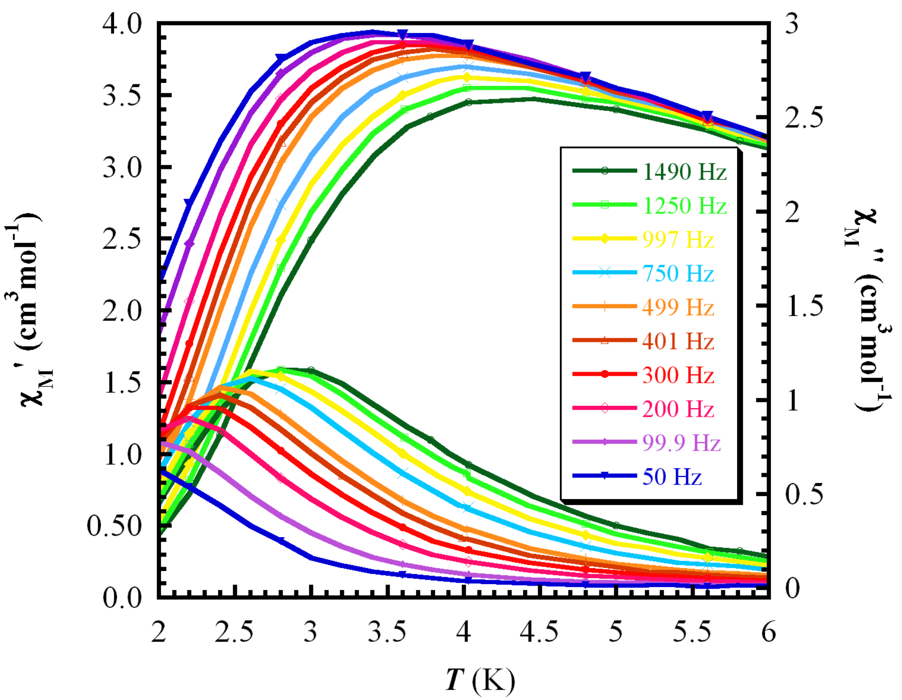


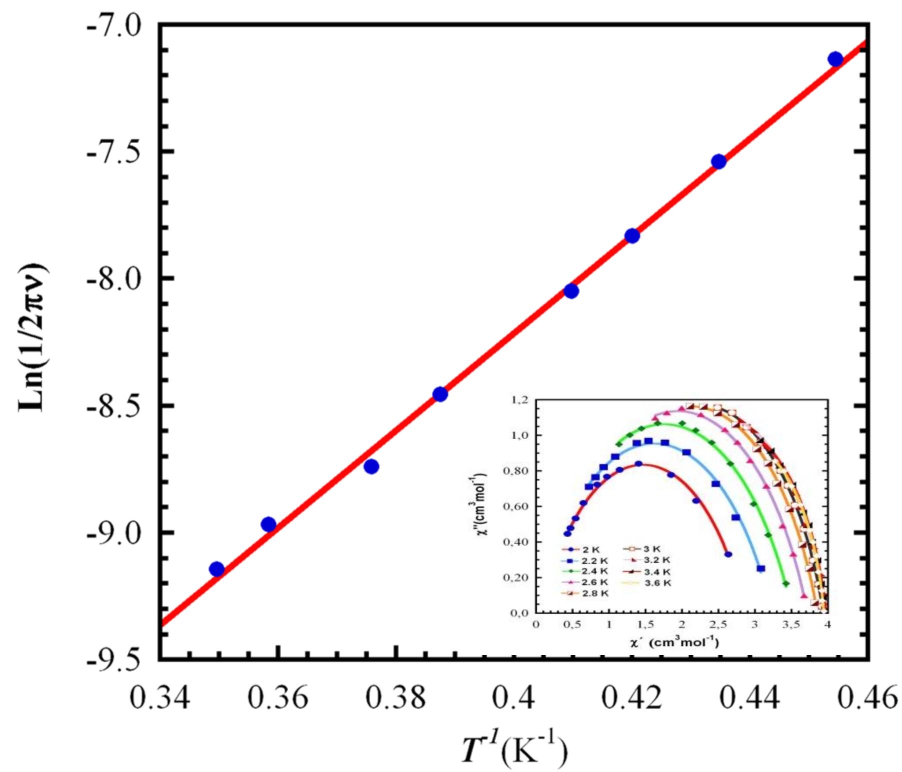


J(Gd-Cu1) = J(Gd-Cu2) = 5 cm^{-1} and J(Gd-Mo) =-1 cm^{-1}
J(Mo-Cu1) = -3 cm^{-1}
J(Mo-Cu2) =7 cm^{-1}

First heterotrimetallic 3d-4d-4fSingle Chain Magnet

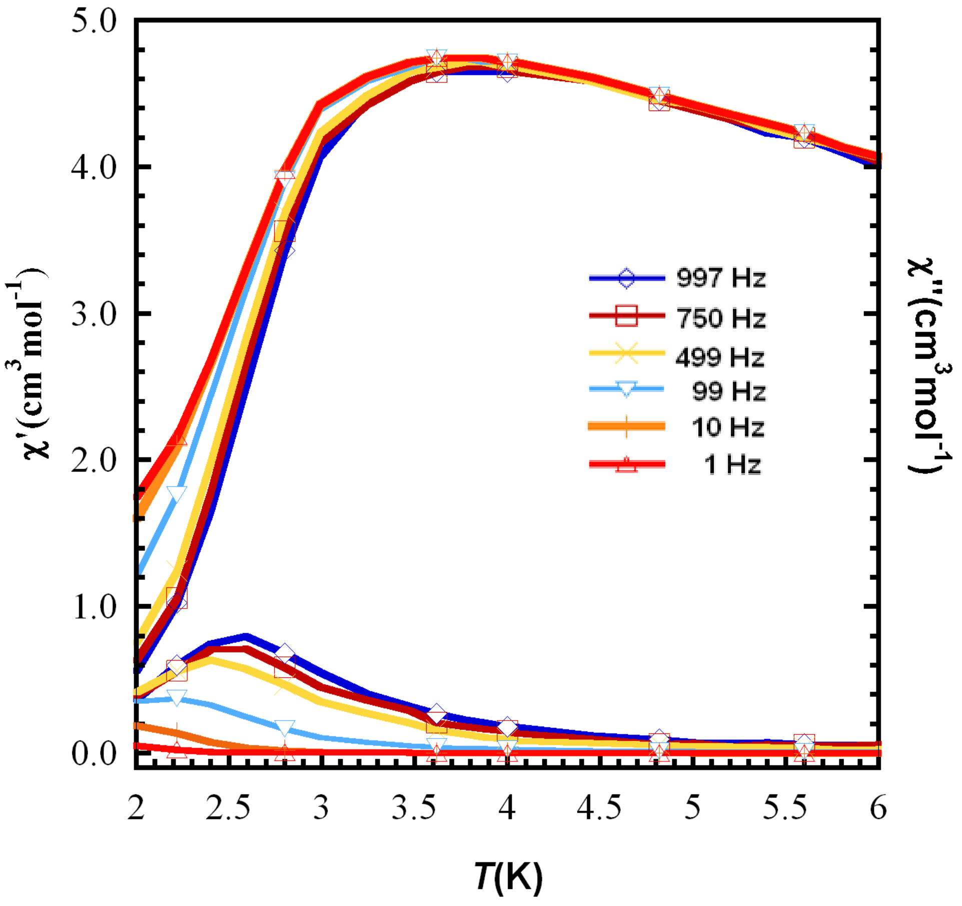
Cu(II)Dy(III)Mo(V)



