

# Molecular Metal Wires: From Homonuclear Metal Strings to Heteronuclear Metal Strings

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# ***From Homonuclear Metal String Complexes to Heteronuclear Metal String Complexes***

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## **I. Homonuclear Metal String Complexes**

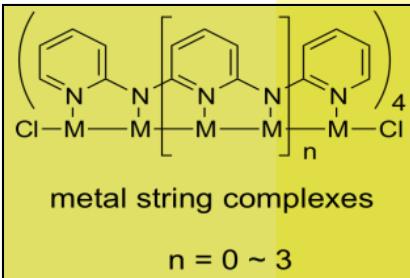
- Synthesis and structure of newly designed ligands and unique metal string complexes
- Multinuclear metal-metal multiple bonds
- Single molecular conductance & I-V characteristics
- New generation of the metal string complexes  
Naphthyridyl amino ligands ; asymmetrical ligands ; chiral ligands.

## **II. Heteronuclear Metal String Complexes**

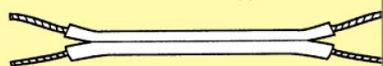
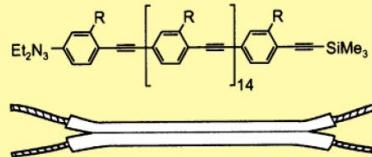
- Heterotrinuclear metal string complexes  
 $M_A-M_B-M_A$  ;  $M_A-M_A-M_B$  ;  $M_A-M_B-M_C$
- Heteropentanuclear metal string complexes  
NDR effect on  $NiRu_2Ni_2$  metal string  
 $NiPtCo-CoPd$  &  $Mo \equiv MoNiMo \equiv Mo$  metal strings

## **III. Conclusion**

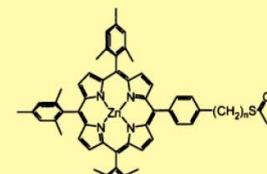
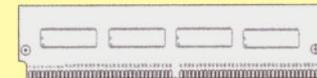
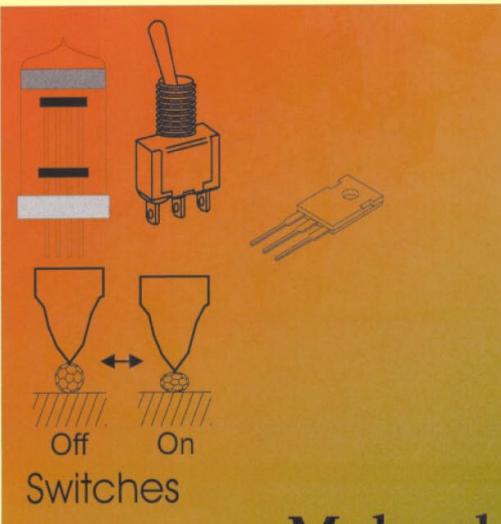
## Metal Wires



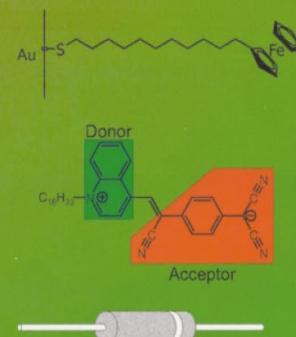
## Wire



## Molecular Electronics



Memory



Diodes/Rectifiers

ANGEWANDTE  
CHEMIE  
© WILEY-VCH

*"For the greatest benefit to mankind"*  
Alfred Nobel



The Royal Swedish Academy of Sciences has decided to award the

# 2016 NOBEL PRIZE IN CHEMISTRY

to:

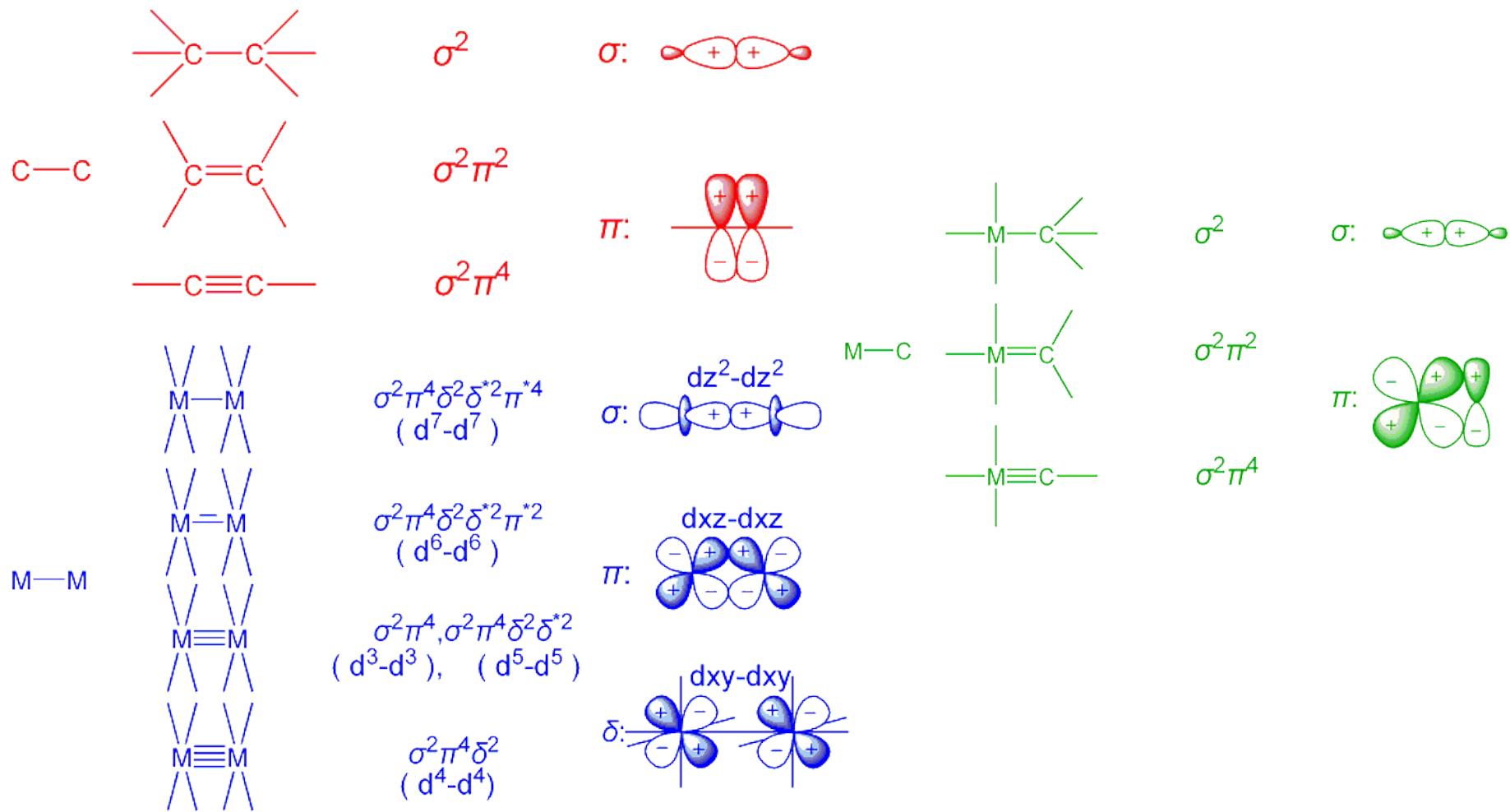


Illustrations: Niklas Elmehed, Nobel Prize Medal;  
Nobel Foundation, Photo: Lovisa Engblom

# Jean-Pierre Sauvage Sir J. Fraser Stoddart Bernard L. Feringa

*"for the design and synthesis of molecular machines"*

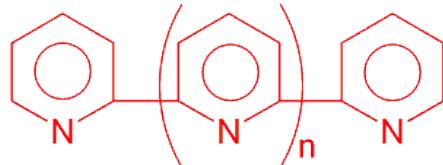
# Chemical Bonding



New Type of Bonding

- 1) Multi-layered Bonding
- 2) Multinuclear Metal-Metal Multiple Bonding

## Oligo-( $\alpha$ -Pyridyl)



$n=0$  bipyridine

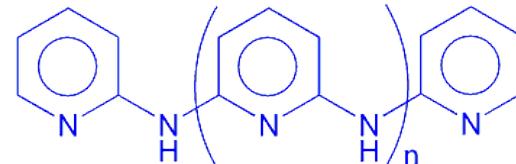
$n=1$  terpyridine

$n=2$  quaterpyridine

$n=3$  quinquepyridine

$n=4$  sexipyridine

## Oligo-( $\alpha$ -Pyridyl)amino



$n=0$  dipypyridylamine  
dpaH (N3)

$n=1$  tripyridylamine  
tpdaH<sub>2</sub> (N5)

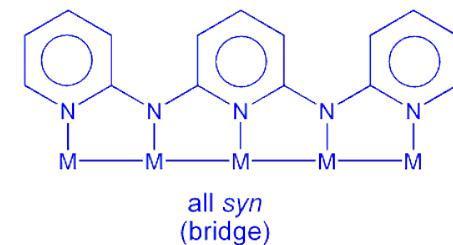
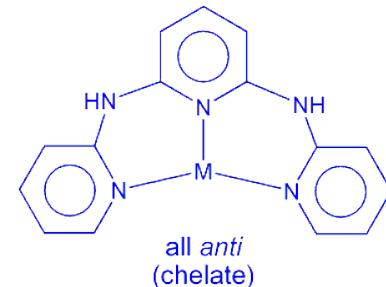
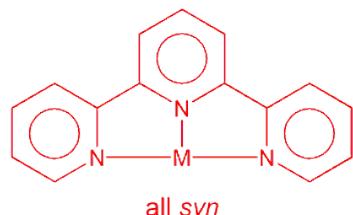
$n=2$  tetrapyridyltriamine  
teptaH<sub>3</sub> (N7)

$n=3$  pentapyridyltetramine  
PeptaH<sub>4</sub> (N9)

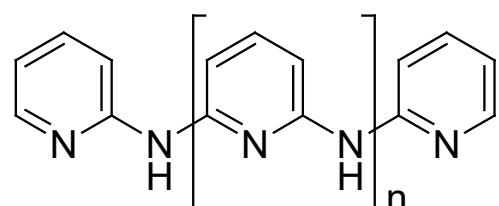
$n=4$  (N11) ;  $n=5$  (N13) ..... $n=7$  (N17)  
..... $n=11$  (N25)

## Comparisons of Complexation

- ★ 5 member chelating vs 4 or 6 member chelating ring
- ★ anionic radical vs anion by deprotonation
- ★ all syn-form (chelate) vs all anti- or all syn-form (chelate) (bridge)

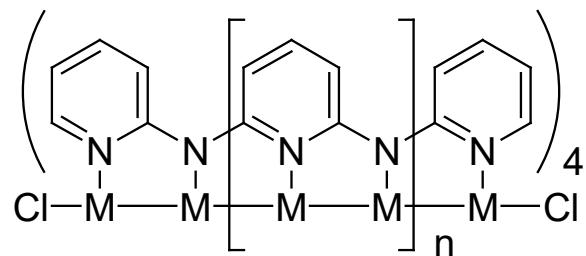
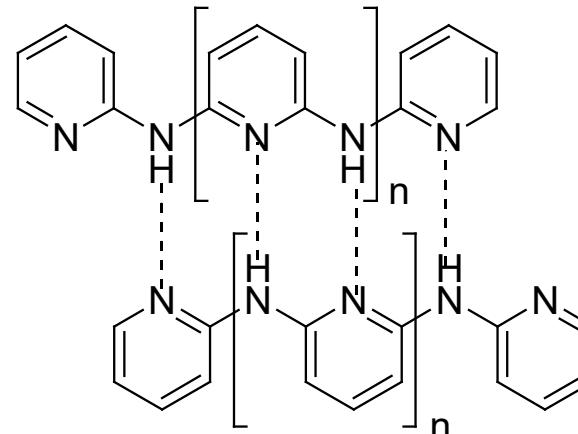


# Oligo-( $\alpha$ -Pyridyl)-amino ligands



oligo- $\alpha$ -pyridylamino ligands

self-recognition



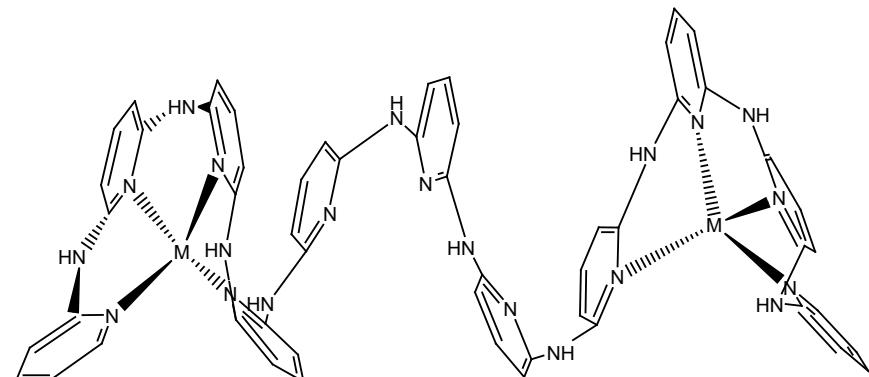
metal string complexes of quadruple helix

M = Ni, Co, Cr, Ru, Rh and Cu.

n = 0 ~ 3

M<sup>2+</sup>

hydrogen bonding dimer of double helix

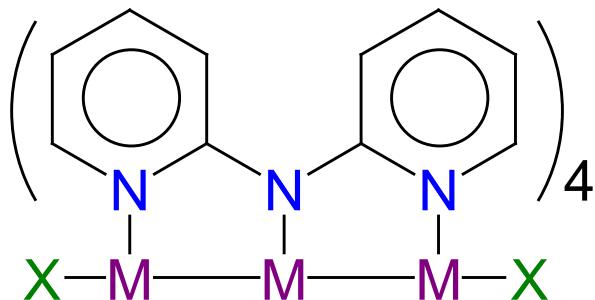


metal complex of single helix

M = Cu

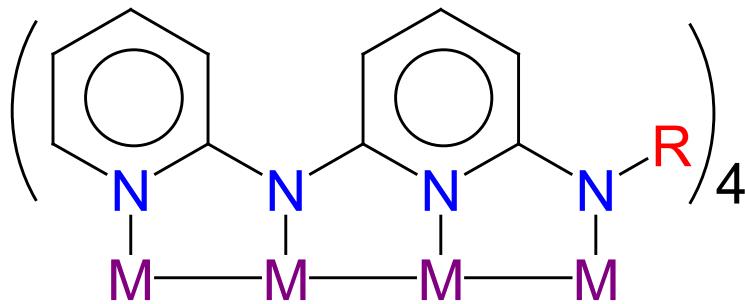
# Metal String Complexes

I.



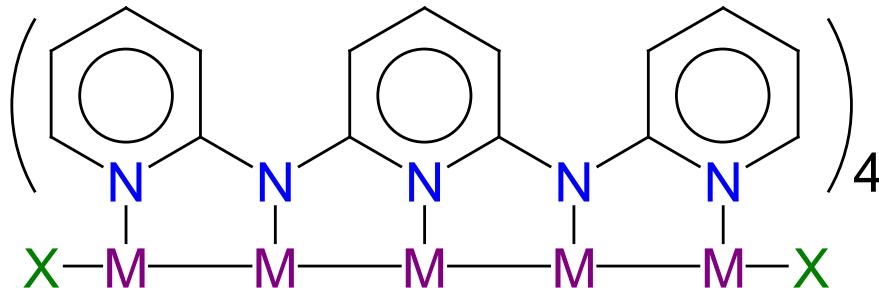
$[M^{II}]_3(\mu_3\text{-dpa})_4X_2]$   
(M = Ni<sup>II</sup>, Cr<sup>II</sup>, Co<sup>II</sup>, Ru<sup>II</sup>, Rh<sup>II</sup>, Cu<sup>II</sup>)

II.

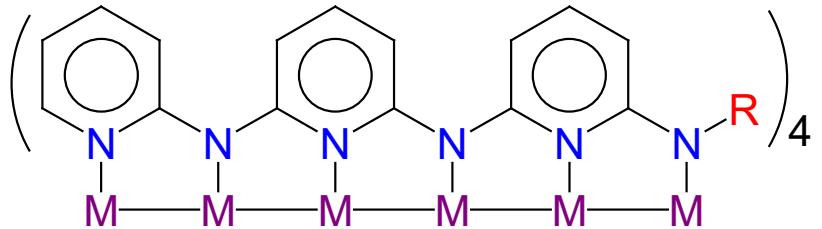
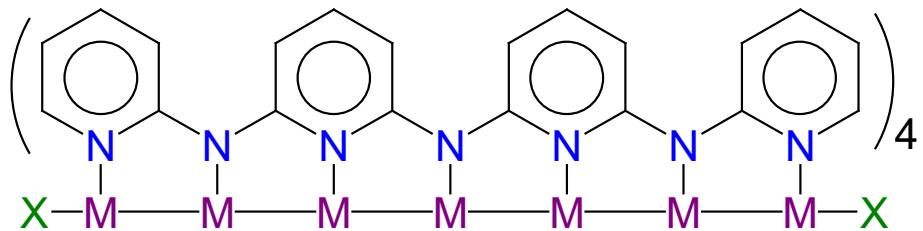
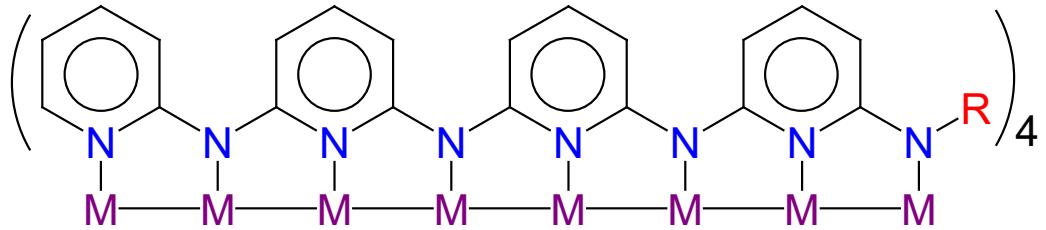
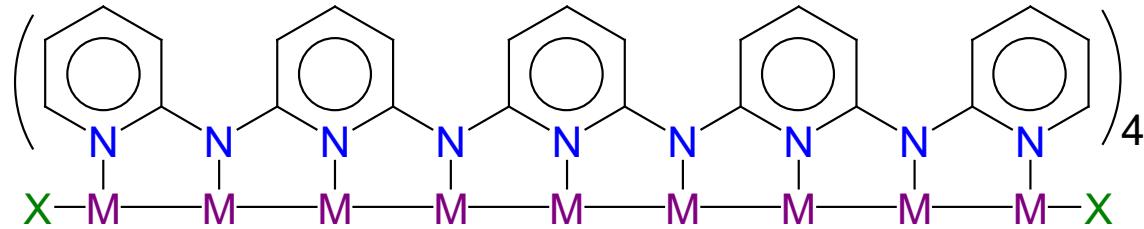


$[M^{II}]_4(\mu_4\text{-dpda})_4$   
(M = Ni<sup>II</sup>, Cr<sup>II</sup>, Co<sup>II</sup>)

III.



$[M^{II}]_5(\mu_5\text{-tpda})_4X_2]$   
(M = Ni<sup>II</sup>, Cr<sup>II</sup>, Co<sup>II</sup>, Ru<sup>II</sup>)

**IV.** $[M^{II}_6(\mu_6\text{-trptra})_4]$   
(M = Ni<sup>II</sup>, Co<sup>II</sup>)**V.** $[M^{II}_7(\mu_9\text{-tepta})_4X_2]$   
(M = Ni<sup>II</sup>, Cr<sup>II</sup>, Co<sup>II</sup>)**VI.** $[M^{II}_8(\mu_8\text{-tepta})_4]$   
(M = Ni<sup>II</sup>)**VII.** $[M^{II}_9(\mu_9\text{-pepta})_4X_2]$   
(M = Ni<sup>II</sup>, Cr<sup>II</sup>)

# Metal-Metal Bonding for Second-Row Transition Metal [Ru<sub>3</sub>(dpa)<sub>4</sub>X<sub>2</sub>] & [Rh<sub>3</sub>(dpa)<sub>4</sub>X<sub>2</sub>]



-7.313 eV



-10.223 eV



-10.508 eV



-10.799 eV



-11.895 eV



-11.927 eV



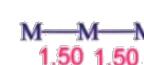
-11.973 eV



-13.104 eV

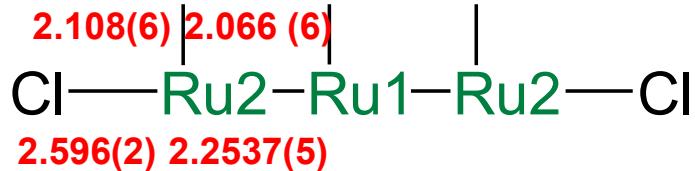
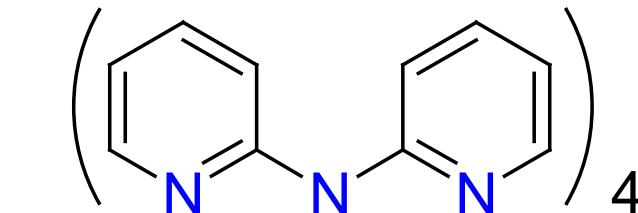
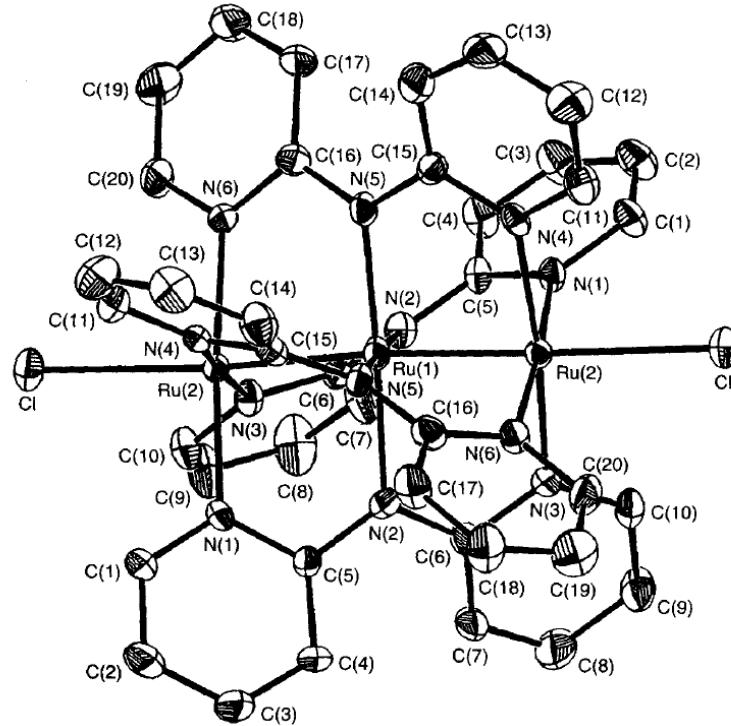