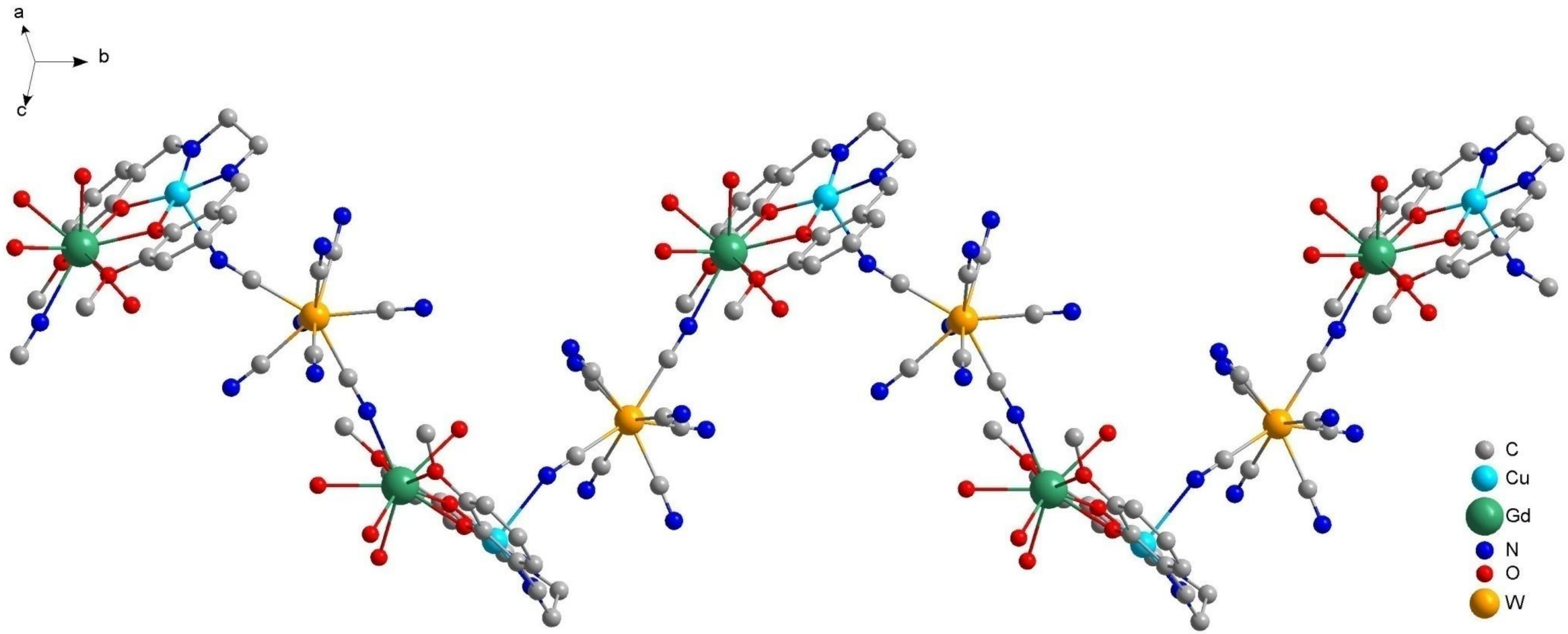


τ_0 = 1.28·10^{-7} s; U_{eff}/k_B= 19.1 K

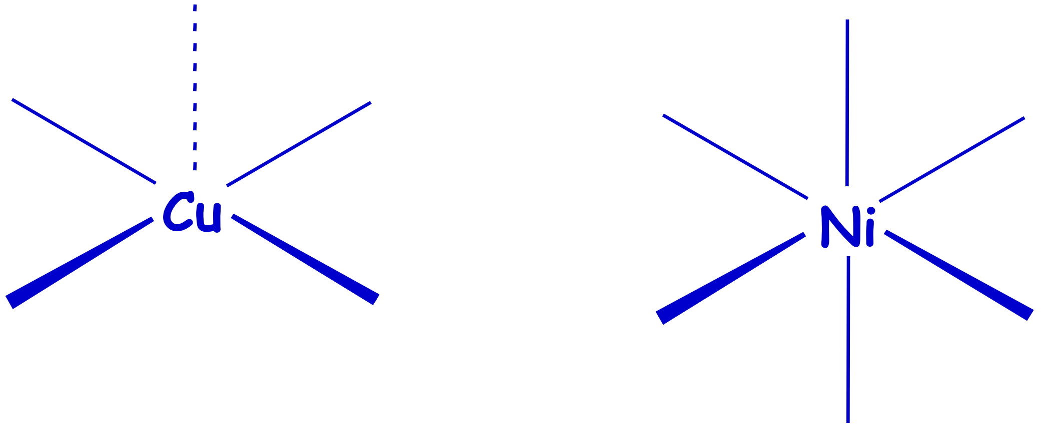
…and the Cu(II)Dy(III)W(V) derivative:



Slight modification of the diamine induces a different network topology

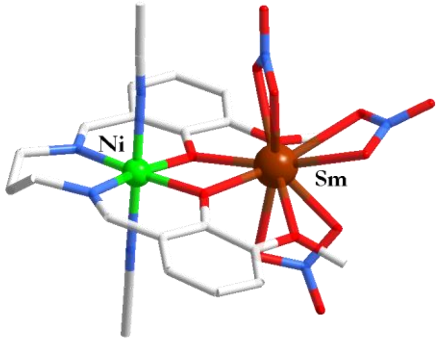


The apical interaction with the copper(II) ion precludes the (strong) coupling of the three metal ions