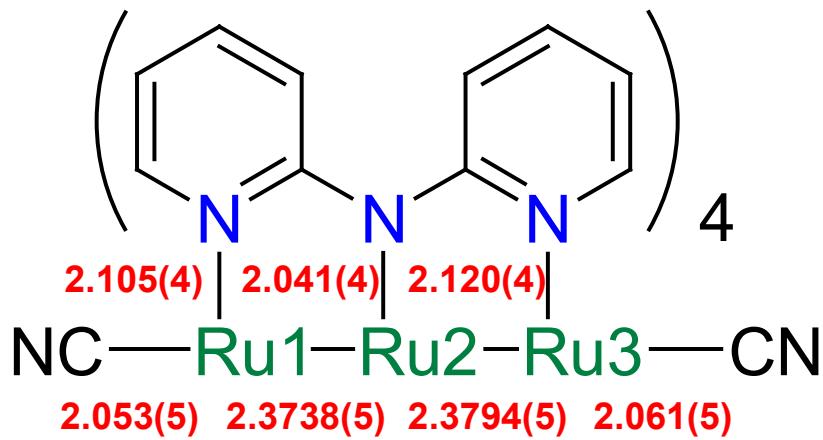
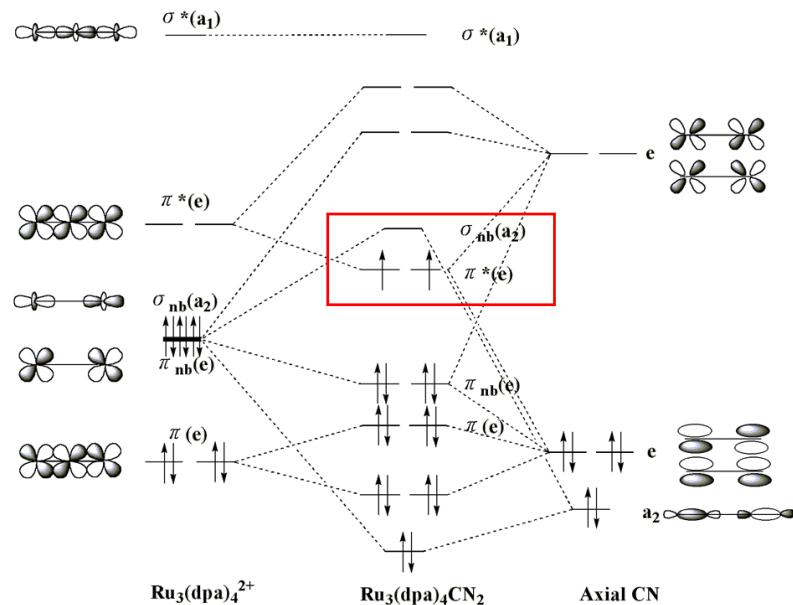
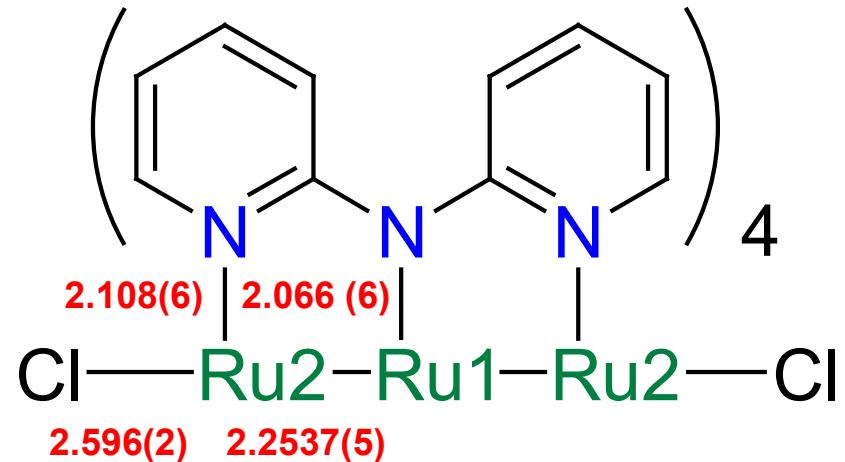
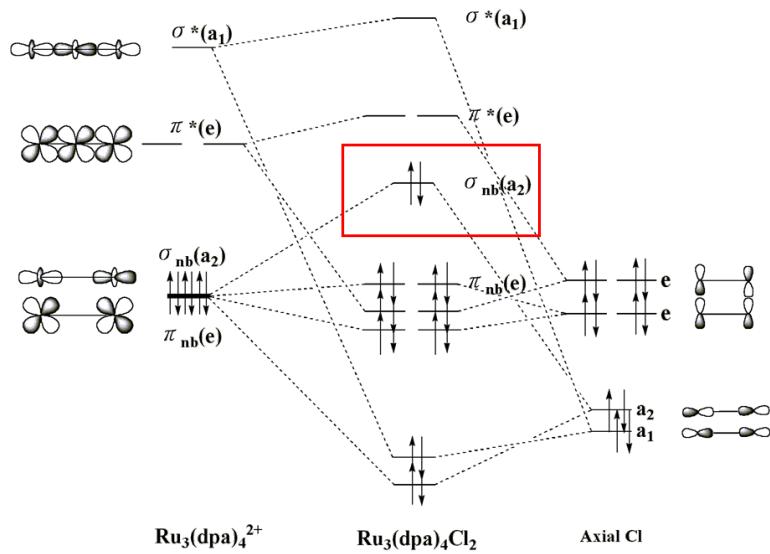
-13.118 eV



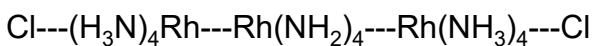
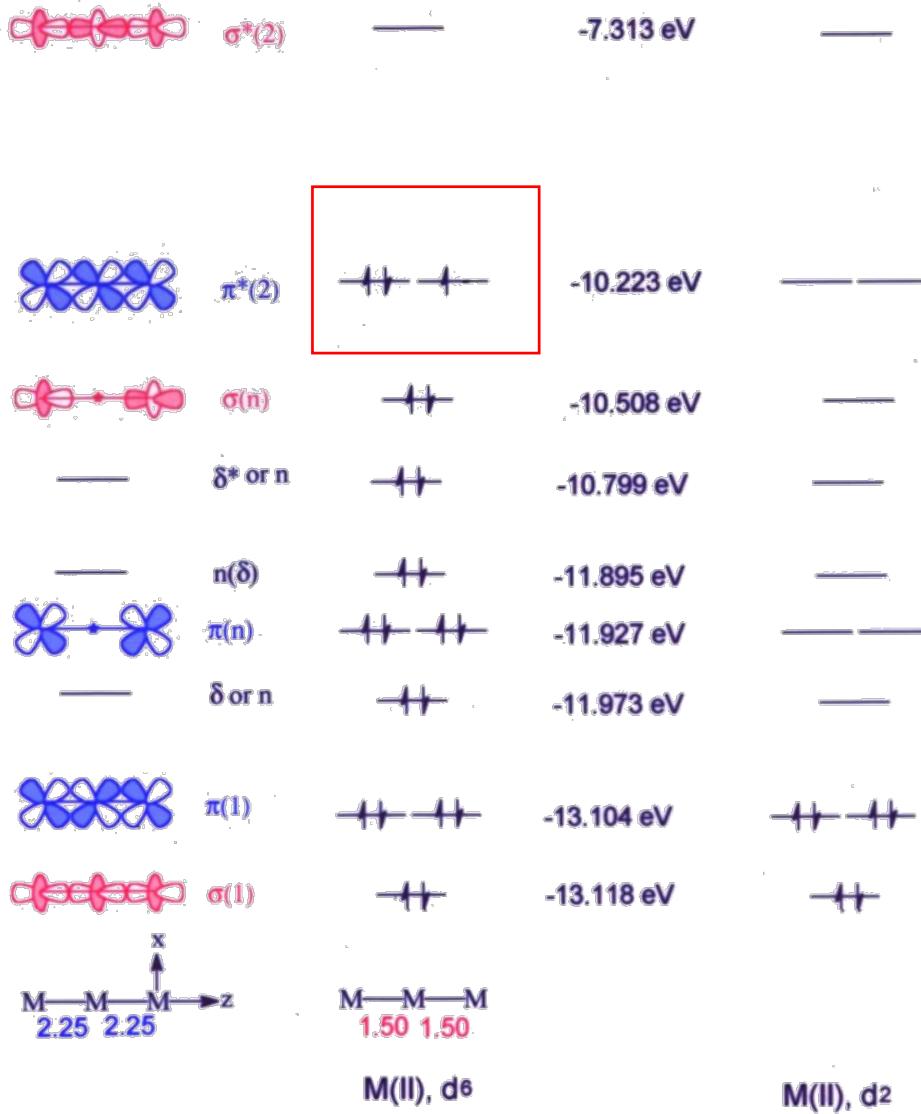
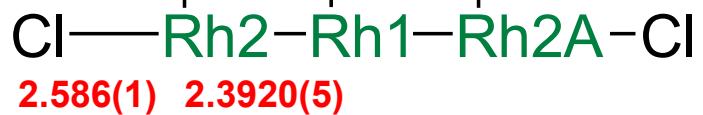
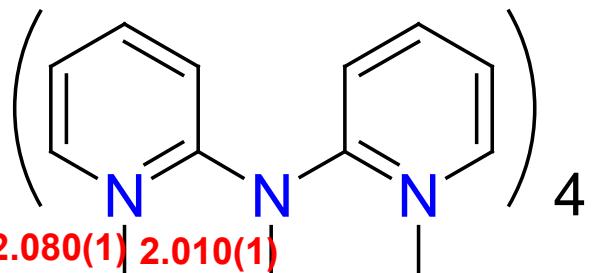
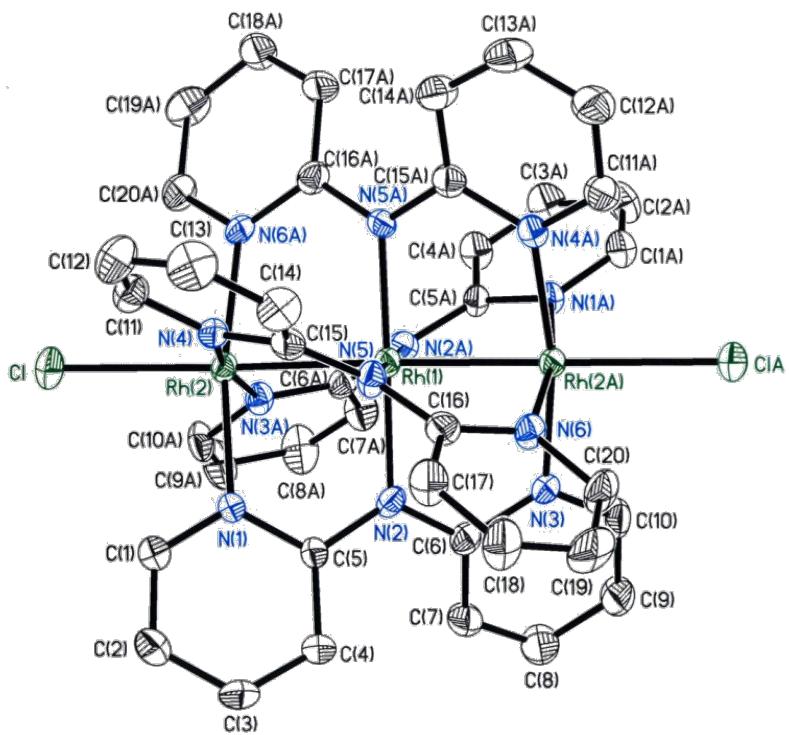
M(II), d<sub>6</sub>

M(II), d<sub>2</sub>

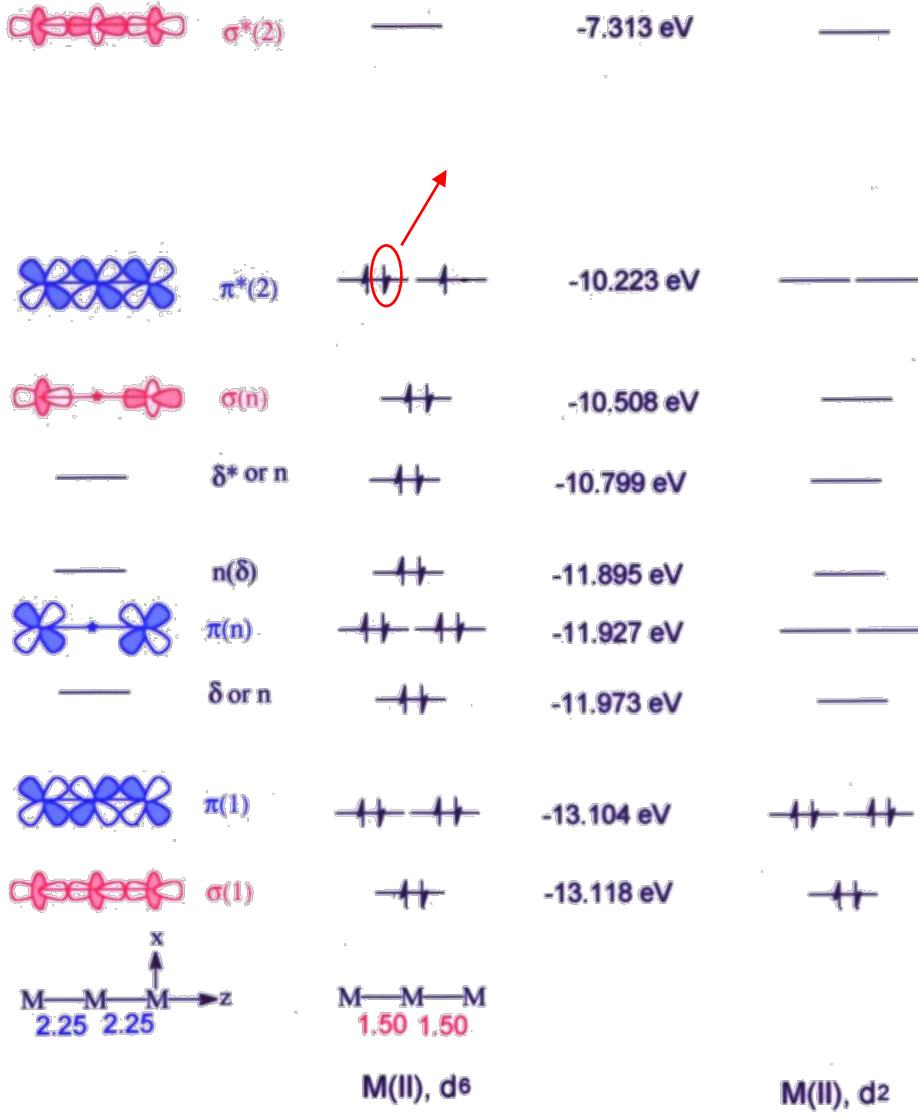
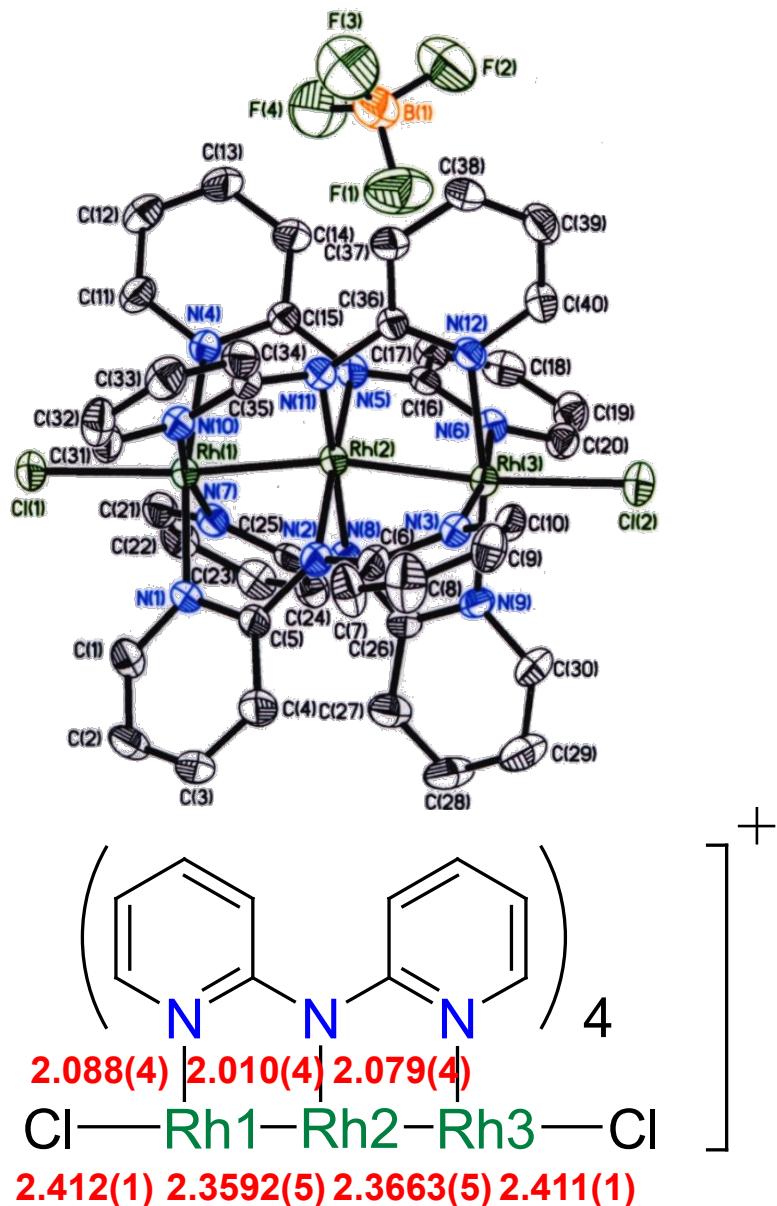




# [Rh<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>]



# $[\text{Rh}_3(\text{dpa})_4\text{Cl}_2](\text{BF}_4)$



Cl---(H<sub>3</sub>N)<sub>4</sub>Rh---Rh(NH<sub>2</sub>)<sub>4</sub>---Rh(NH<sub>3</sub>)<sub>4</sub>---Cl

# Comparison of Dinuclear and Trinuclear M-M bonds

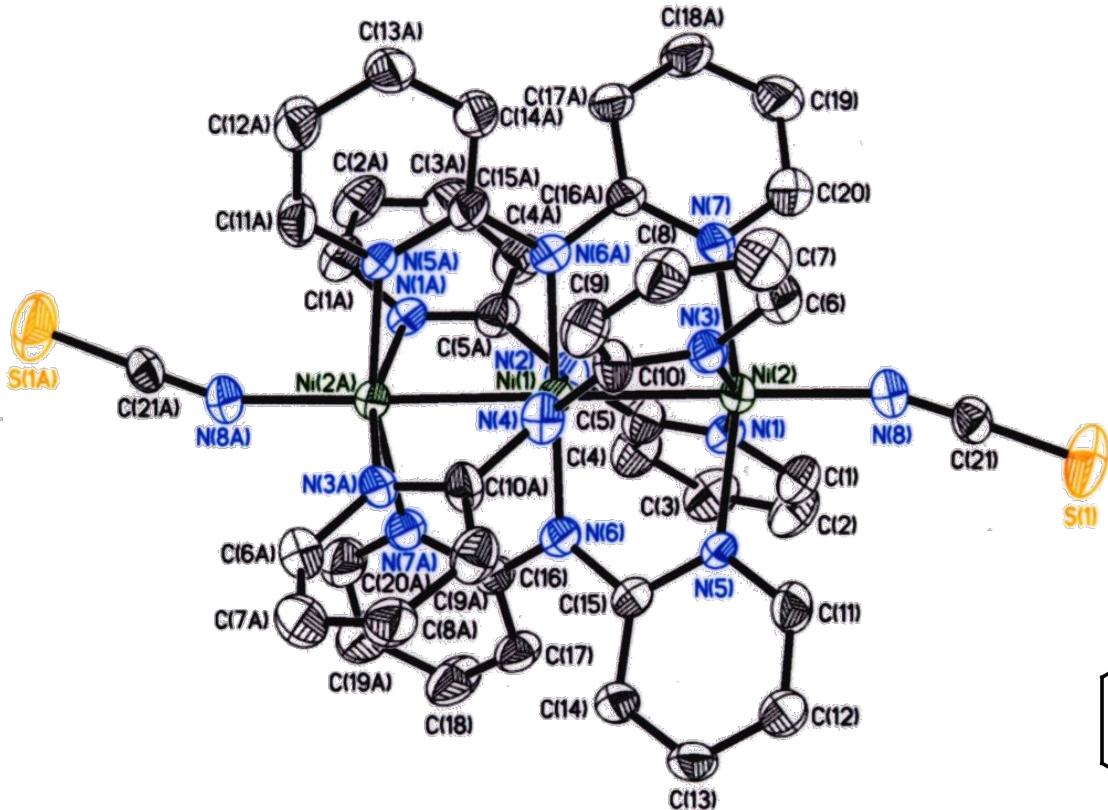
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Complex	Configuration	Bond Order	M-M Bond Length
[Mo <sub>2</sub> (OAc) <sub>2</sub> ]	$\sigma^2\pi^4\delta^2$	4	2.093(1)
[Ru <sub>2</sub> (OAc) <sub>4</sub> Cl]	$\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$	2.5	2.267(1)
[Ru <sub>2</sub> (OAc) <sub>4</sub> (THF) <sub>2</sub> ]	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$	2.0	2.261(3)
[Rh <sub>2</sub> (OAc) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] (ClO <sub>4</sub> ) H <sub>2</sub> O	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$	1.5	2.316(2)
[Rh <sub>2</sub> (OAc) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ]	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	1.0	2.3855(5)
[Cr <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> Cl <sub>2</sub> ]	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^2)$	3/2	2.339(2), 2.381(2)
[Co <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> X <sub>2</sub> ] <sup>a</sup>	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2}\sigma_n^2)\pi^{*3}$	1.5/2	2.290(3) ~ 2.344(3)
[Ni <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> X <sub>2</sub> ] <sup>b</sup>	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2}\sigma_n^2)\pi^{*4}\sigma^{*2}$	0	2.380(2) ~ 2.447(7)
[Ru <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> Cl <sub>2</sub> ]	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2}\sigma_n^2)$	3/2	2.2537(5)
[Ru <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> (CN) <sub>2</sub> ]	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2})\pi^{*2}$	2/2	2.3738(5)
[Rh <sup>II,II,III</sup> <sub>3</sub> (dpa) <sub>4</sub> Cl <sub>2</sub> ](BF <sub>4</sub> )	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2}\sigma_n^2)\pi^{*2}$	2/2	2.3626(5)
[Rh <sup>II</sup> <sub>3</sub> (dpa) <sub>4</sub> Cl <sub>2</sub> ]	$\sigma^2\pi^4(\delta^2\delta_n^2\pi_n^4\delta^{*2}\sigma_n^2)\pi^{*3}$	1.5/2	2.3920(5)