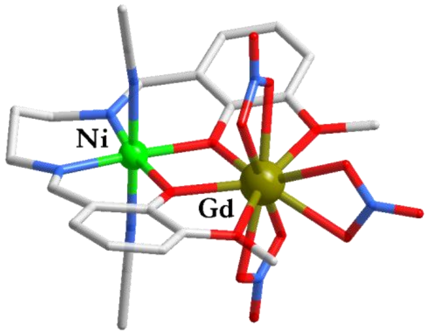


$(d_{x^2-y^2})^1$

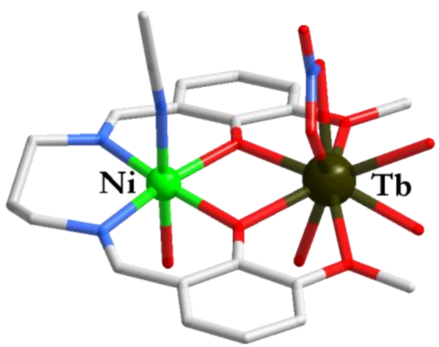
$(d_{x^2-y^2})^1(d_{z^2})^1$



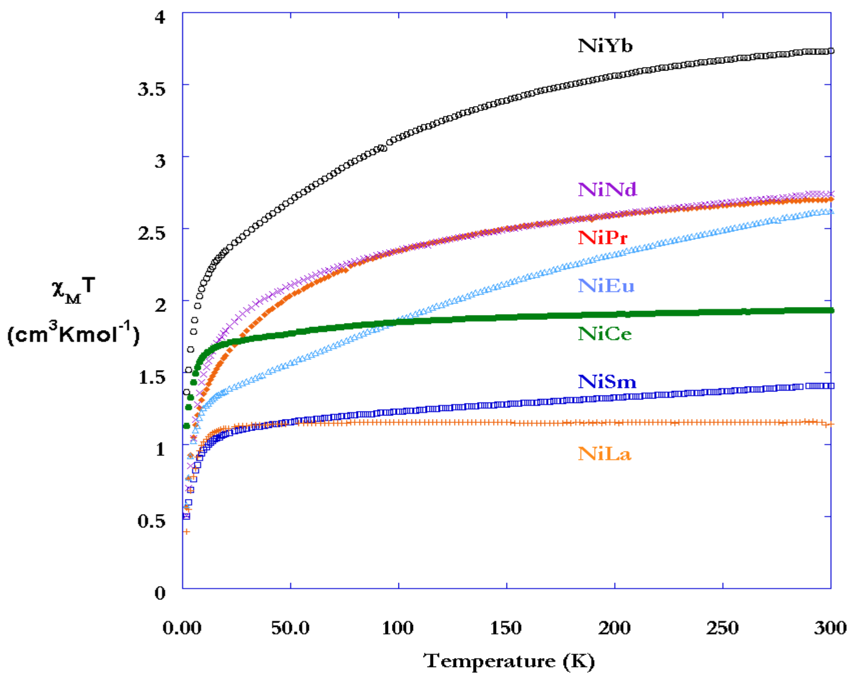
$[Ni(valpn)Ln^{III}(NO_3)_3(CH_3CN)_2](CH_3CN)(H_2O)$
$(Ln^{III} = Pr^{III}, Nd^{III}, Sm^{III})$



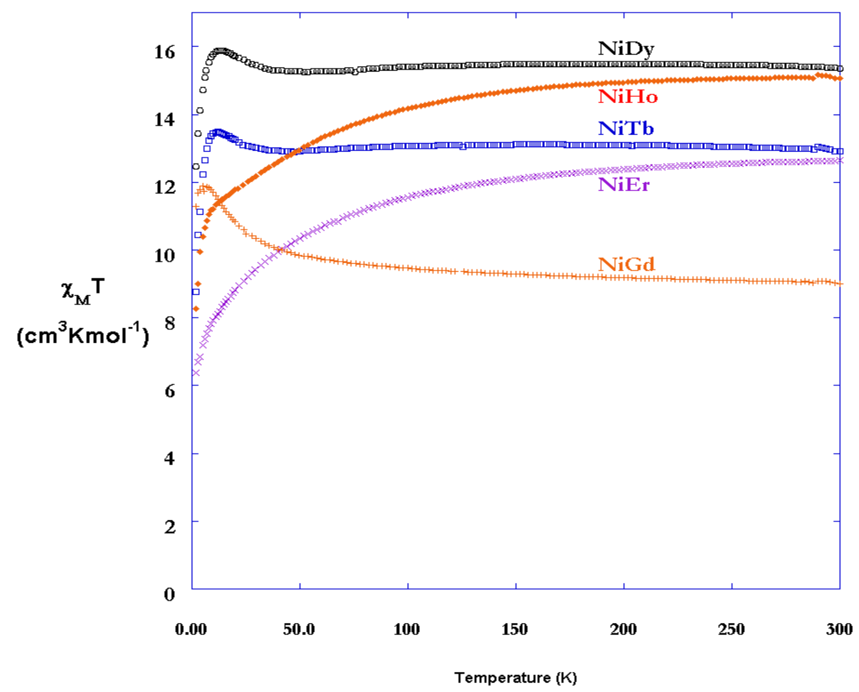
$[Ni(valpn)Ln^{III}(NO_3)_3(CH_3CN)_2](CH_3CN)$
$(Ln^{III} = Eu^{III}, Gd^{III}, Dy^{III})$



$[Ni(valpn)Ln^{III}(NO_3)(CH_3CN)(H_2O)_4](NO_3)_2(H_2O)$
$(Ln^{III} = Tb^{III})$

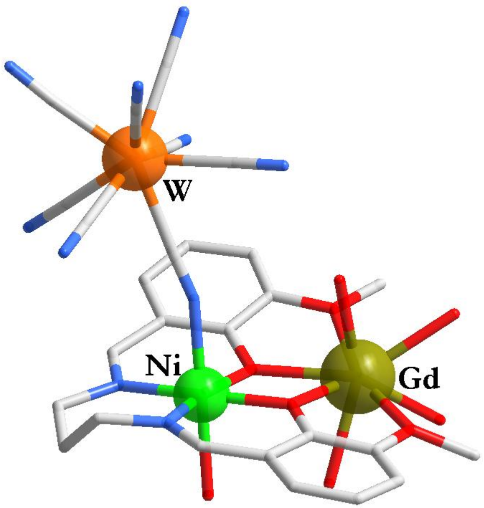


NiYb
NiNd
NiPr
NiEu
NiCe
NiSm
NiLa
$\chi_M T$ (cm^3Kmol^{-1})
0
0.5
1
1.5
2
2.5
3
3.5
4
0.00
50.0
100
150
200
250
300
Temperature (K)