**a:** X = Cl<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>CN    **b:** X = Cl<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>CN, CN<sup>-</sup>

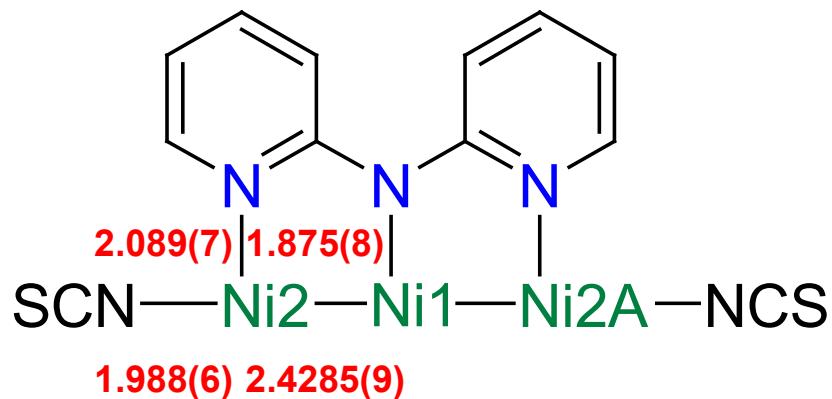
# Metal String Complexes of Nickel System

## Trinickel Metal String $[\text{Ni}_3(\text{dpa})_4(\text{NCS})_2]$

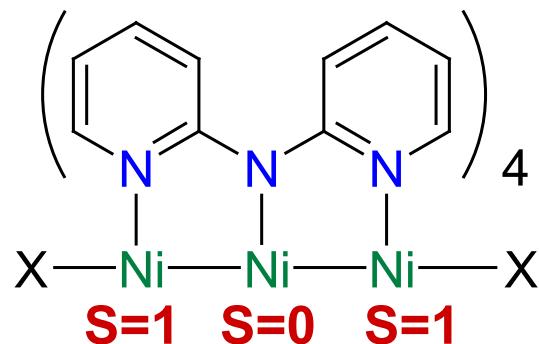
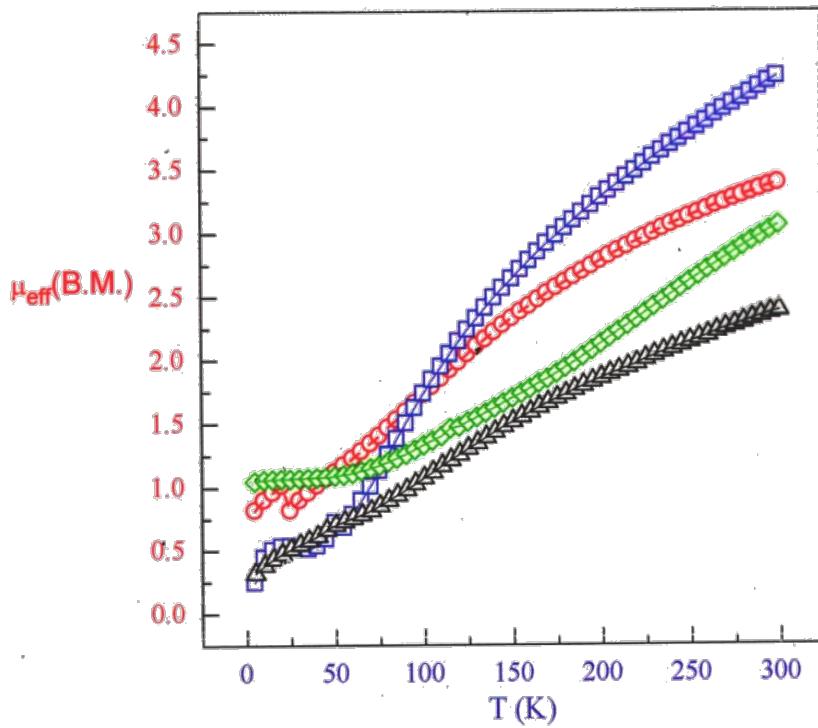


$$R1 = 0.050 \quad [I > 2\sigma(I)]$$

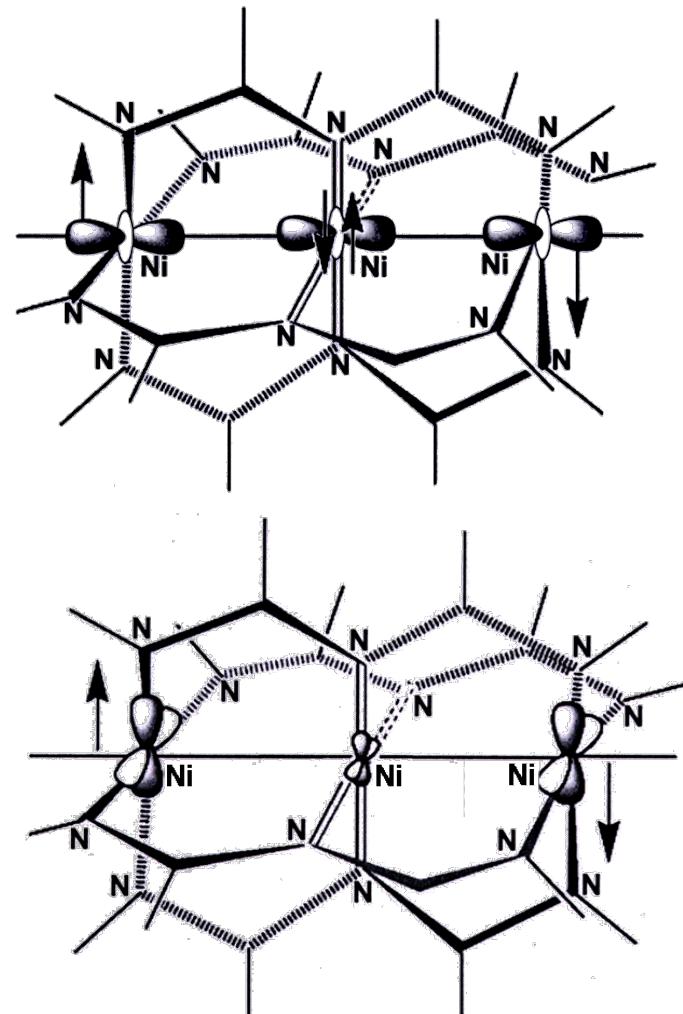
$$wR2 = 0.091 \quad [I > 2\sigma(I)]$$



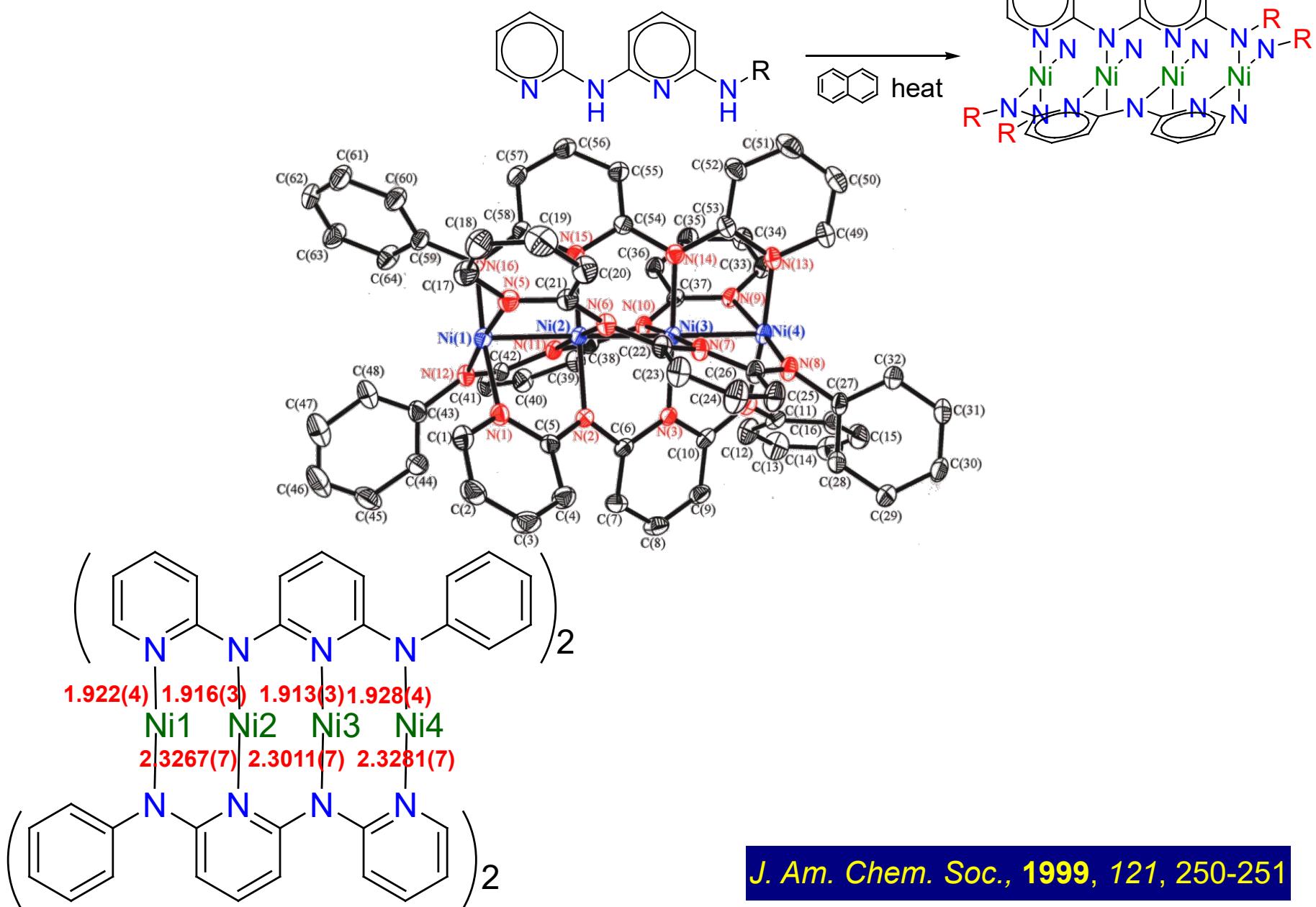
# Magnetism of Trinickel Metal Strings

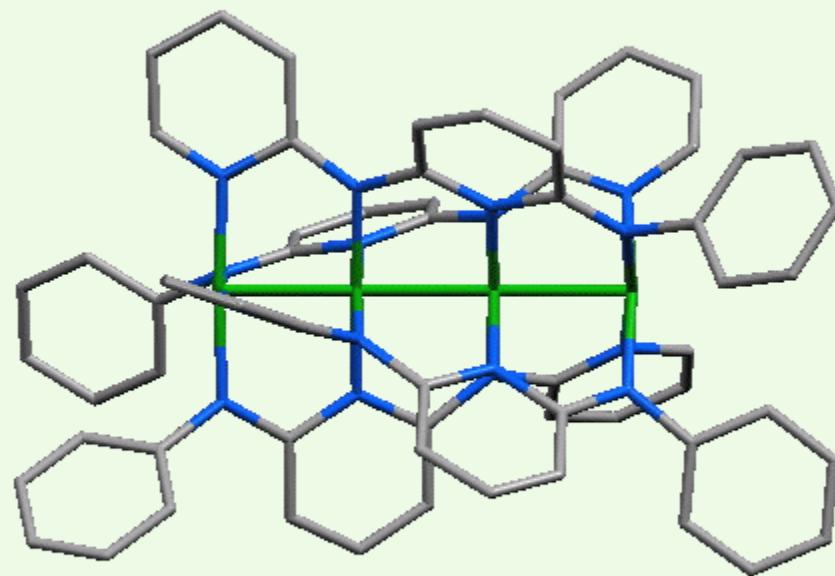


X = Cl, NCS, N<sub>3</sub><sup>-</sup>, C<sub>3</sub>H<sub>7</sub>CN

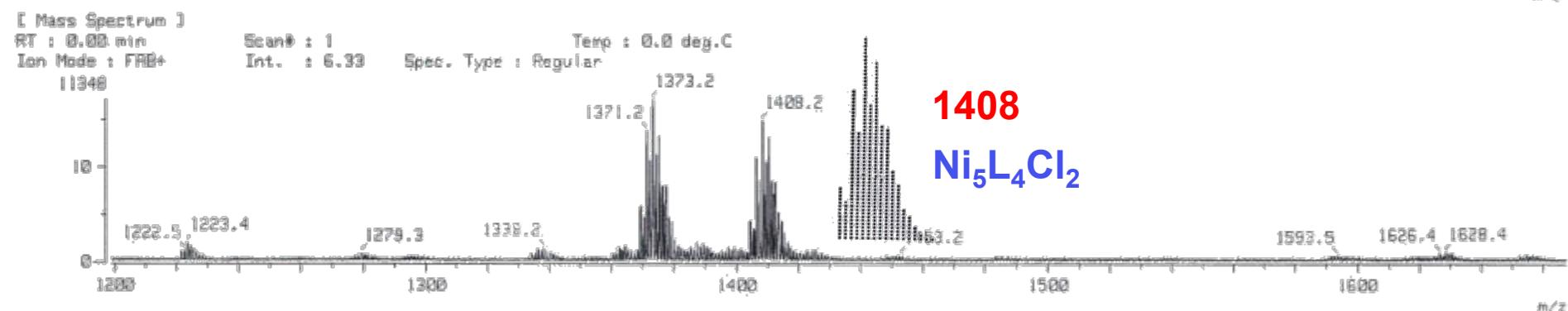
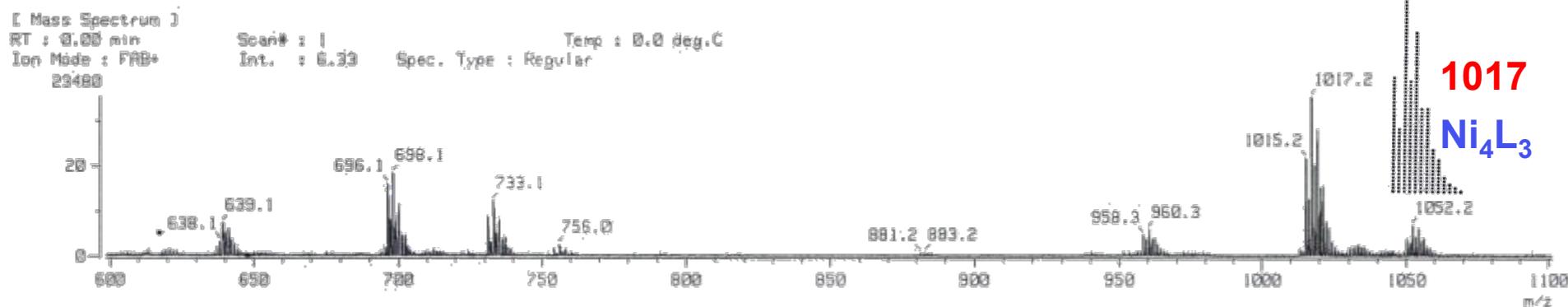
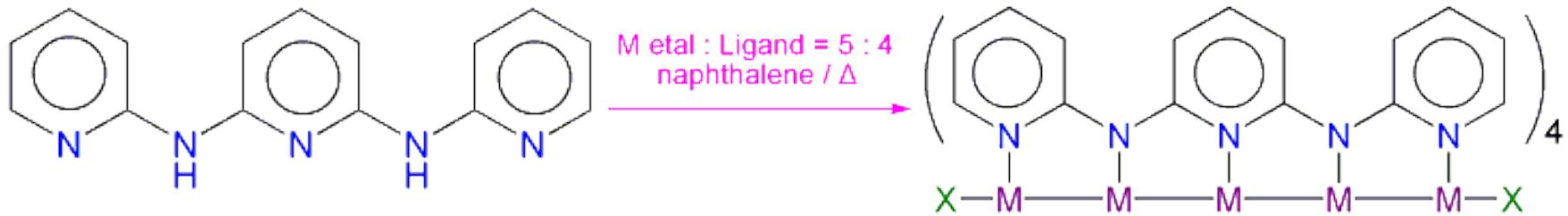


# Tetranickel Metal String $[Ni_4(phdpda)_4]$



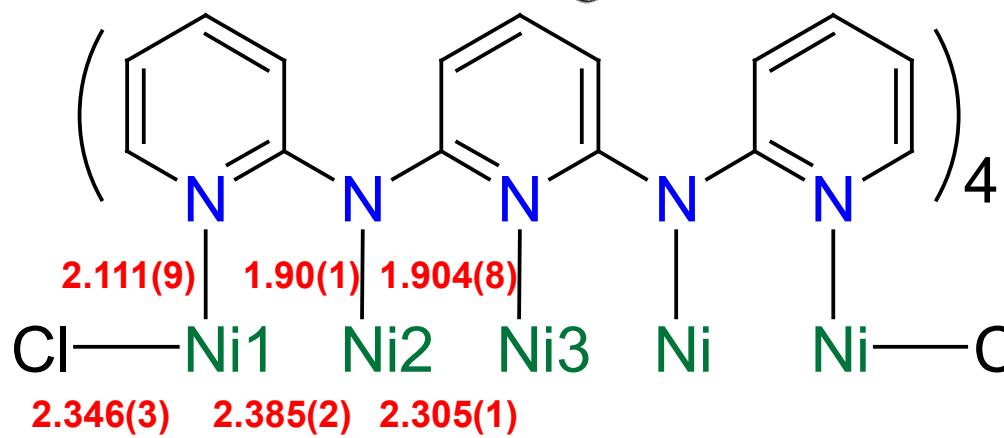
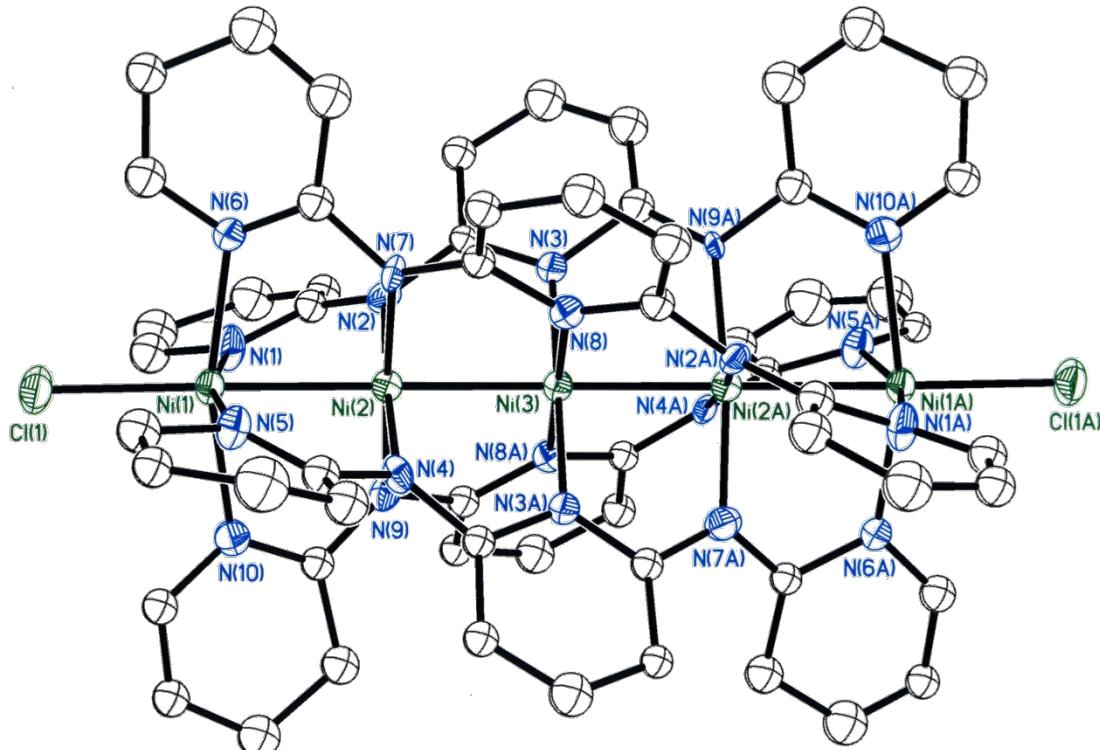


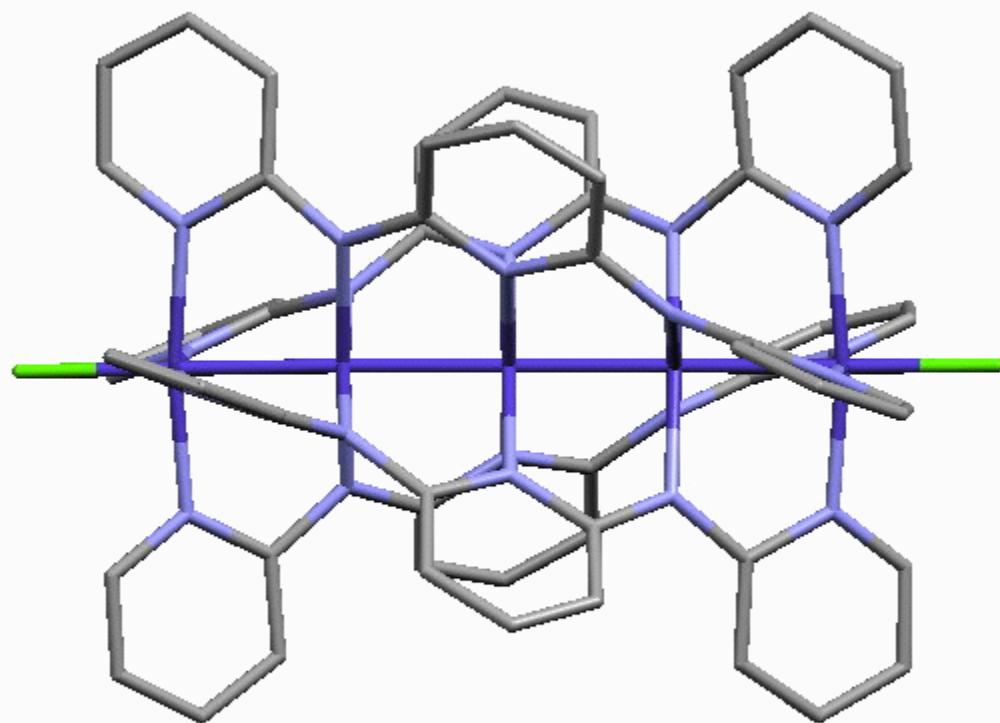
# Pantanickel Metal String $[Ni_5(tpda)_4Cl_2]$

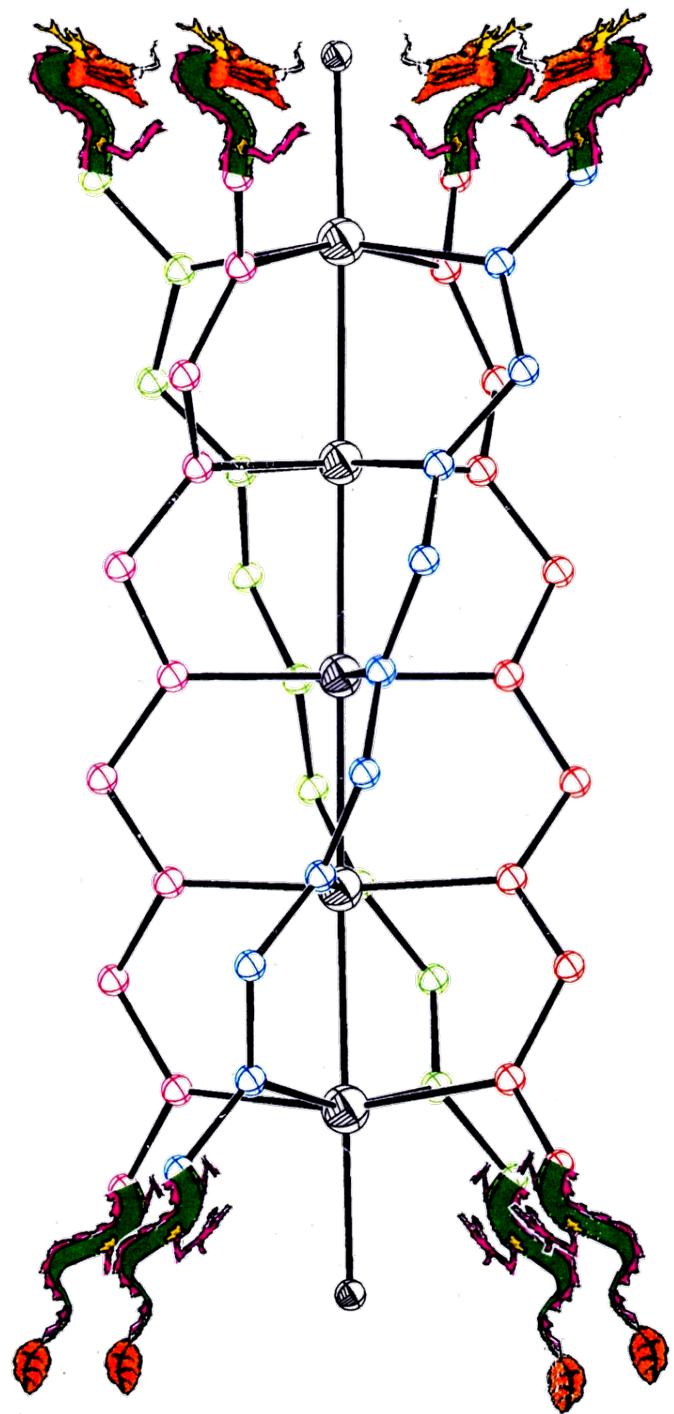


**1408**  
 **$Ni_5L_4Cl_2$**

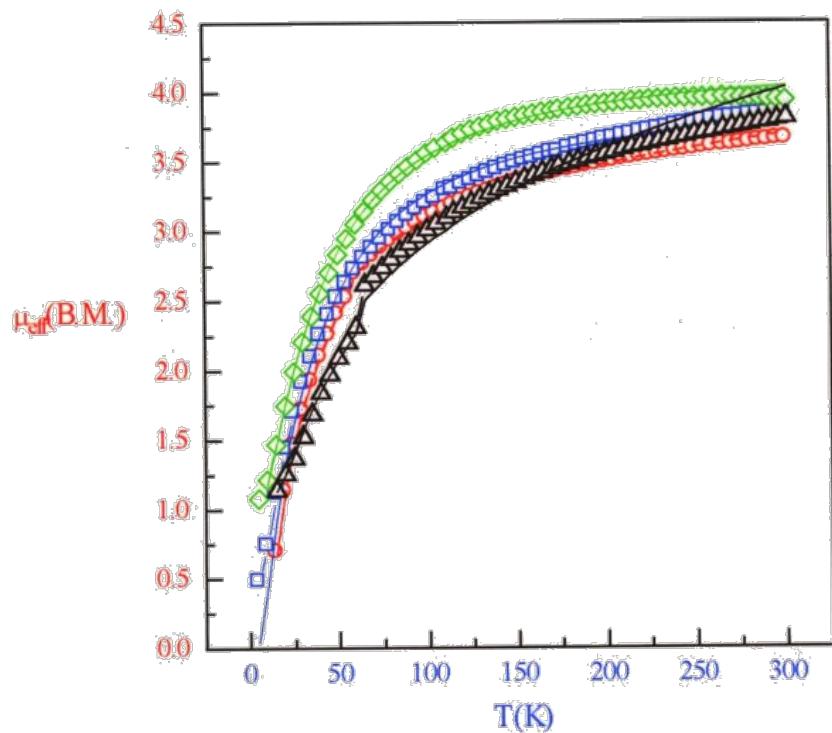
**1017**  
 **$Ni_4L_3$**



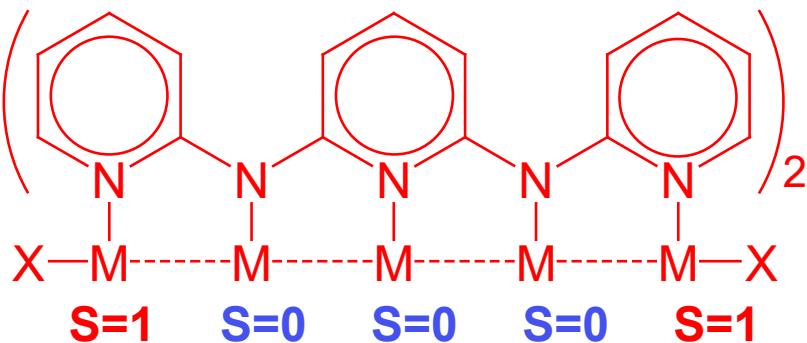
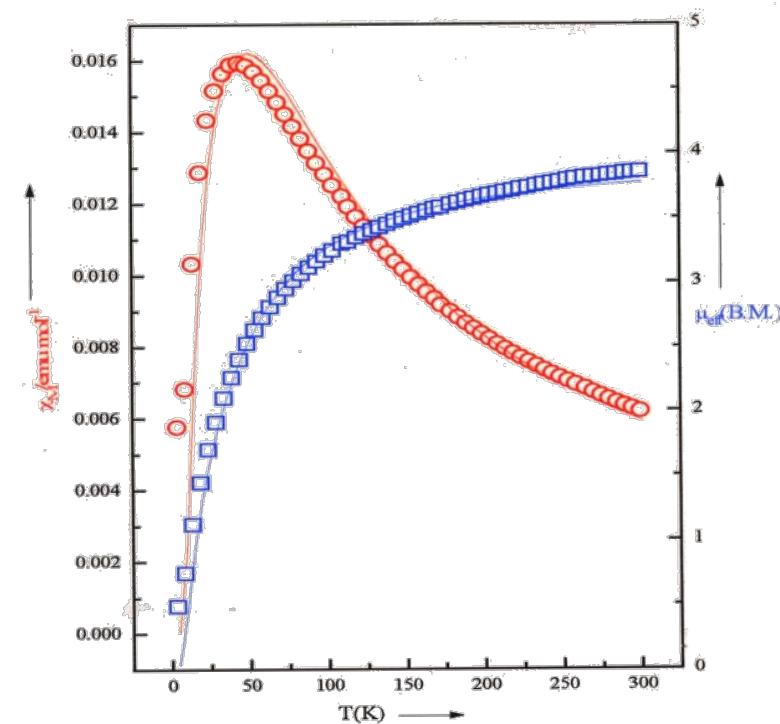




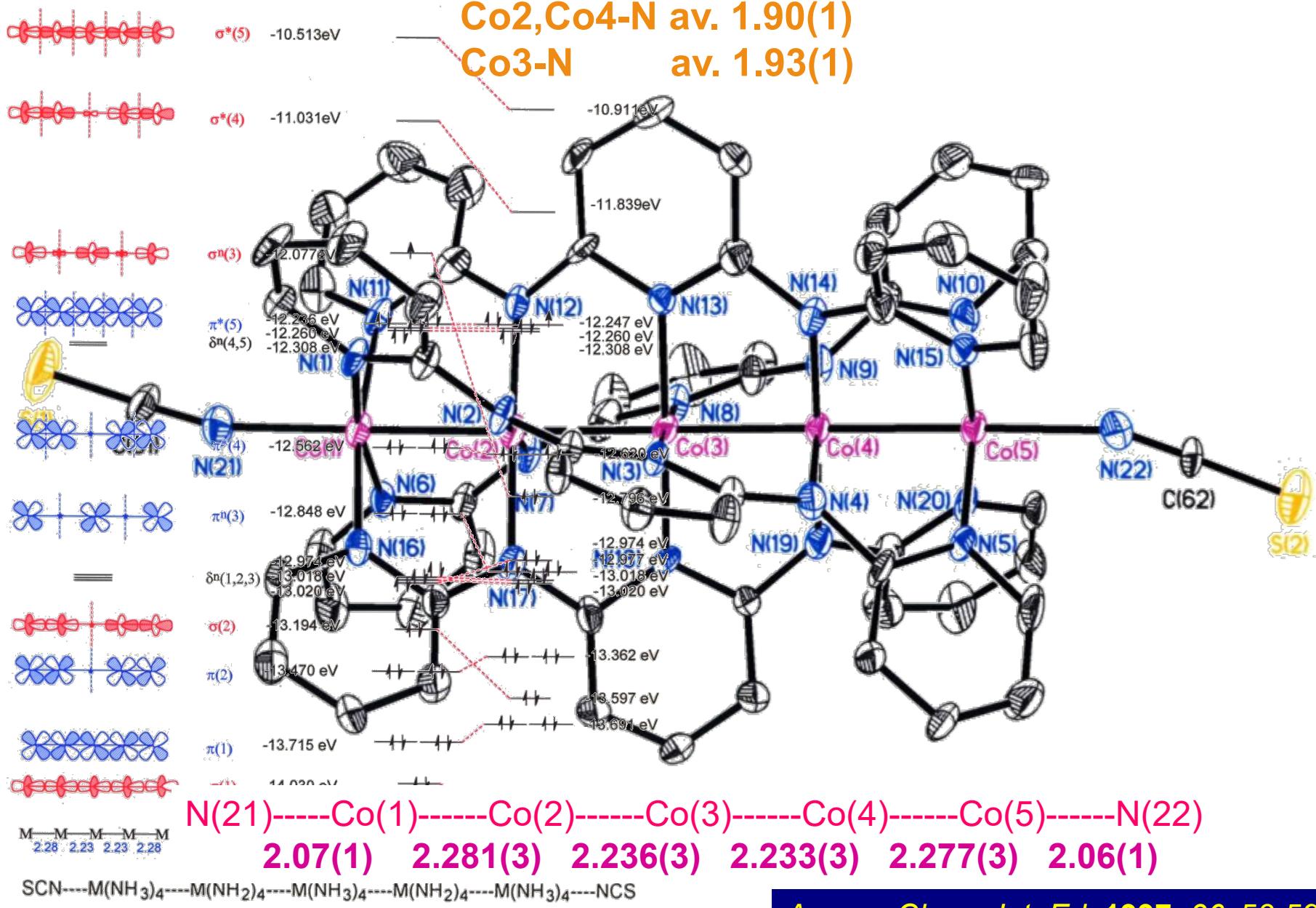
# Magnetism of Pentanickel Metal Strings



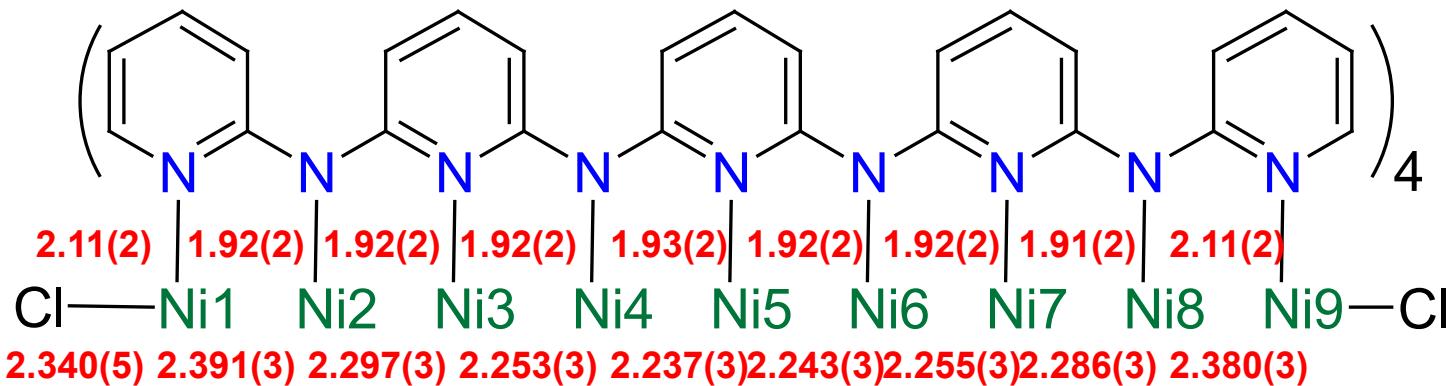
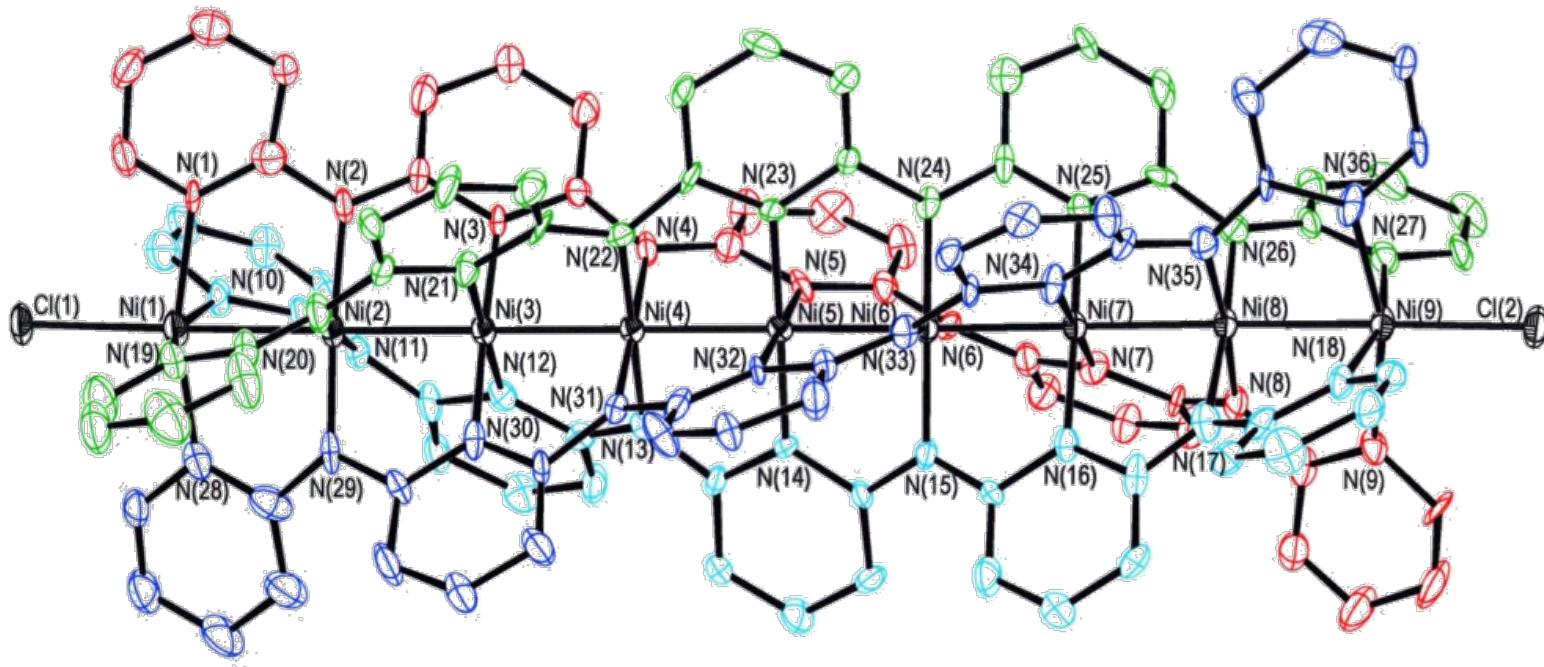
- $\text{Ni}_5(\text{tpda})_4(\text{CN})_2$ ,  $J_{15} = -6.40 \text{ cm}^{-1}$
- $\text{Ni}_5(\text{tpda})_4(\text{N}_3)_2$ ,  $J_{15} = -8.17 \text{ cm}^{-1}$
- ◇—  $\text{Ni}_5(\text{tpda})_4(\text{NCS})_2$ ,  $J_{15} = -9.24 \text{ cm}^{-1}$
- △—  $\text{Ni}_5(\text{tpda})_4(\text{CH}_3\text{CN})_2$ ,  $J_{15} = -9.7 \text{ cm}^{-1}$



# Qualitative MO Diagram of Dicarboxy-Pentanuclear Metal Complexes

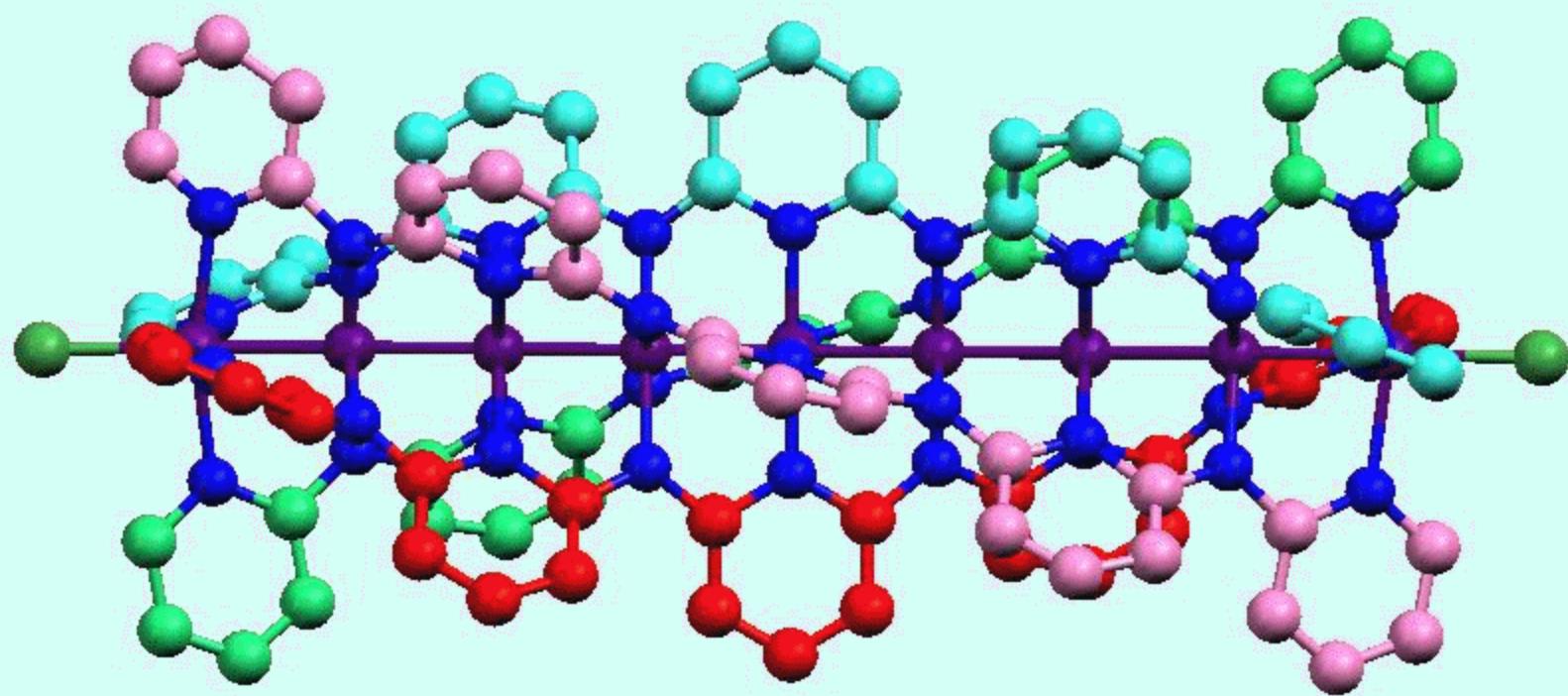


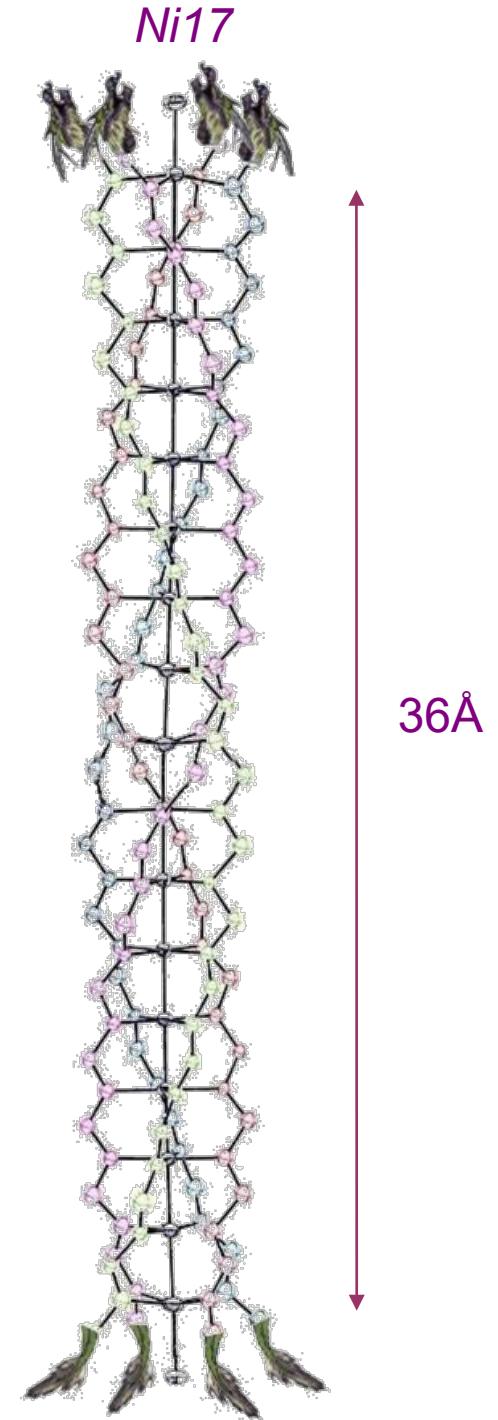
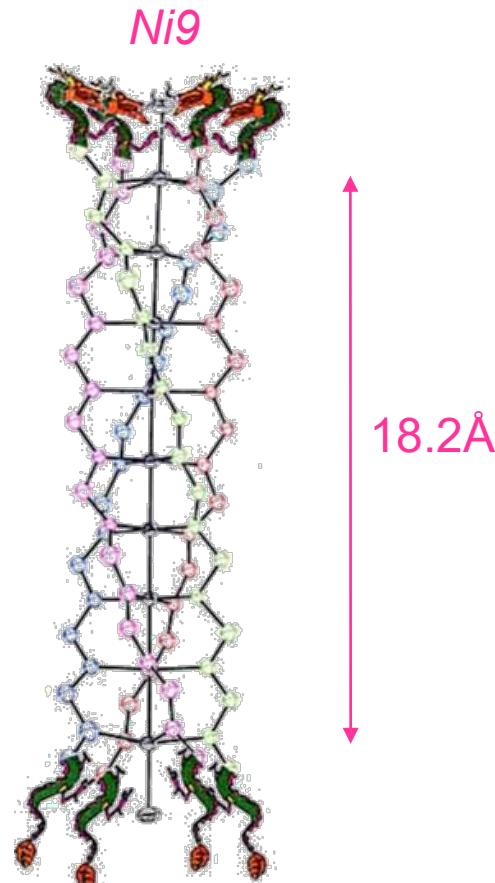
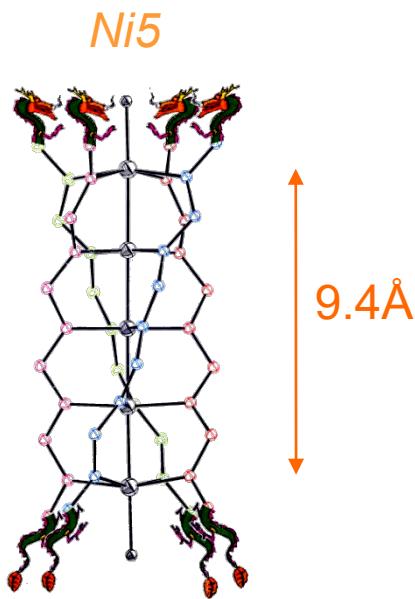
# Nonanickel Metal String $[Ni_9(pepta)_4Cl_2]$