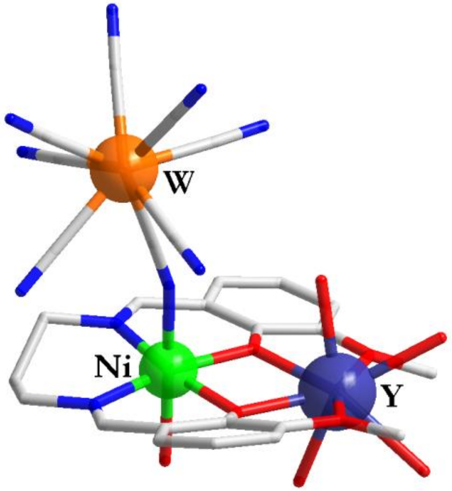


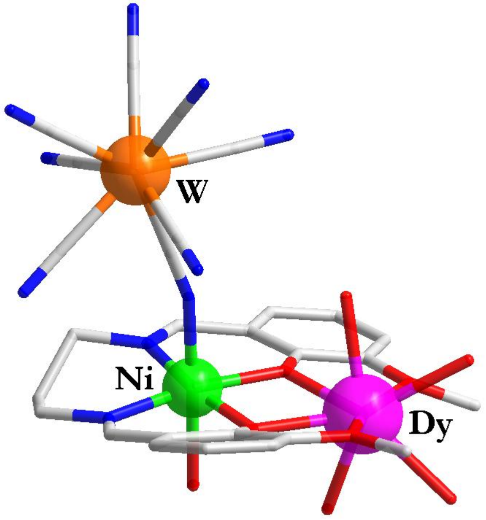
NiDy
NiHo
NiTb
NiEr
NiGd
$\chi_M T$ (cm^3Kmol^{-1})
0
2
4
6
8
10
12
14
16
0.00
50.0
100
150
200
250
300
Temperature (K)