$R1 = 0.12$  [ $I > 2\sigma(I)$ ]

$wR2 = 0.351$  [ $I > 2\sigma(I)$ ]







Temple in Taipei



**Palace Museum at Shengyang, China**



**Garden of Howard International House, Taipei**



**Ninomiya house  
at Tsukuba**



sina 新闻中心

**2017 Miami Open**



**Octahedral Pagoda at Sydney, Australia**



**Quadruple Sky Tower at Moscow, Russia**

# I-V Characteristics by Theoretical Approach

## (1) Linear Multimetal Complex

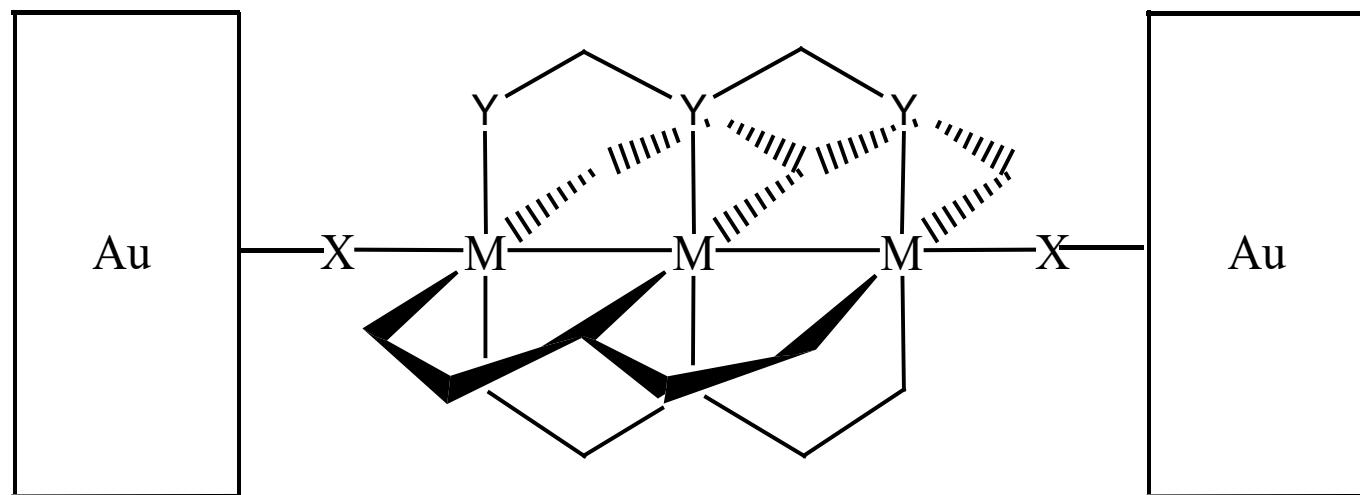


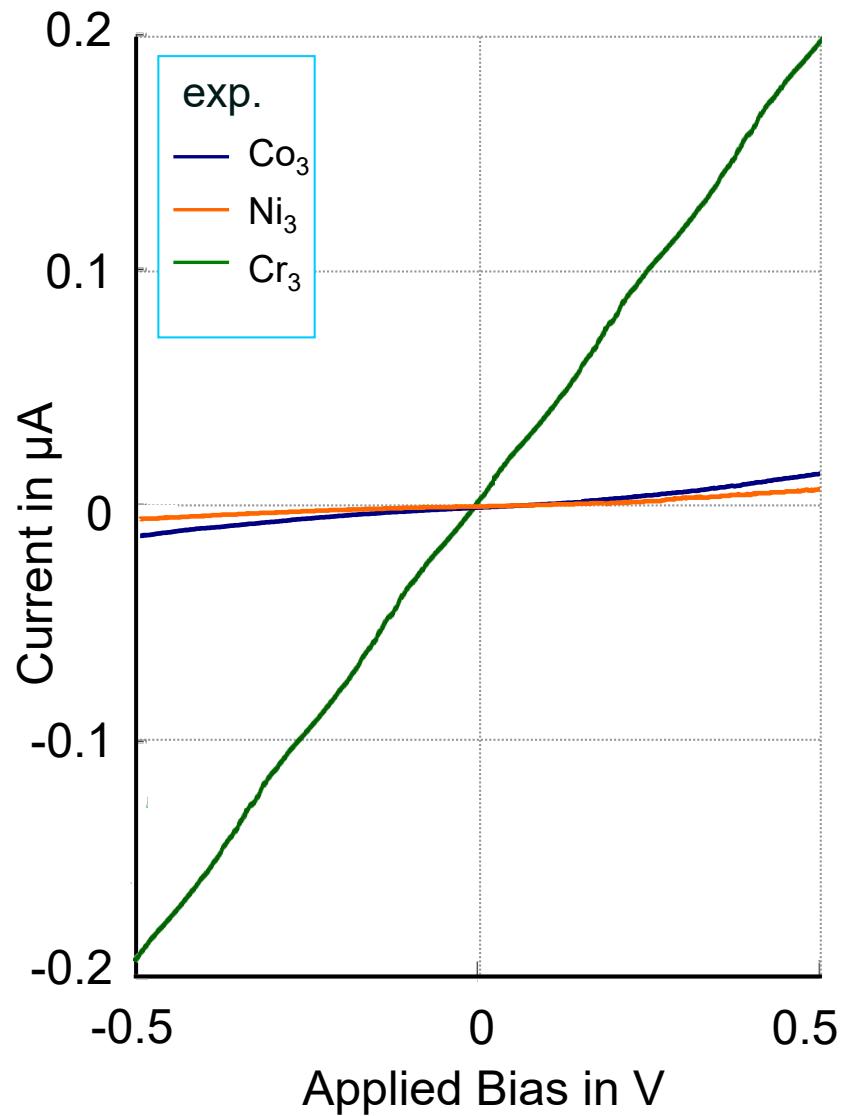
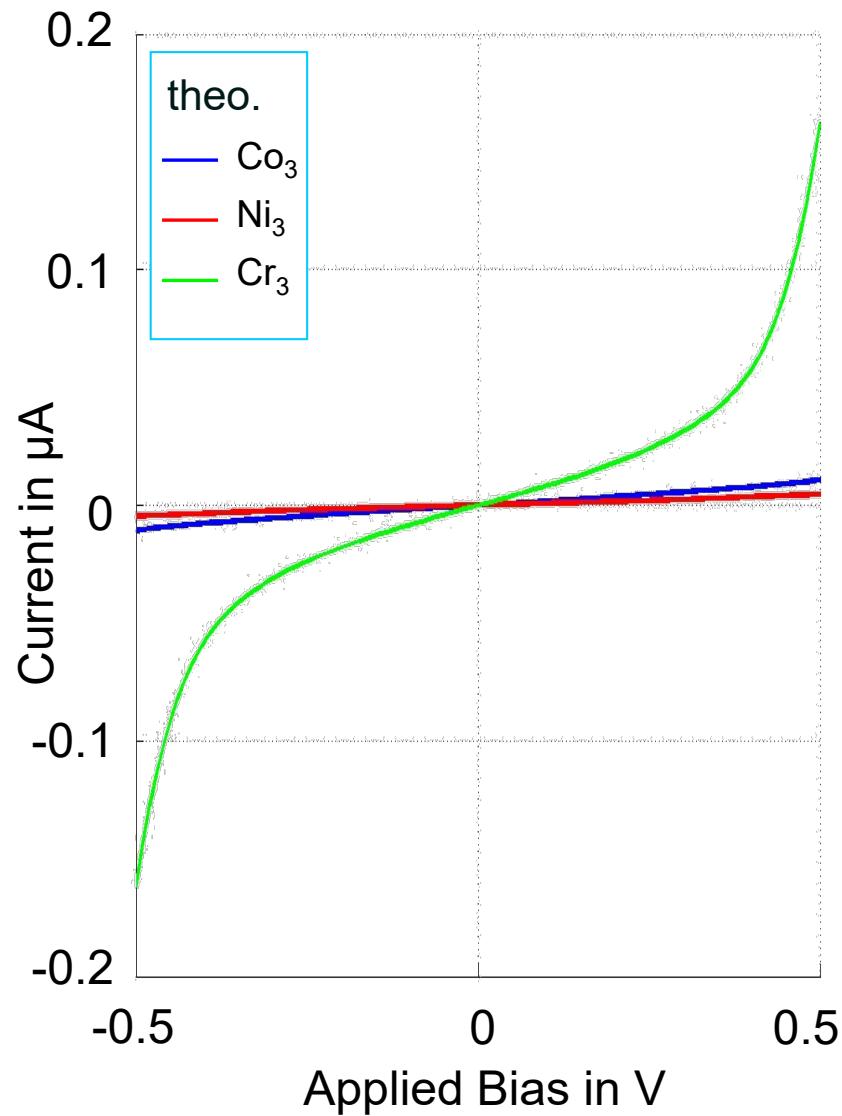
Diagram of the linear multinuclear complexes  $ML_4X_2$ . M = Co, Ni , Cr ; L =  $\mu_3$ -dpa ; X = NCS.

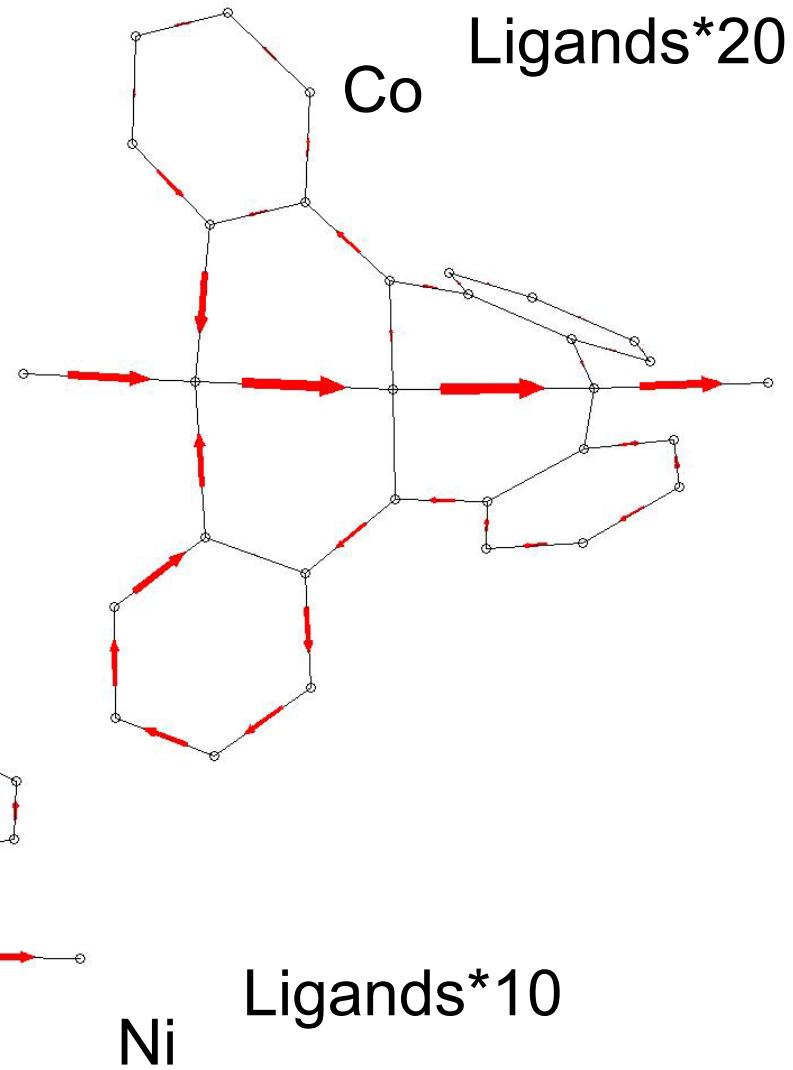
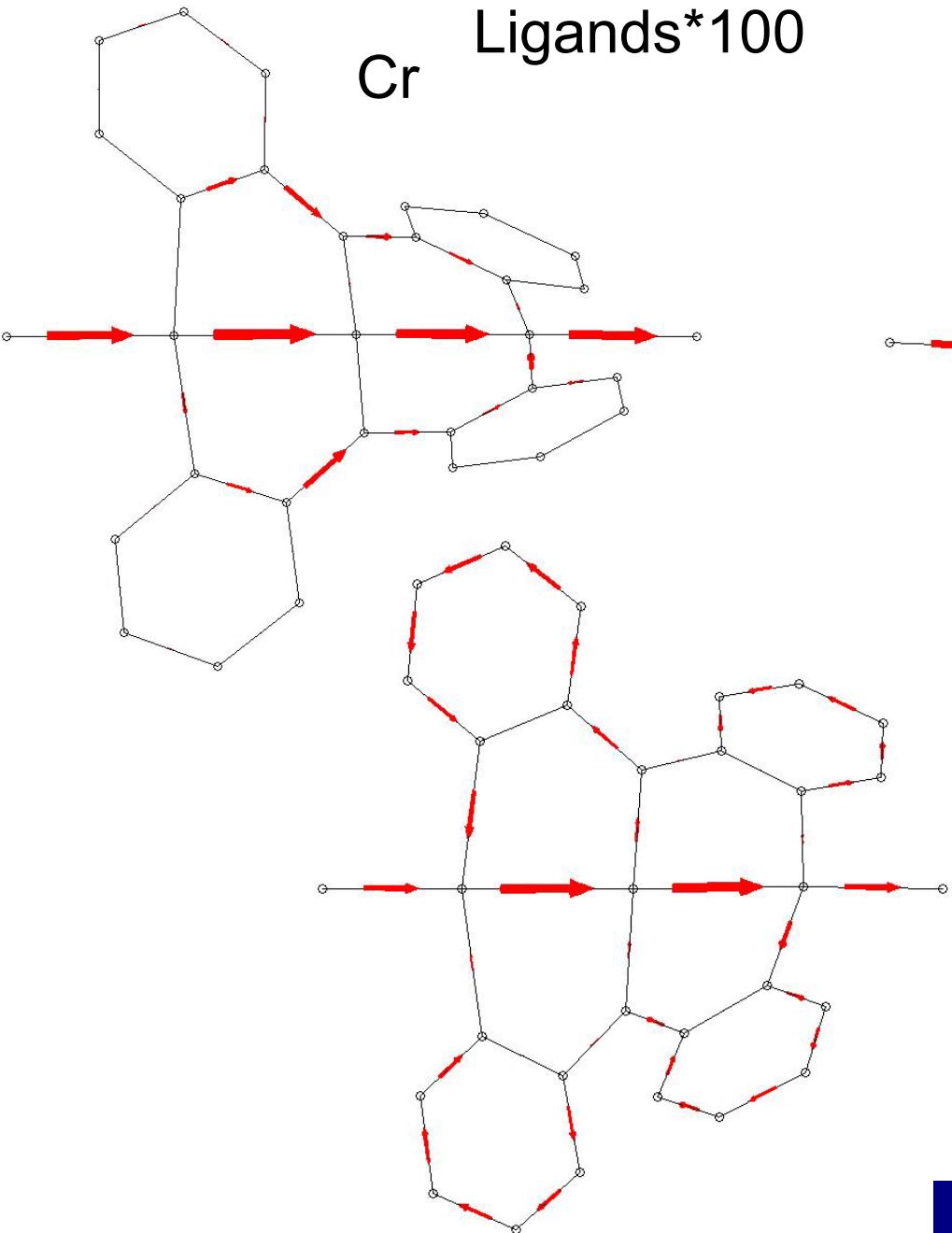
## (2) Non-equilibrium Green's function

Coherent transport model

# I-V Characteristics—theory v.s. experiment

---

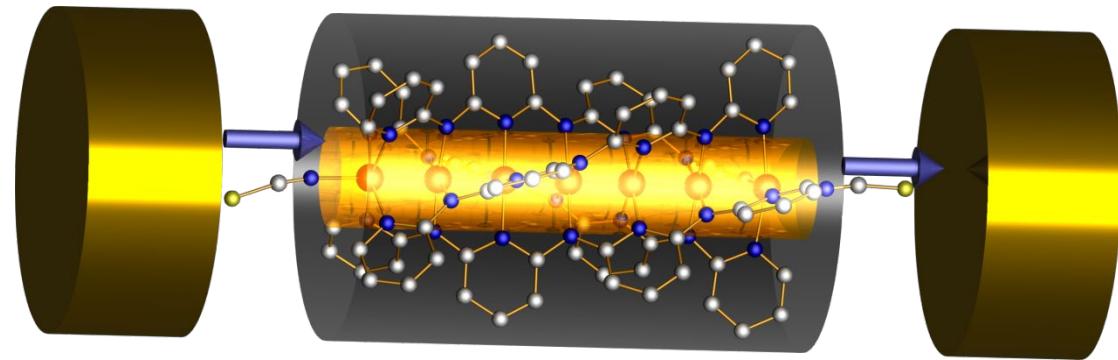




**Ni** Ligands\*10

*J. Phys. Chem. C. 2010, 114, 3641.*

EMACs are indeed the smallest electrical wires!



Charges transport across central metal string, while the internal current is insulated from outside by the surrounding  $\pi$ -conjugated functional group!

Metal string



Conductor

Ligands

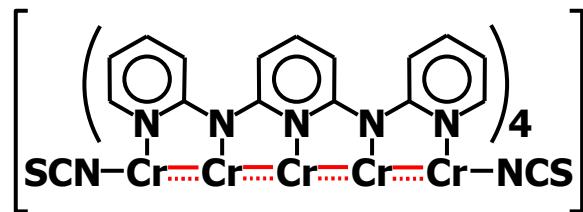


Insulator

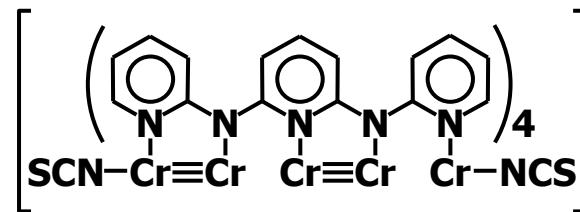
# Measurements of Single Molecular Conductance

Angew. Chem. Int. Ed. 2006, 45, 5814—5818.

M	Ni	Co	single-molecule resistance ( $M\Omega$ )	
			delocalized	localized
$M_3$	3.3	1.9	0.9	1.2
$M_5$	24.0	10.0	3.2	11.3
$M_7$	130	---	6.9	43.4
$\beta$ (per metal)	0.85	0.69	0.50	0.69
$\beta$ (per Å)	0.39	0.33	0.21	0.30



delocalized



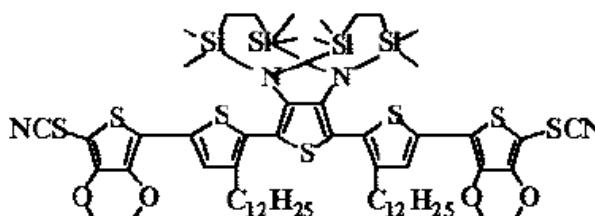
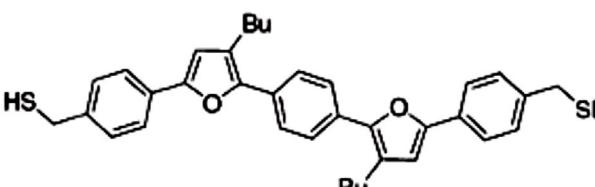
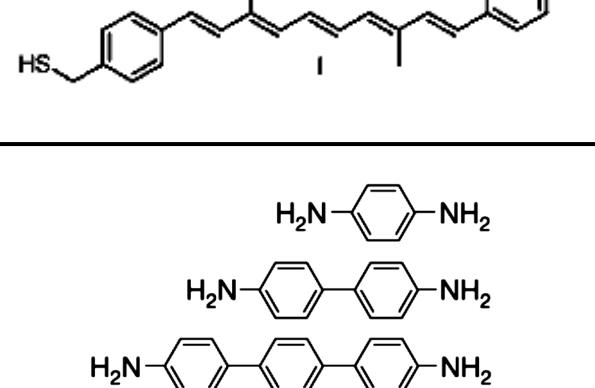
localized

$$R \sim \exp(-\beta d)$$

$\beta$ : tunneling decay const  
d: gap of molecular junctions

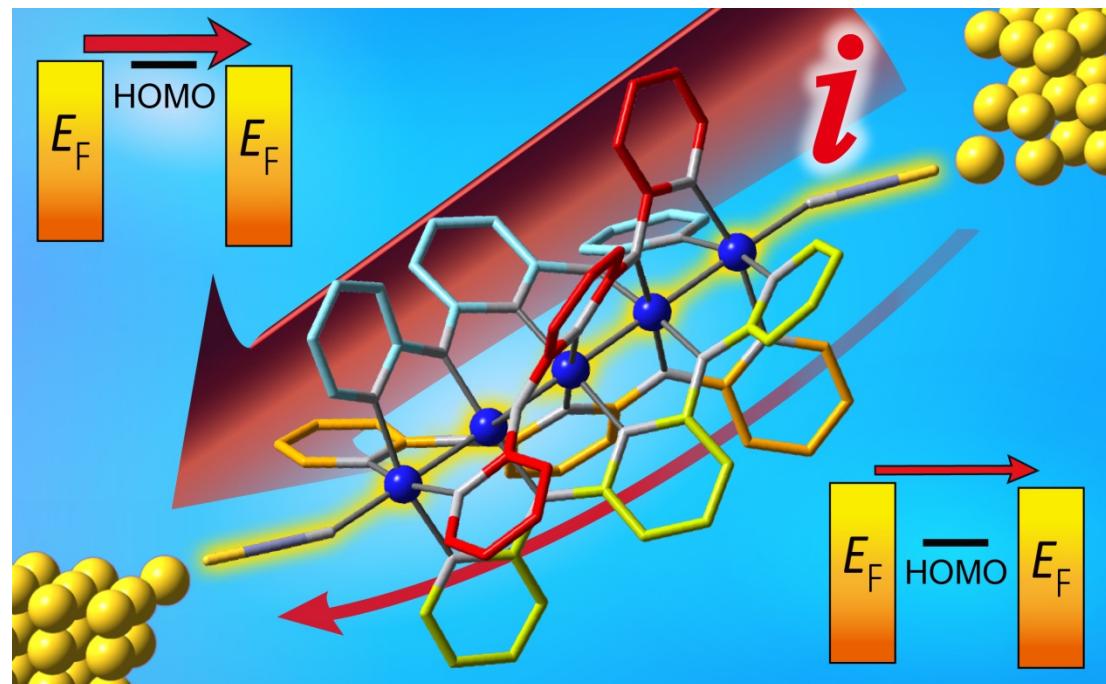
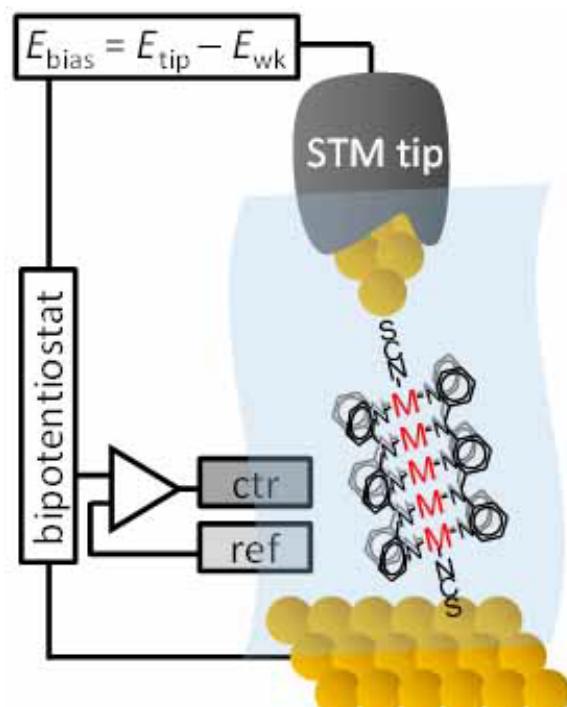
method: STM break junction  
solution: toluene

# List of tunneling decay constants of molecular wires

compounds	$\beta$ ( $\text{\AA}^{-1}$ )	R/length	reference
	0.1	<b>9.1 MΩ</b> $L = 2.3 \text{ nm}$	<i>Nano Lett.</i> 2008, 8, 1237.
	0.13	<b>198 MΩ</b> $L = 2.2 \text{ nm}$	<i>Chem. Commun.</i> 2007, 3074.
Carotenoid Polyenes	0.22	<b>485 MΩ</b> $L = 2.5 \text{ nm}$	<i>JACS</i> 2005, 127, 1384.
	0.4	<b>72.2 MΩ</b> $L = 1.4 \text{ nm}$	<i>Nature</i> 2006, 442, 904.

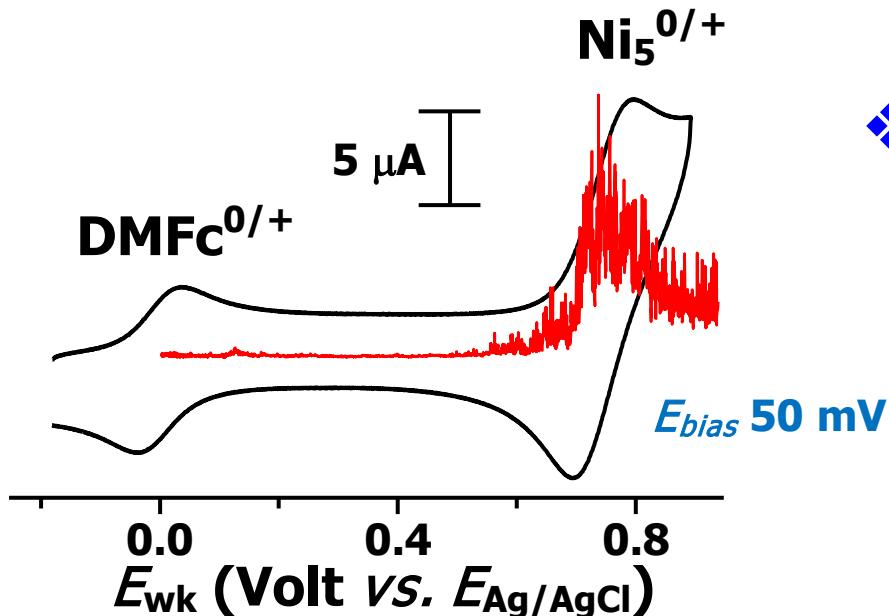
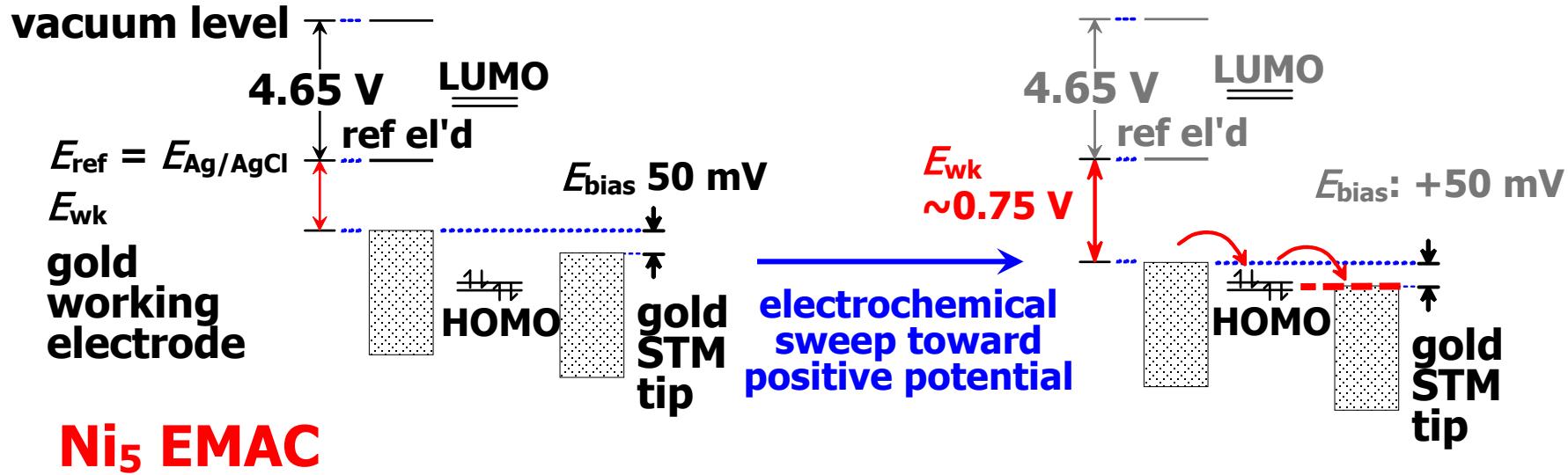
# Energy-Level Alignment for Single-Molecule Conductance of Extended Metal-Atom Chains

## Molecular Switch gated by electrochemical potential



$E_{\text{bias}}: 50 \text{ mV}$   
solution: propylene carbonate

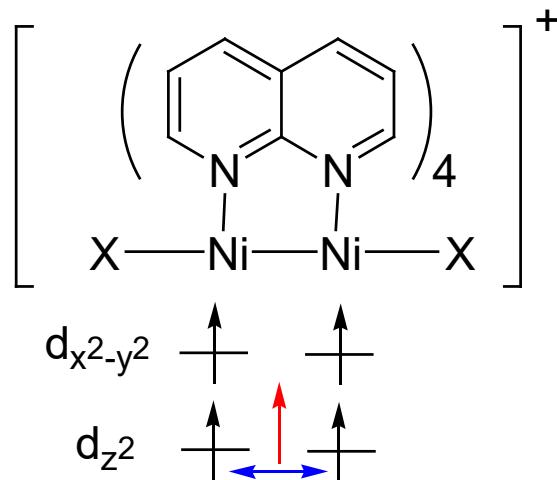
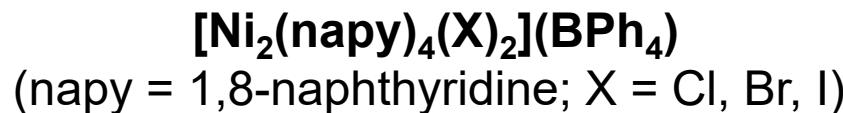
# Measurements of Single Molecular Conductance under Electrochemical Control



- ❖ alignment between electrode Fermi & molecule MOs  
⇒ resonance tunneling  
⇒ stronger current

# New generation of metal string complexes

How to design the new generation of metal string complexes with enhanced metal-metal interactions or novel properties ??



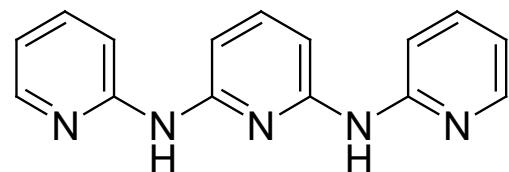
fully delocalized, class III compound

Inorg. Chem., 1974, 19, 1985  
Inorg. Chem., 1978, 17, 2760  
Chem. Eur. J., 2002, 8, 3660

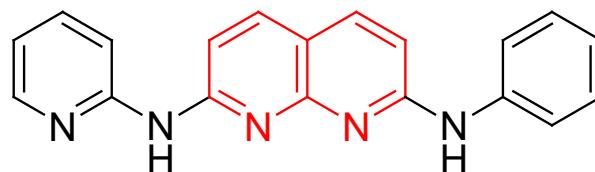
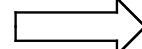
# Introducing the MV dinickel units incorporate into metal framework



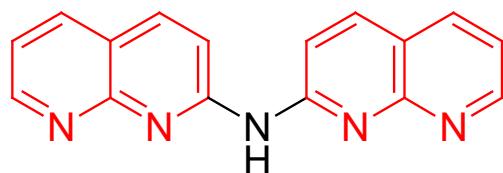
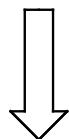
## Design of ligand systems



tripyridyldiamine (H<sub>2</sub>tpda)

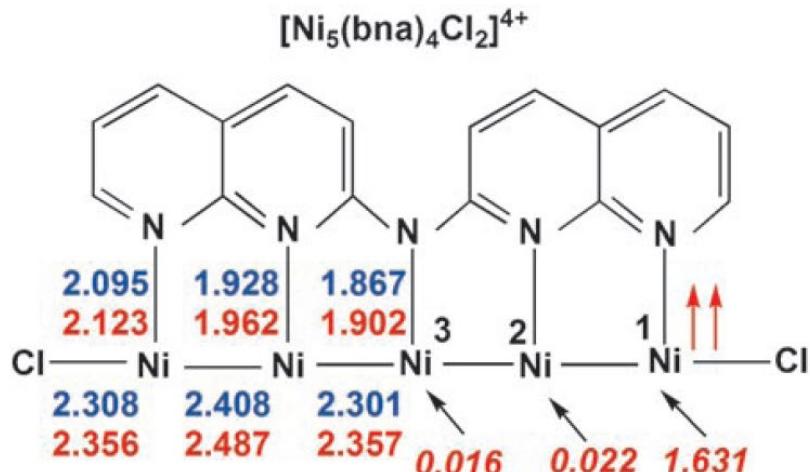
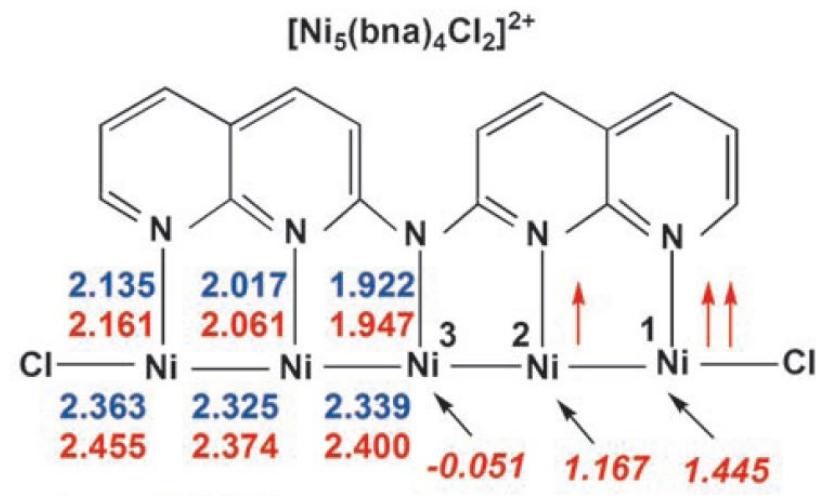
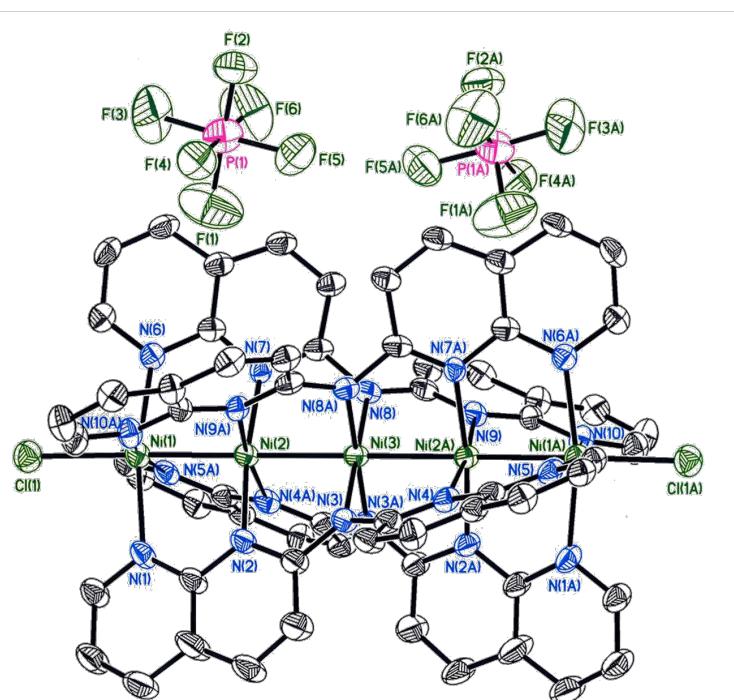


H<sub>2</sub>bpyany

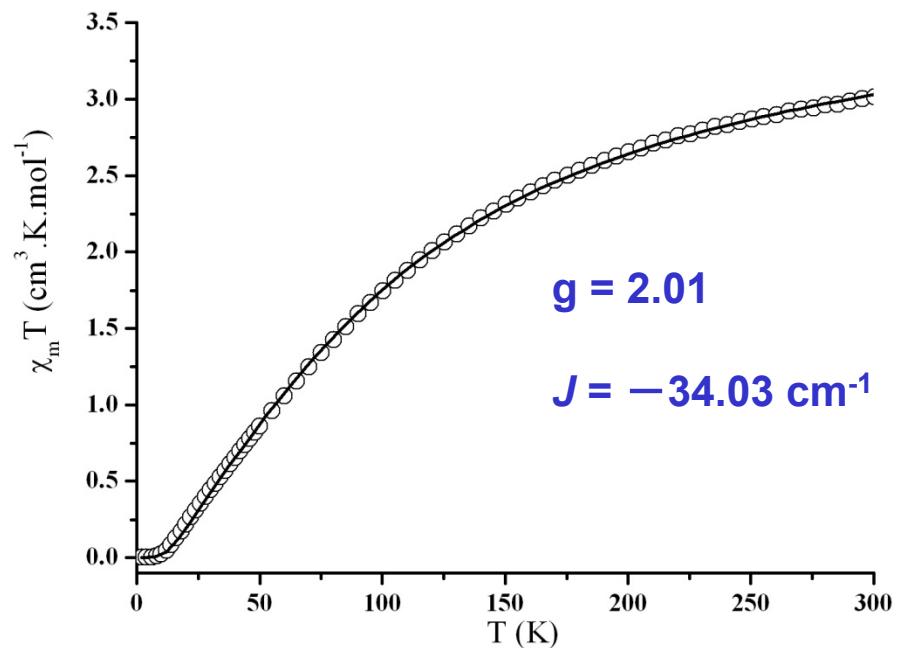
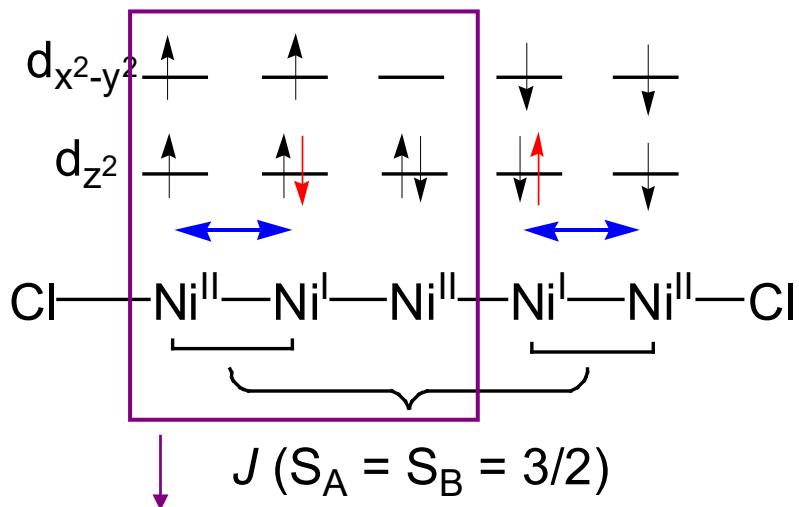


bisnaphthyridylamine (Hbnna)

# 2-electrons reduced MV pentanickel metal string $[Ni_5(bna)_4Cl_2]^{2+}$



# Mechanism (delocalization)



$d_{x^2-y^2}$	0.83	0.82	0.01
$d_{z^2}$	0.60	0.35	0.06

partially delocalized

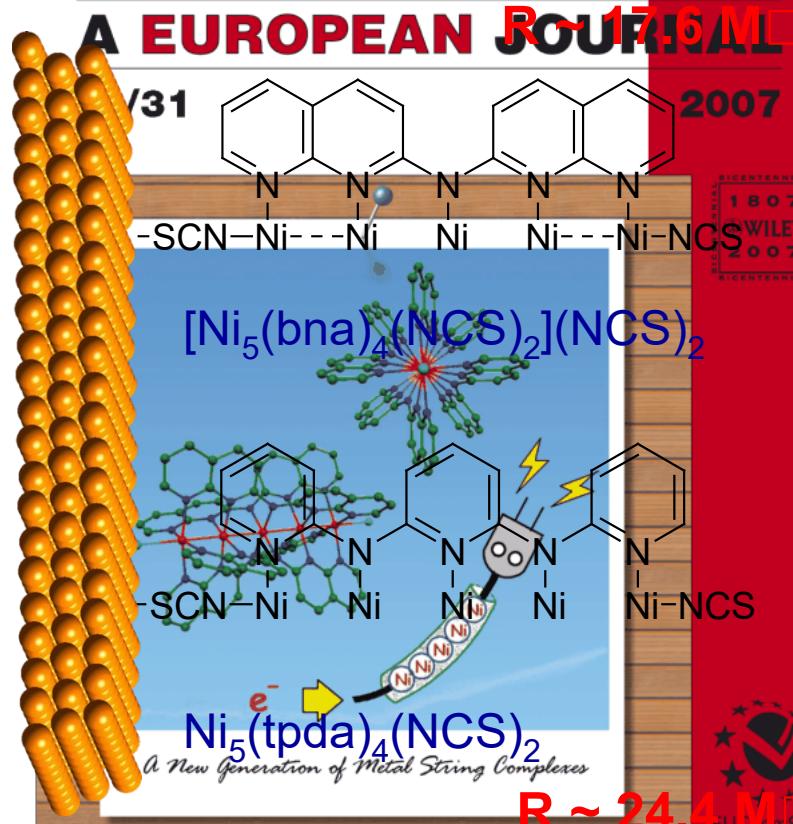


The  $\beta$ -spin electron will partially delocalized between two Ni atoms through the sigma pathway