Novel high-spin heterotrimetallics

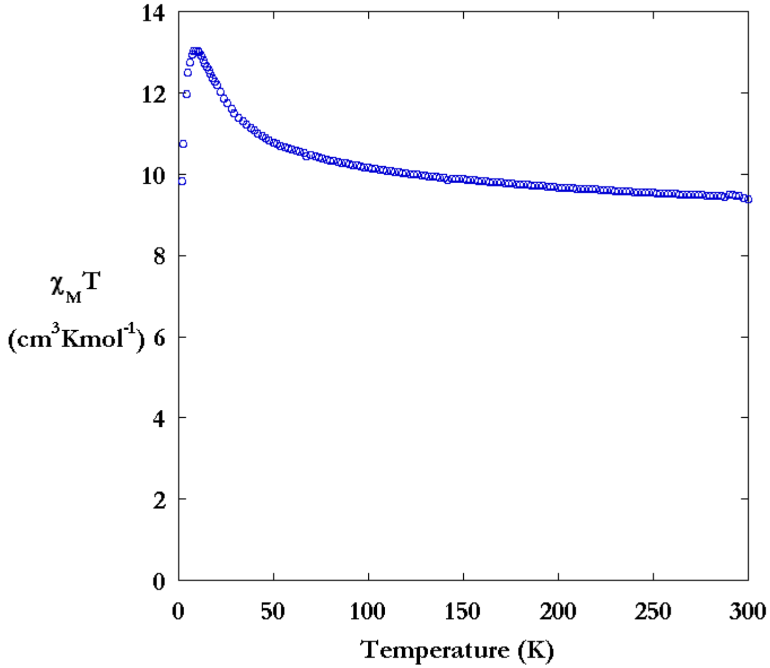


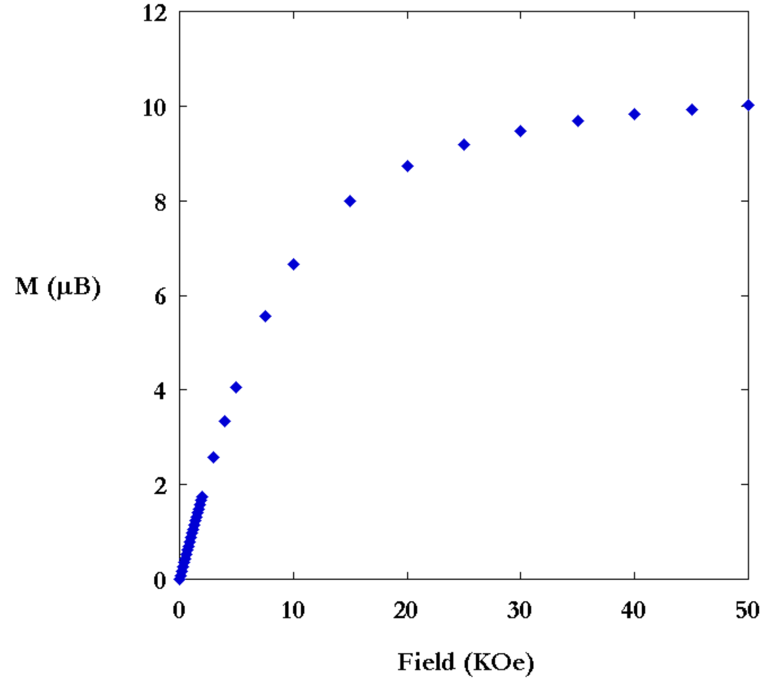
isostructural





$[Ni(valpn)Gd(H_2O)_5W(CN)_8](H_2O)_2$

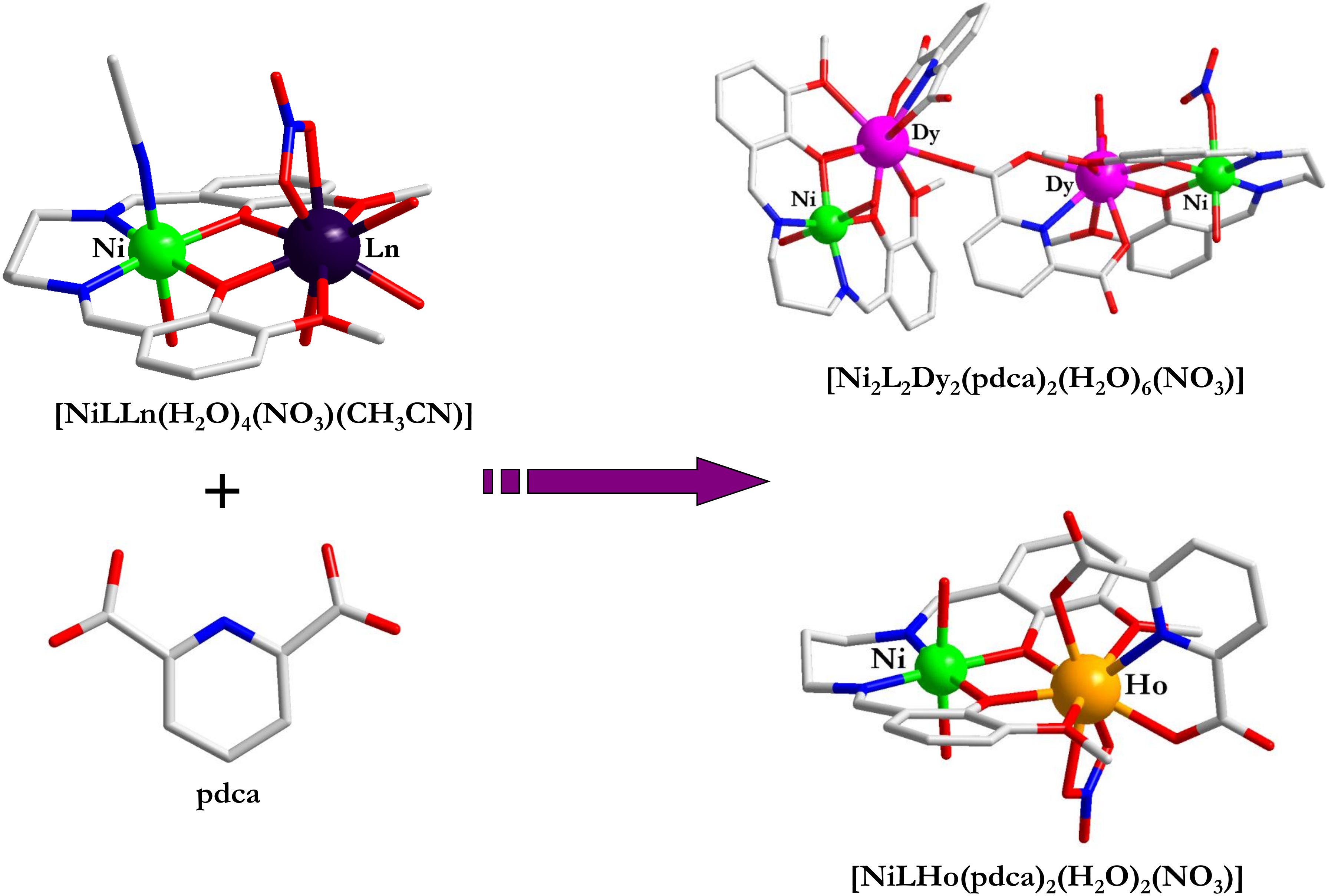




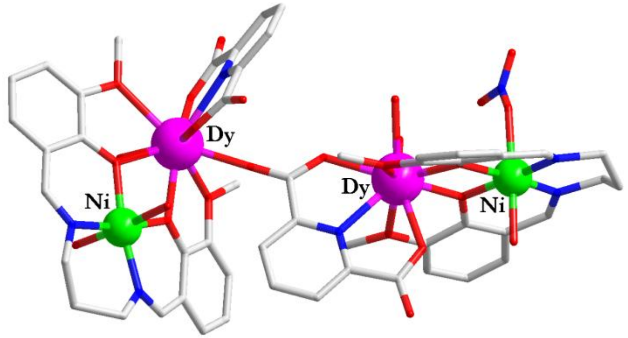
J_{NiGd} = +4.1 cm^{-1}; J_{NiW} = +44.4 cm^{-1}

D. Visinescu, J.-P. Sutter et al., *J. Am. Chem. Soc.* **2006**, *128*, 10202: J_{NiW} = +37.3 cm^{-1}

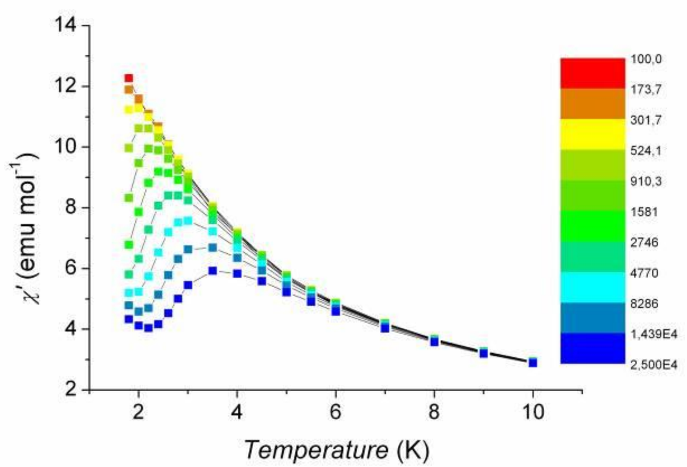
Organizing SMMs into well-defined architectures

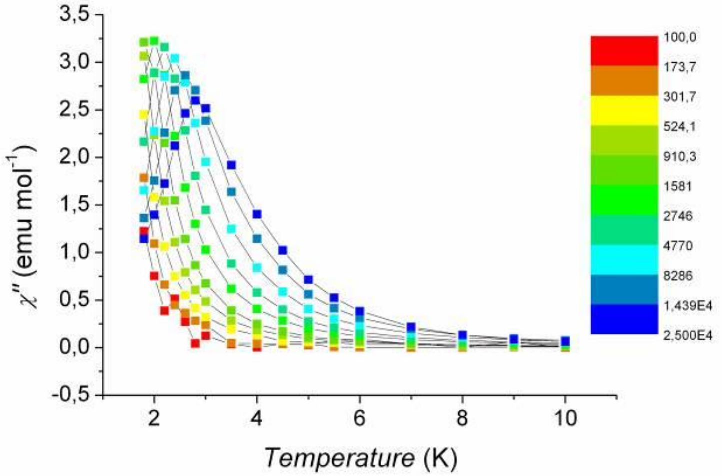


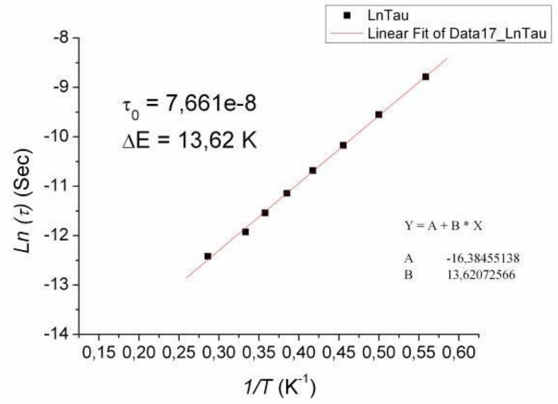
T. D. Pasatoiu, M. Etienne, A. M. Madalan, M. Andruh, R. Sessoli, *Dalton Trans.*, **2010**, *39*, 4802.



A dimer of SMMs

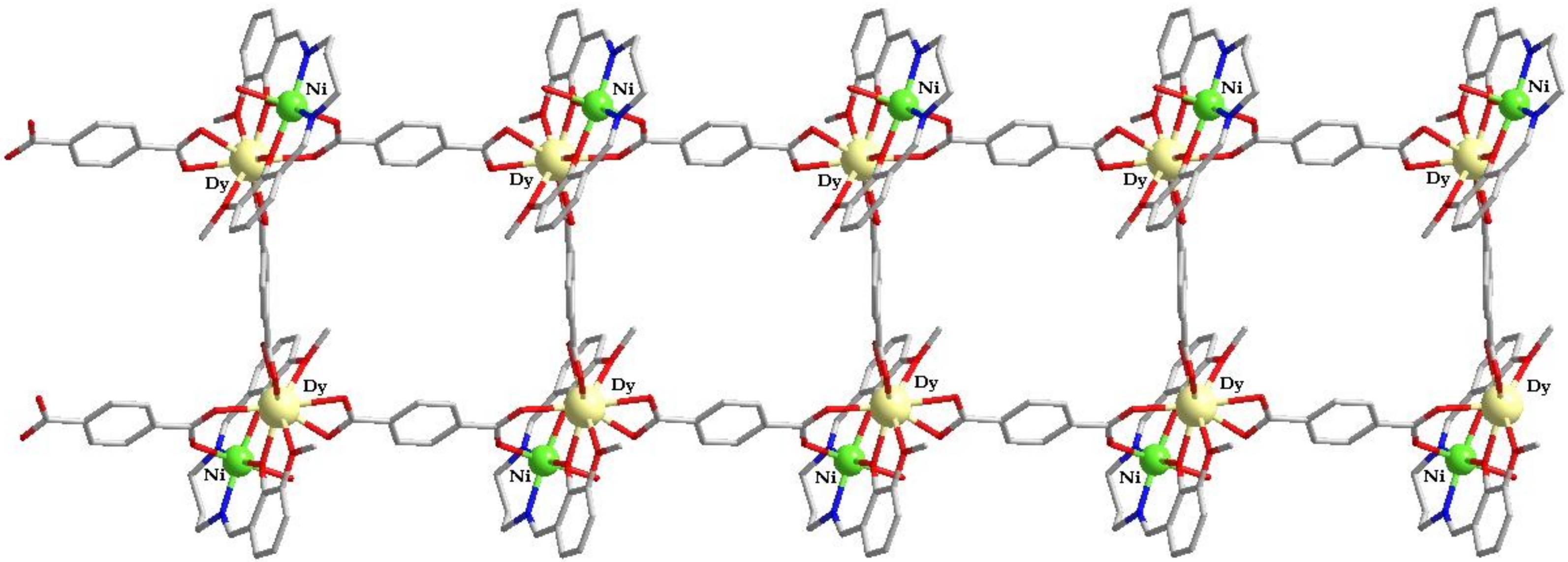




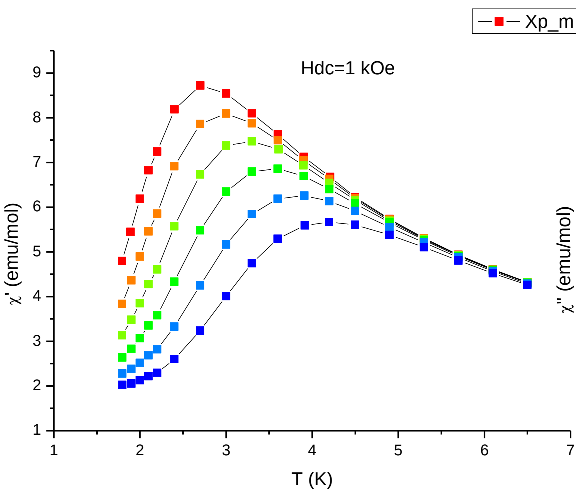


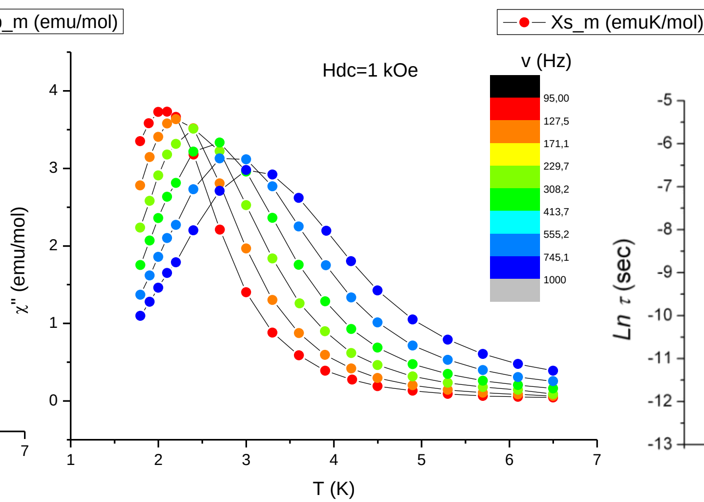
Static field: 750 Oe

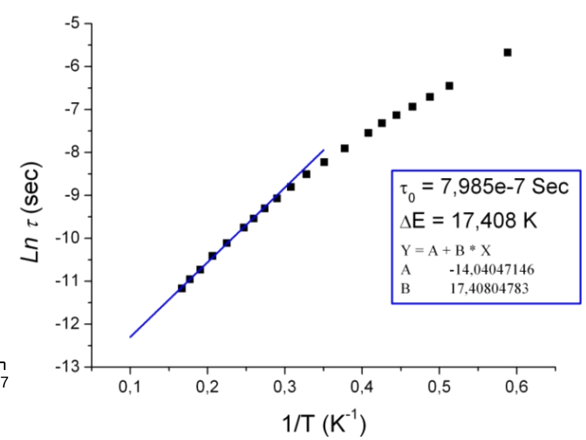
...and chains of SMMs



Static field: 1000 Oe



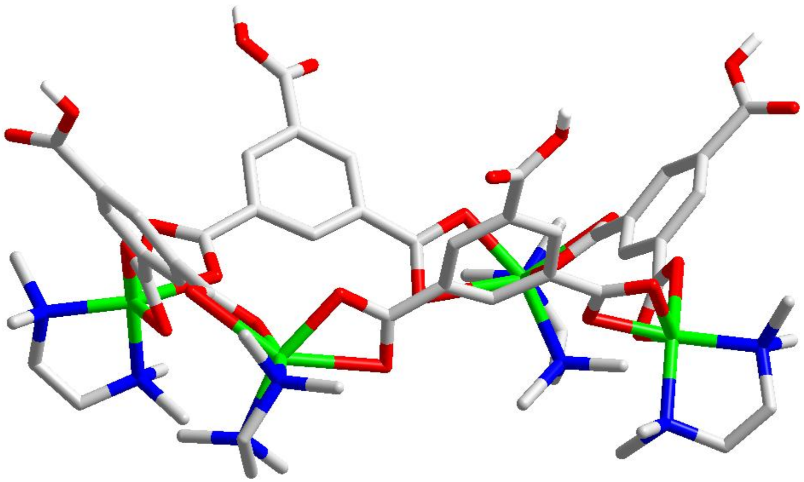