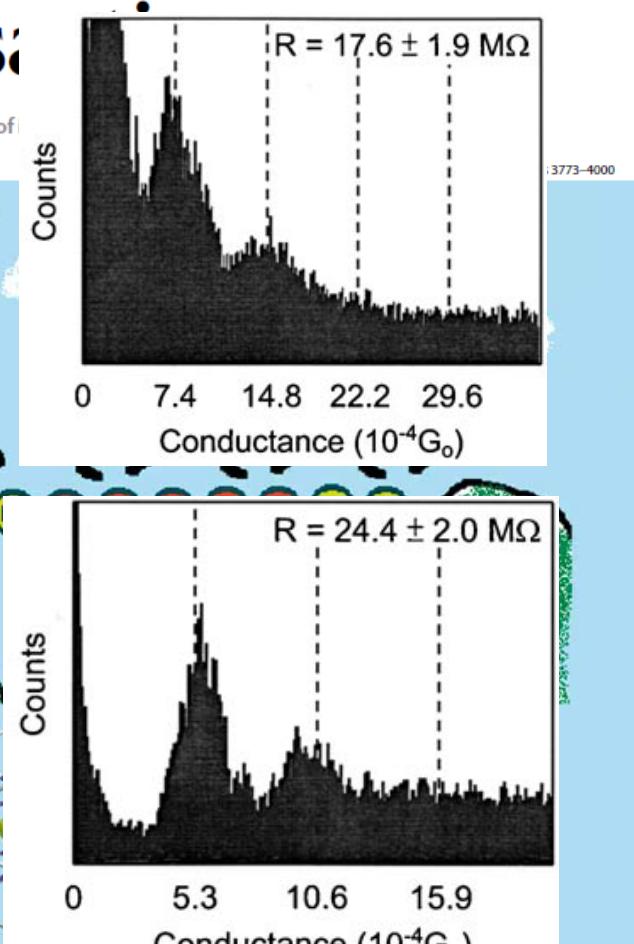
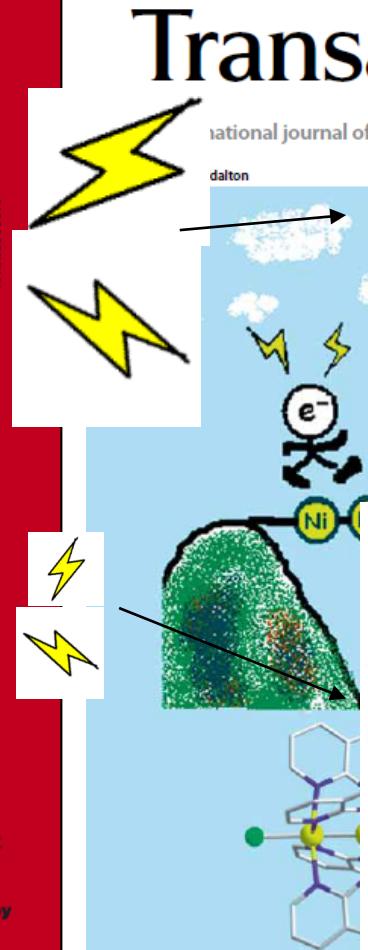
# Conductance measurement of MV metal

string complex

CHEMISTRY

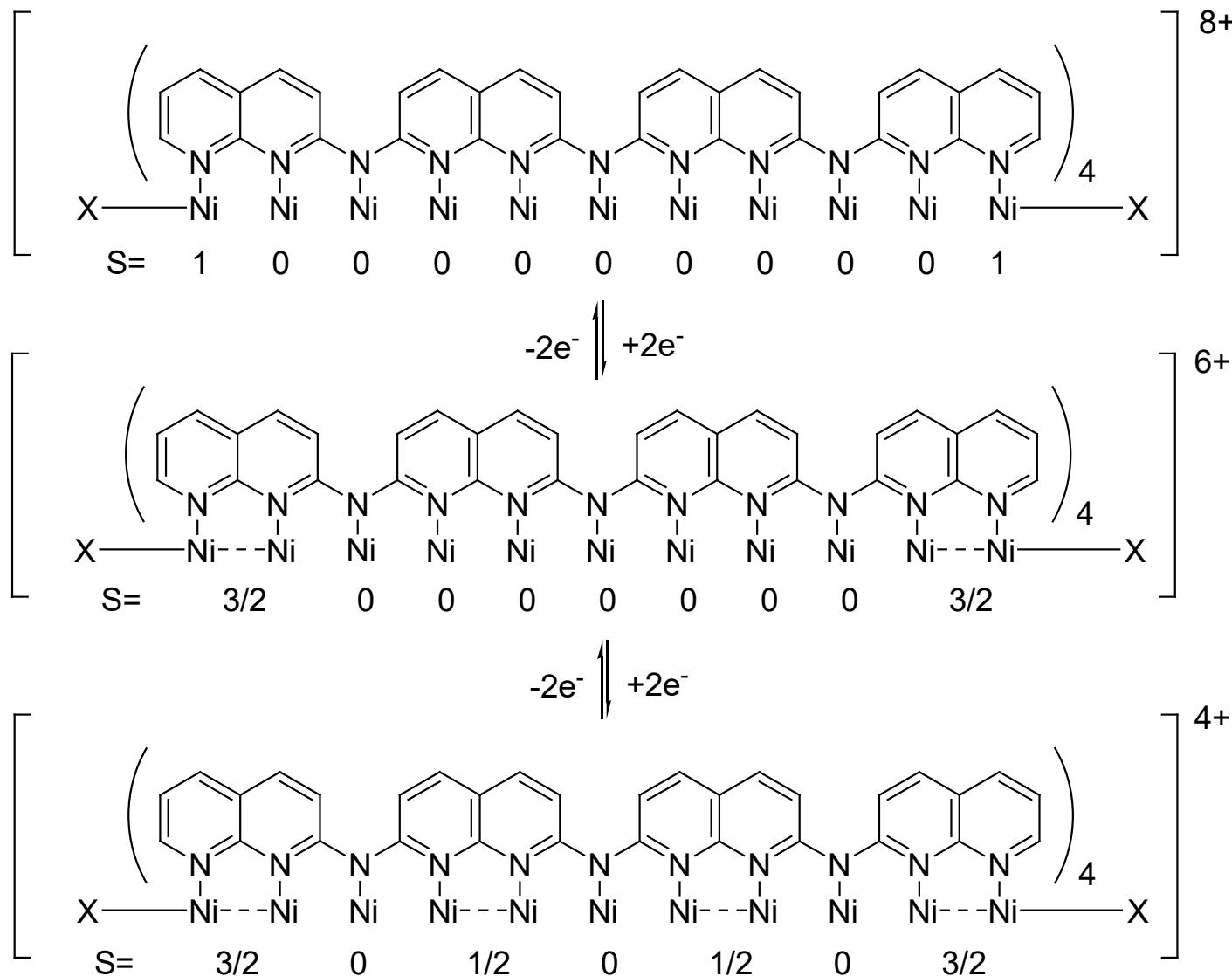


Dalton  
Transac



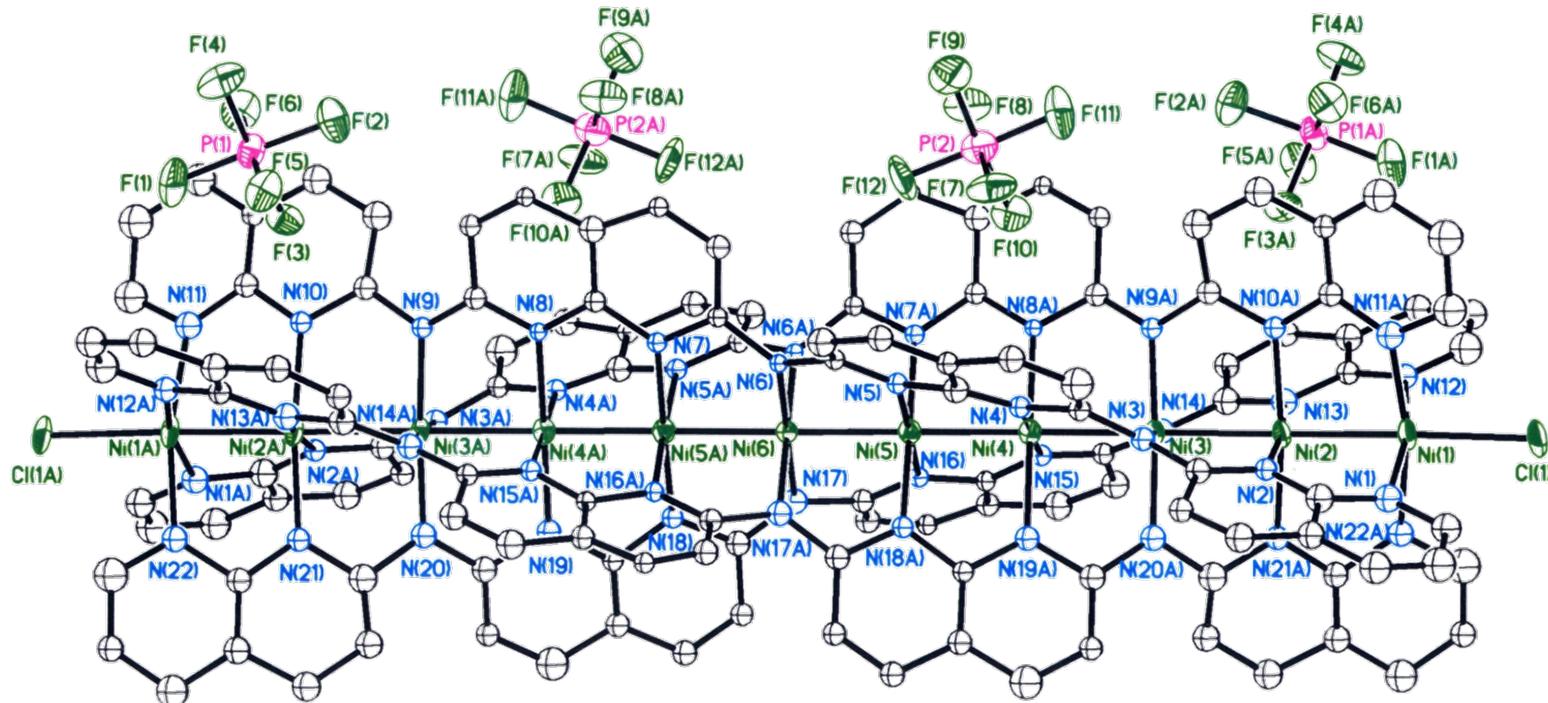
The conductivity of  $[\text{Ni}_5(\text{ona})_4(\text{NCS})_2](\text{NCS})_2$  appears 40% higher than that of  $[\text{Ni}_5(\text{tpda})_4(\text{NCS})_2]$

# *Tetrakis-tetranaphthyridyl-tri-amido Ni<sub>11</sub> system*



# 4-electrons reduced MV undecanickel metal string

## The longest $[Ni_{11}(tenta)_4Cl_2]^{4+}$



Orthorhombic  $Fdd2$

$$a = 21.589(2) \text{ \AA}$$

$$b = 115.289(11) \text{ \AA}$$

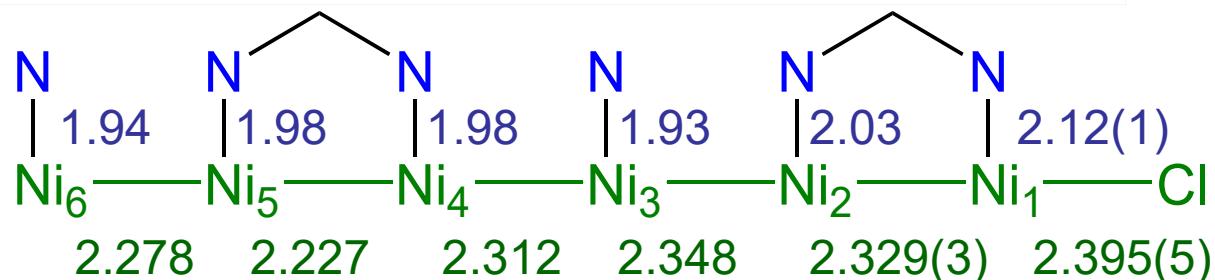
$$c = 13.9168(14) \text{ \AA}$$

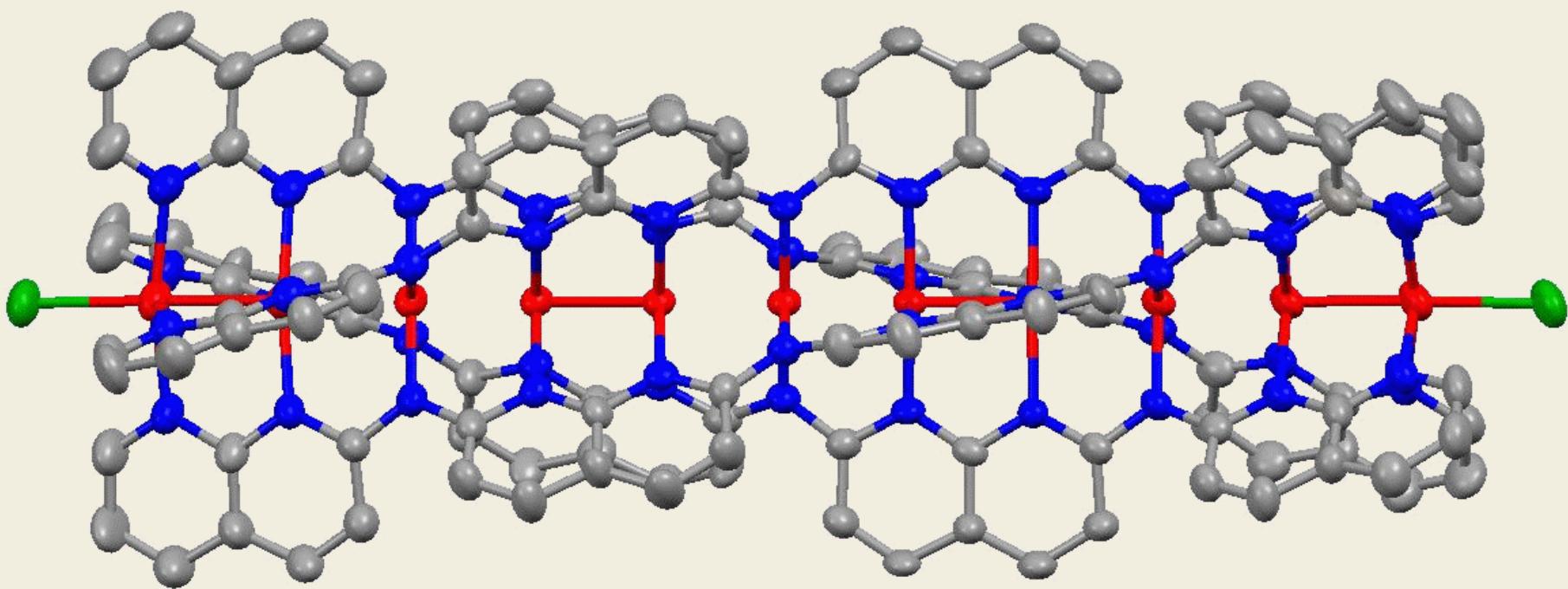
$$\alpha = \beta = \gamma = 90^\circ$$

$$V = 34639(6) \text{ \AA}^3 \quad Z = 8$$

$$R1 = 0.1112 \quad [I > 2\sigma(I)]$$

$$wR2 = 0.2556 \quad [I > 2\sigma(I)]$$





A Journal of the Gesellschaft Deutscher Chemiker

# Angewandte Chemie

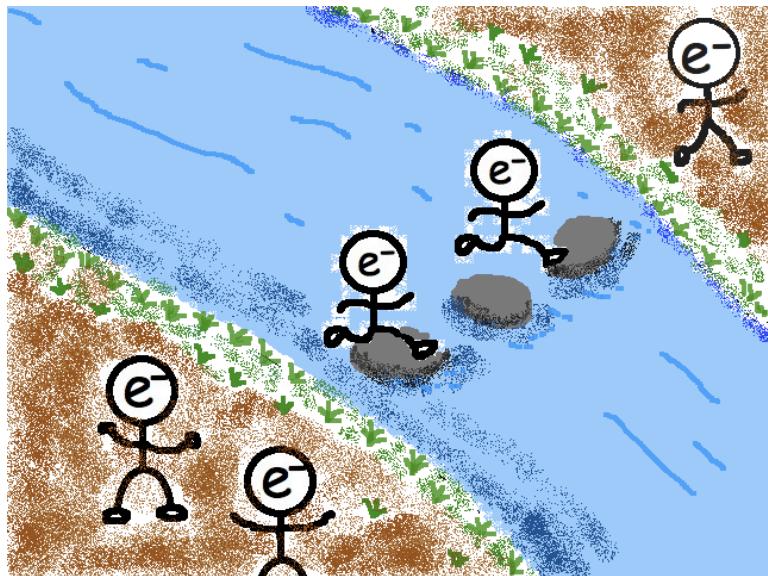
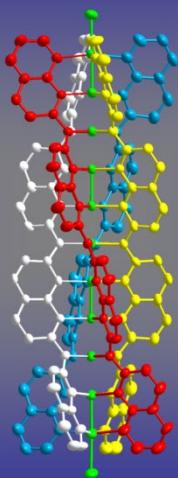
50  
YEARS

International Edition

GDCh

[www.angewandte.org](http://www.angewandte.org)

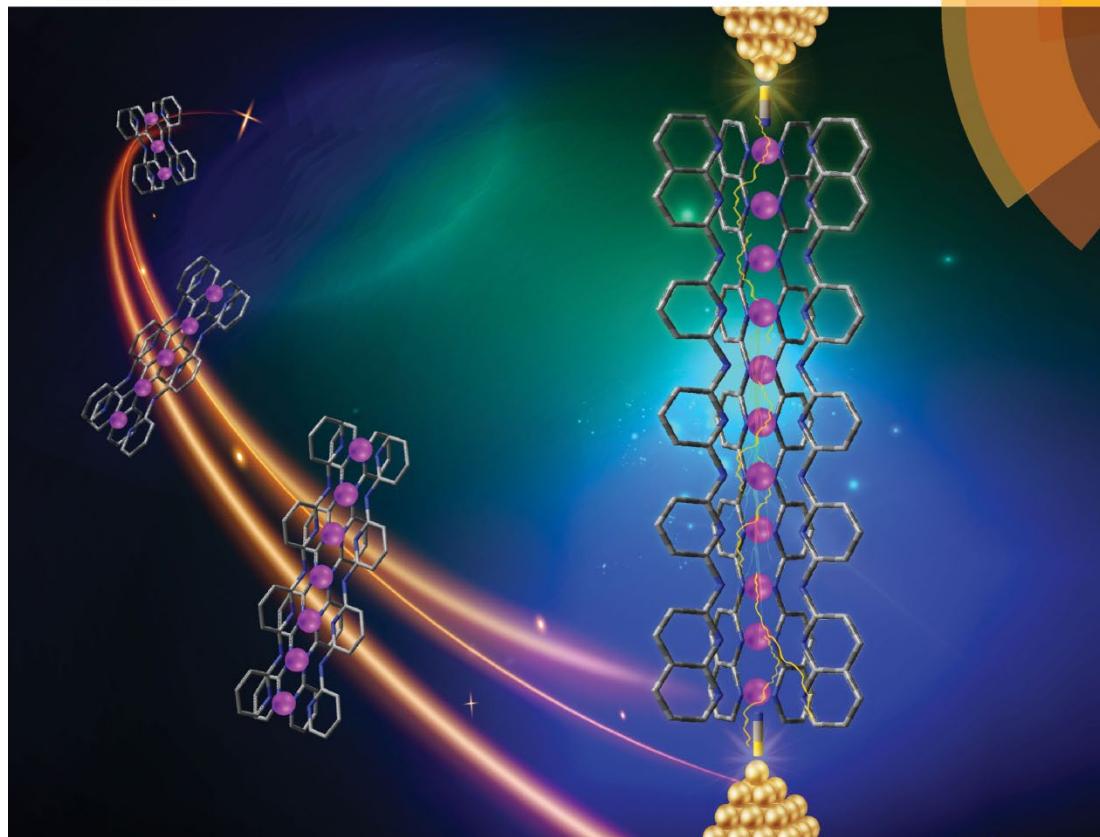
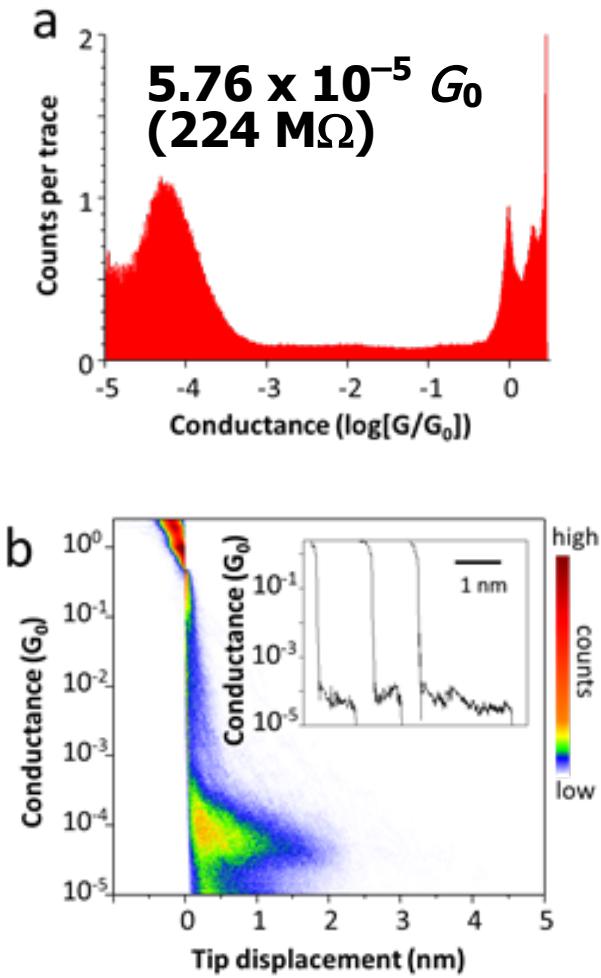
## Mixed-Valence Ni Wire



WILEY-VCH

# ChemComm

Chemical Communications  
rsc.li/chemcomm



ISSN 1359-7345

COMMUNICATION

Chun-hsien Chen, Shie-Ming Peng *et al.*  
A ligand design with a modified naphthyridylamide for achieving the  
longest EMACs: the 1st single-molecule conductance of an undeca-nickel  
metal string