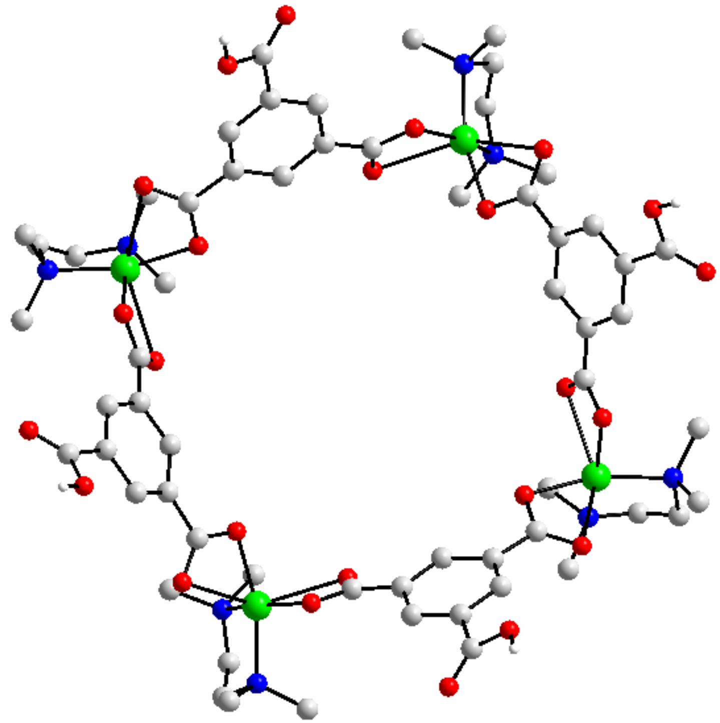


…and back to homometallics

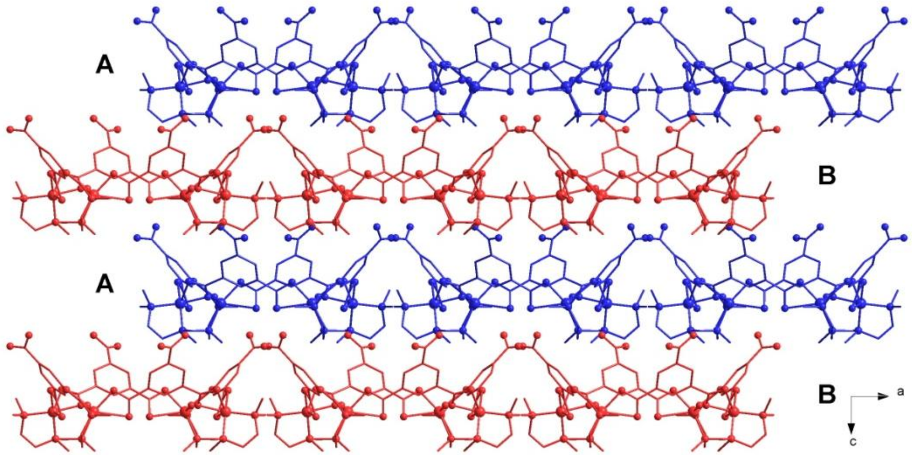
Another way toward porous crystals

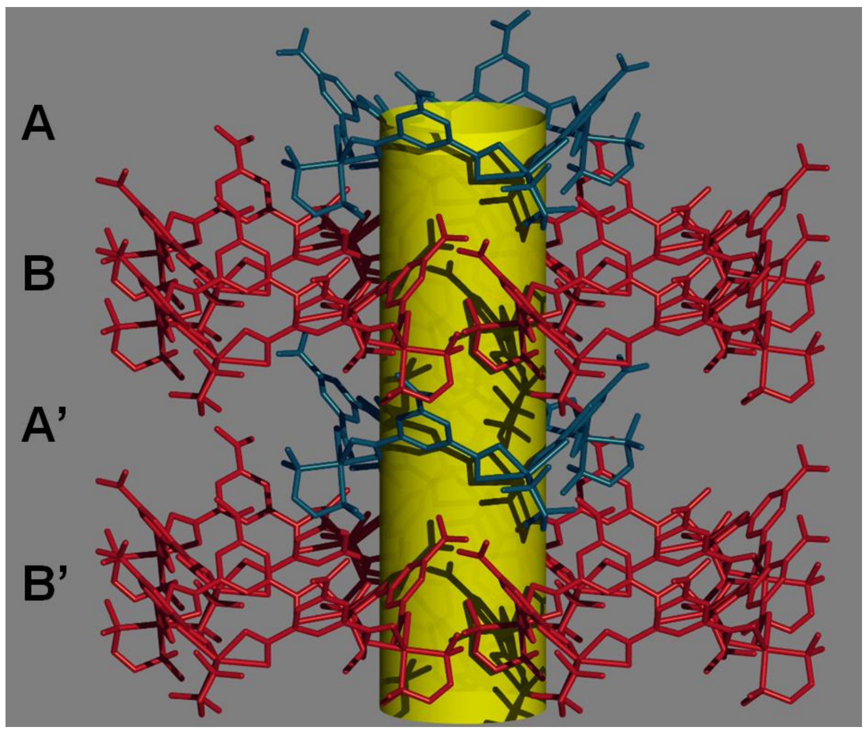
A metallacalixarene

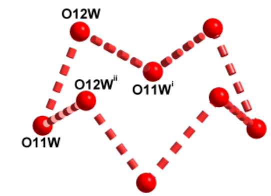




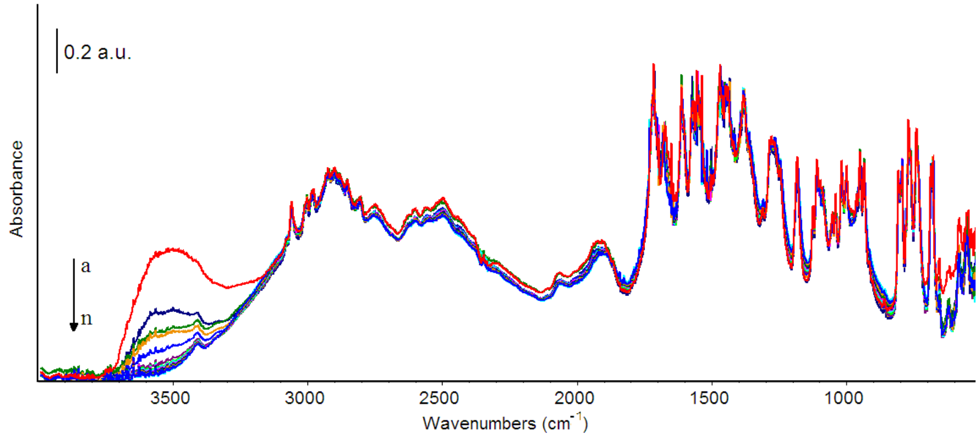
C. D. Ene, A. M. Madalan, C. Maxim, B. Jurca, N. Avarvari, M. Andruh, *J. Am. Chem. Soc.,* **2009,** 131, 4586.

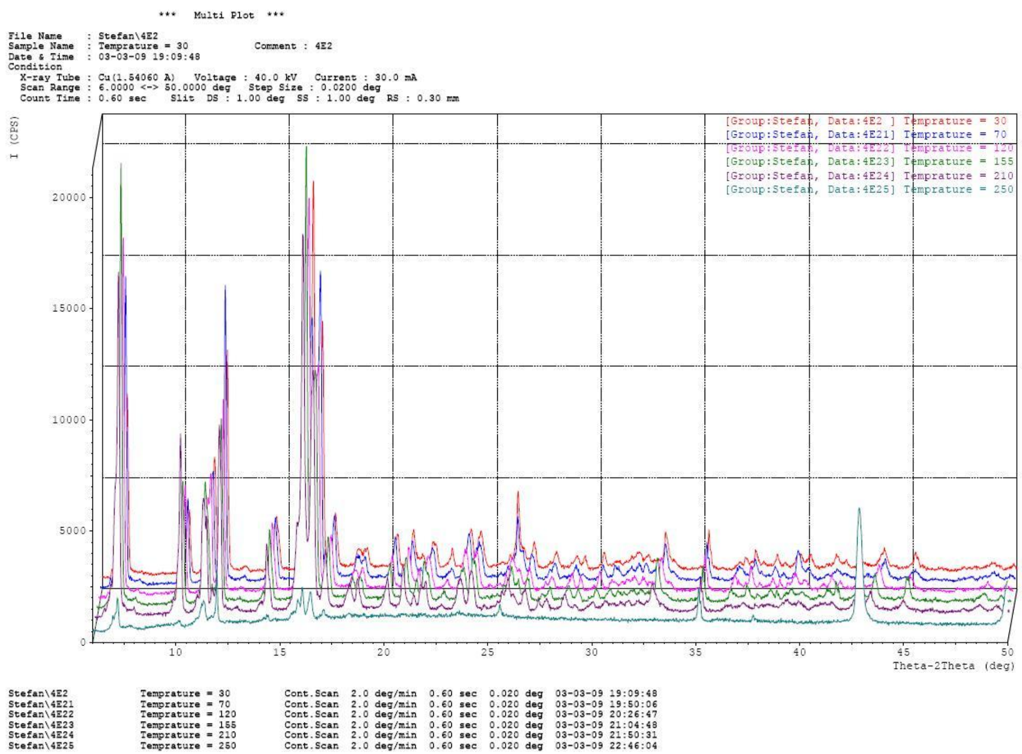




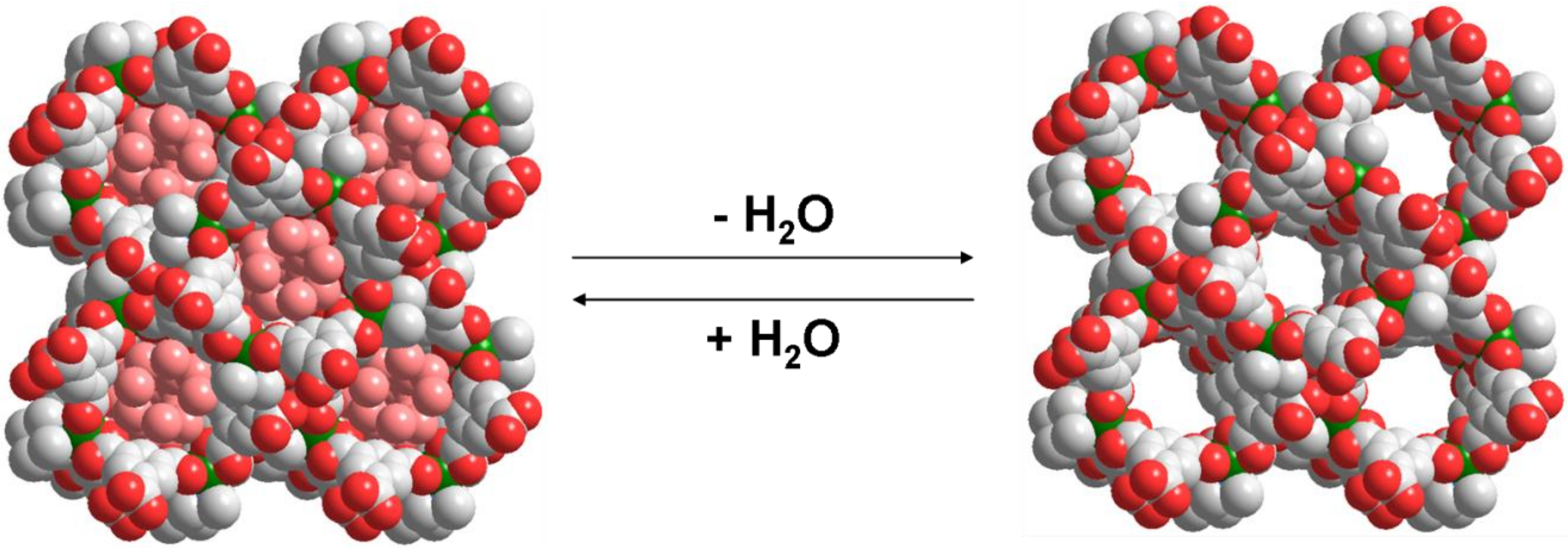


$(H_2O)_8$





Single Crystal to Single Crystal Transformation



- H_2O
+ H_2O