# STM images of $[\text{Ni}_{11}(\text{bnatpya})_4(\text{NCS})_2]^{4+}$

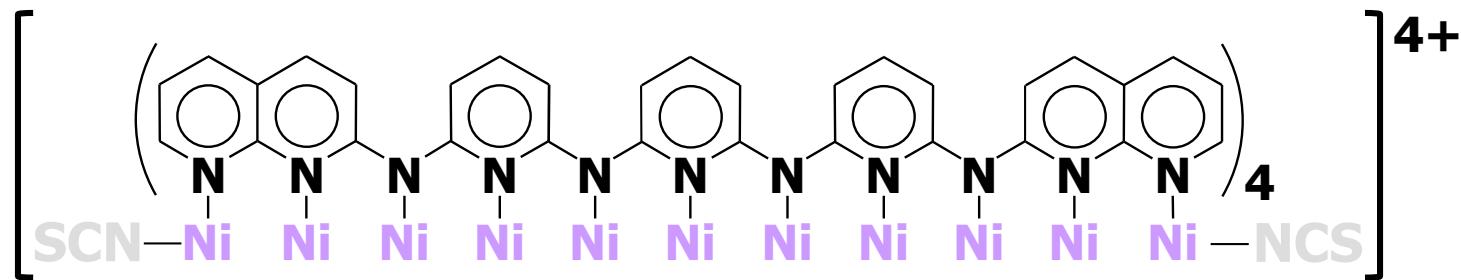
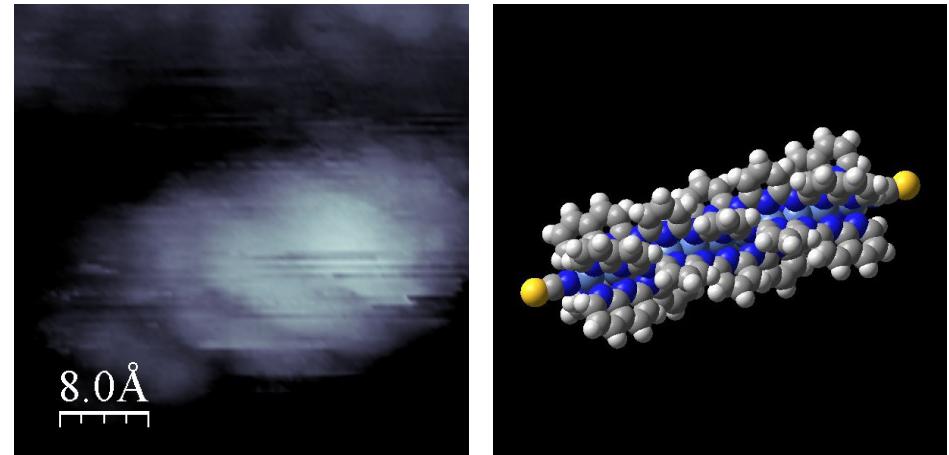
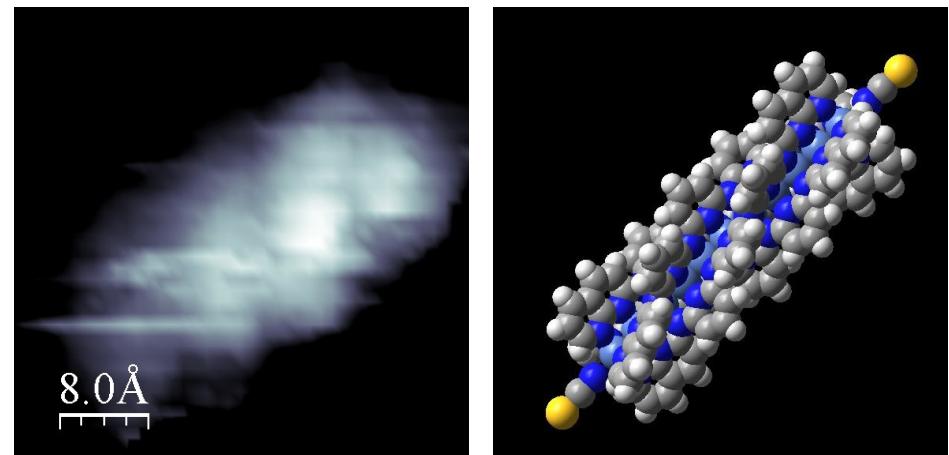
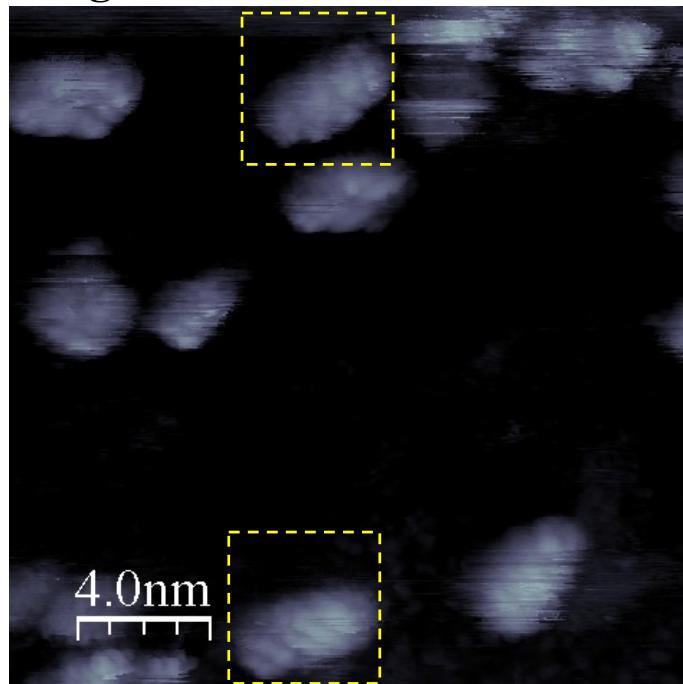


image size: 20 nm x 20 nm

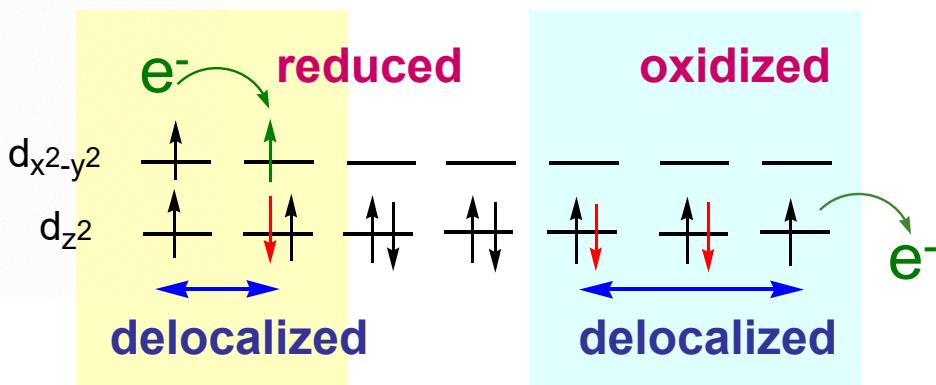
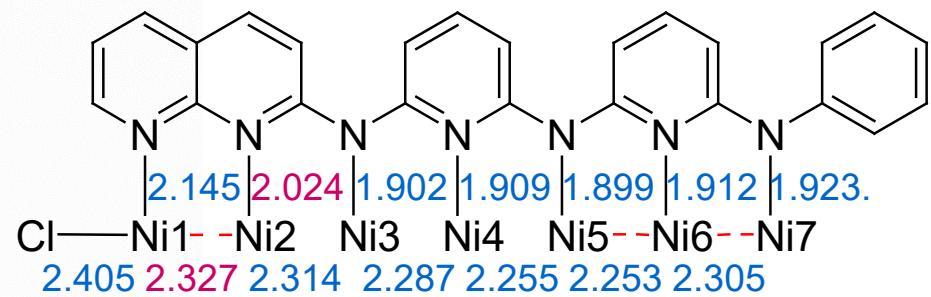
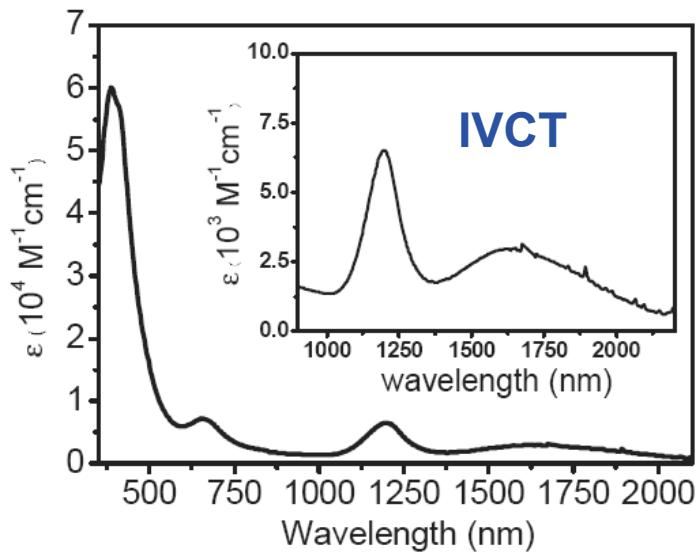
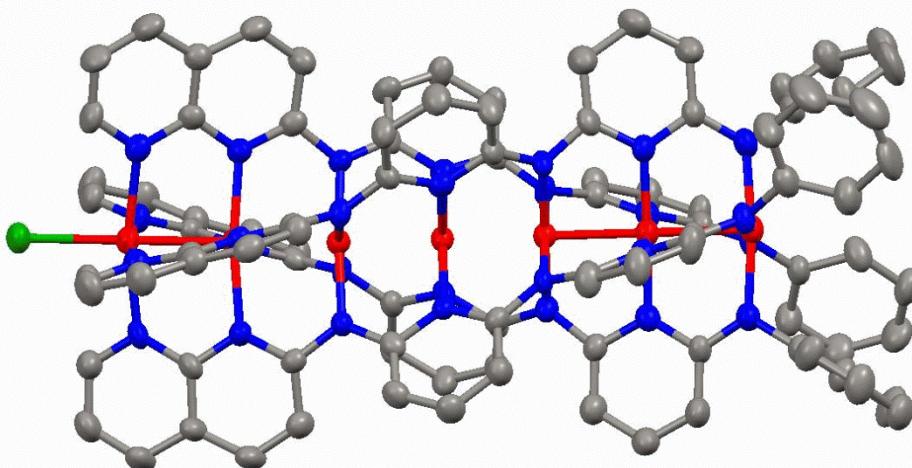


conditions:

UHV-STM at 77 K  
W tip on Au(111)

$E_{\text{bias}}$  1.0 Volt  
 $i_{\text{tunneling}}$  110 pA

# *Disproportionation in metal string:* [Ni<sub>7</sub>(phdptrany)<sub>4</sub>Cl]<sup>1+</sup>

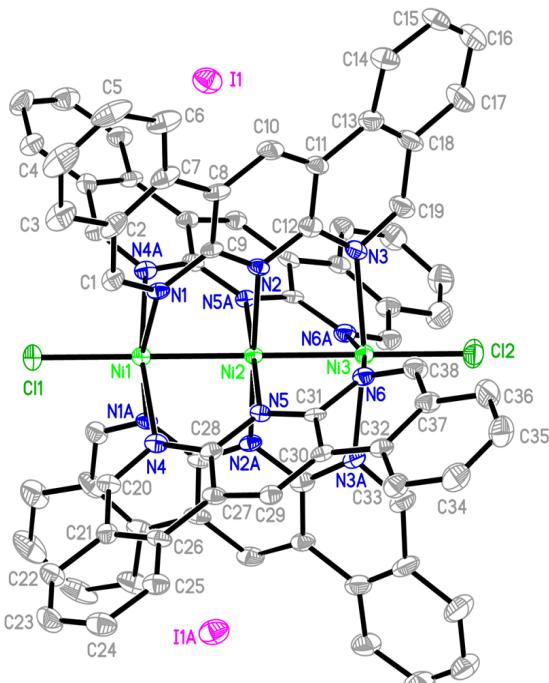
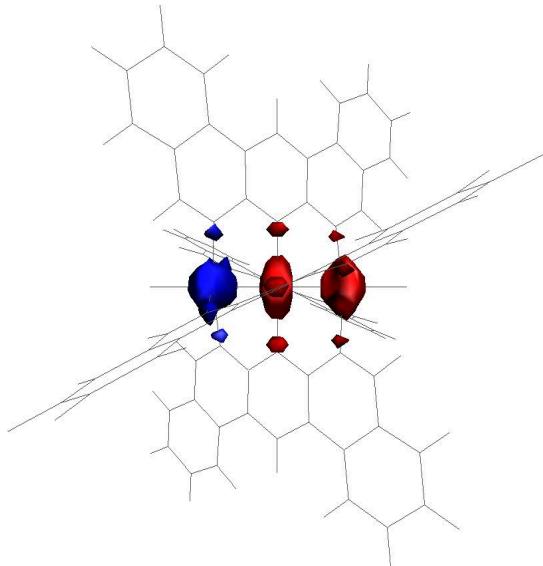


two different MV units,  
charge disproportionate !!

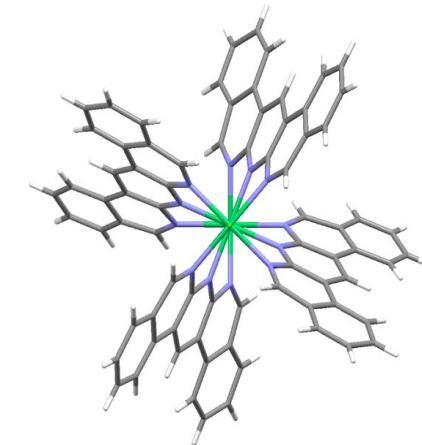
# A Linear Mixed-Valence $[Ni_3]^{5+}$ in Anthyridine Tri-nickel Complex



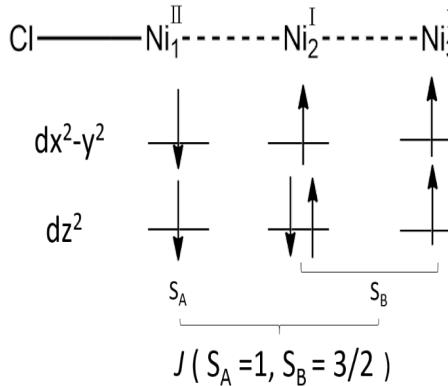
Spin density of  $[Ni_3]^{5+}$



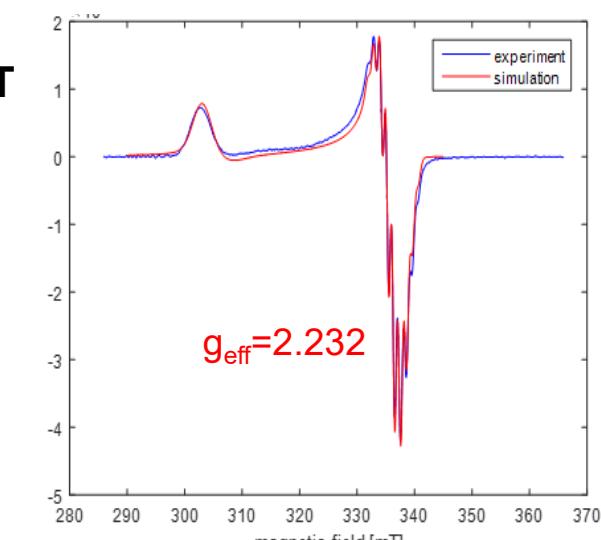
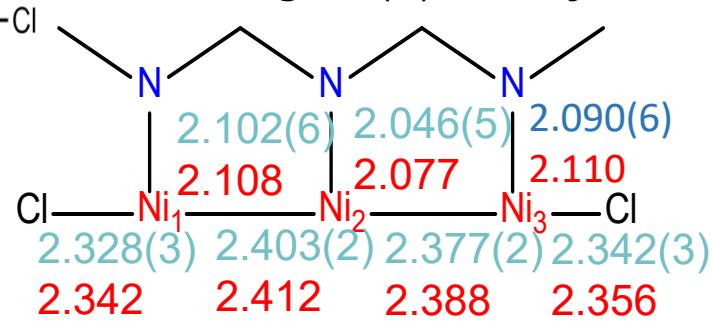
$\angle N\text{-}Ni\text{-}Ni\text{-}N$  angles (about 20-21°)



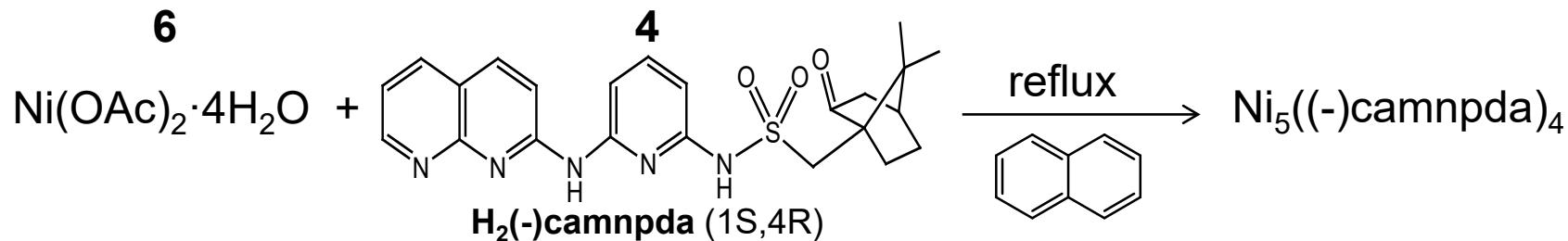
Spin-coupling scheme



Bond lengths (Å) : X-Ray vs DFT



# The synthesis & structure of $\text{Ni}_5((\text{-})\text{camnpda})_4$



$\text{Ni}_5((\text{-})\text{camnpda})_4$

Crystal system **Monoclinic**

Space group **C2**

a = 25.3713 (5) Å

b = 16.7880 (3) Å

c = 26.3214 (5) Å

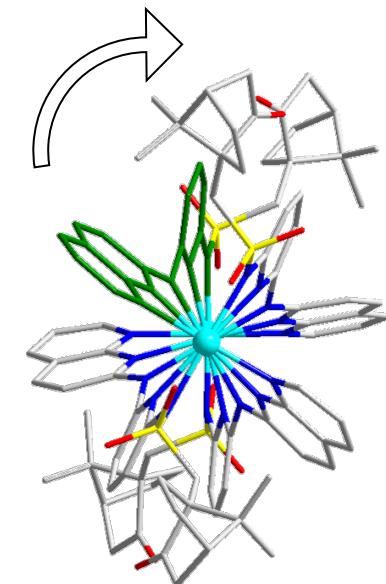
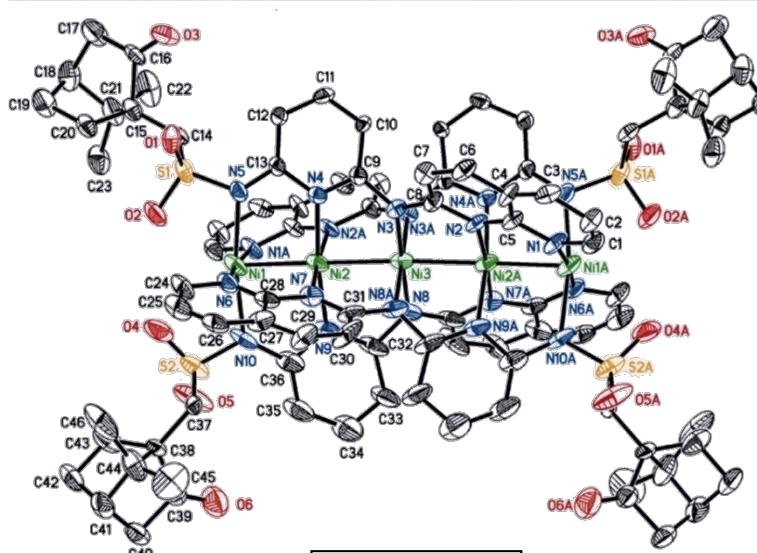
$\alpha$  = 90°

$\beta$  = 106.2702 (8)°

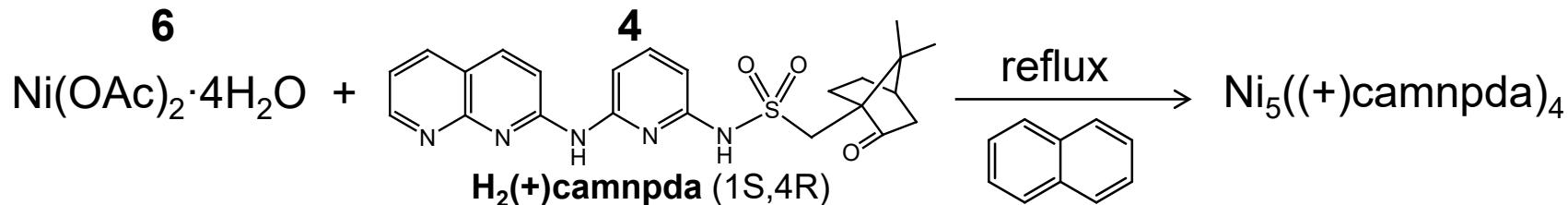
$\gamma$  = 90°

$R_1$  = 0.0778

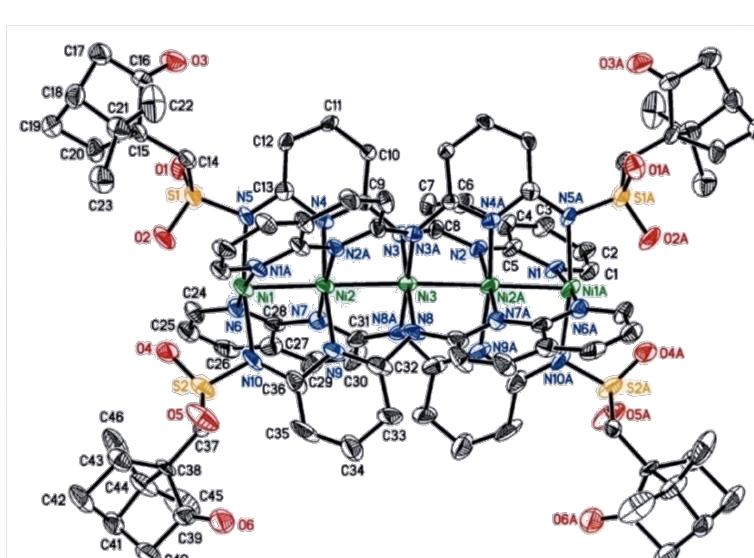
wR<sub>2</sub> = 0.2079



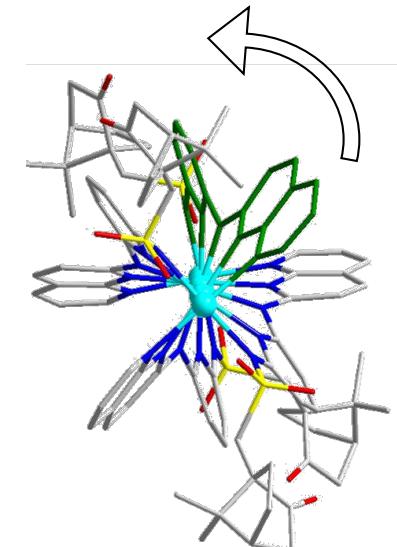
# The synthesis & structure of $\text{Ni}_5((+)\text{camnpda})_4$



<b><math>\text{Ni}_5((+)\text{camnpda})_4</math></b>	
Crystal system	Monoclinic
Space group	C2
a	= 25.3007 (5) Å
b	= 16.7887 (3) Å
c	= 26.4932 (5) Å
$\alpha$	= 90°
$\beta$	= 106.3005 (13)°
$\gamma$	= 90°
$R_1$	= 0.0795
wR <sub>2</sub>	= 0.2134



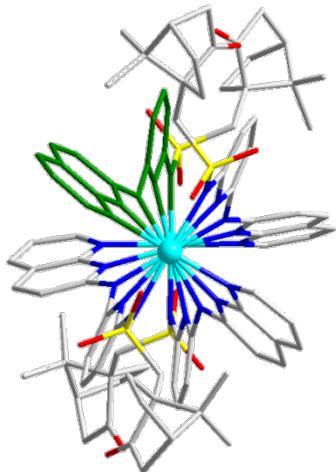
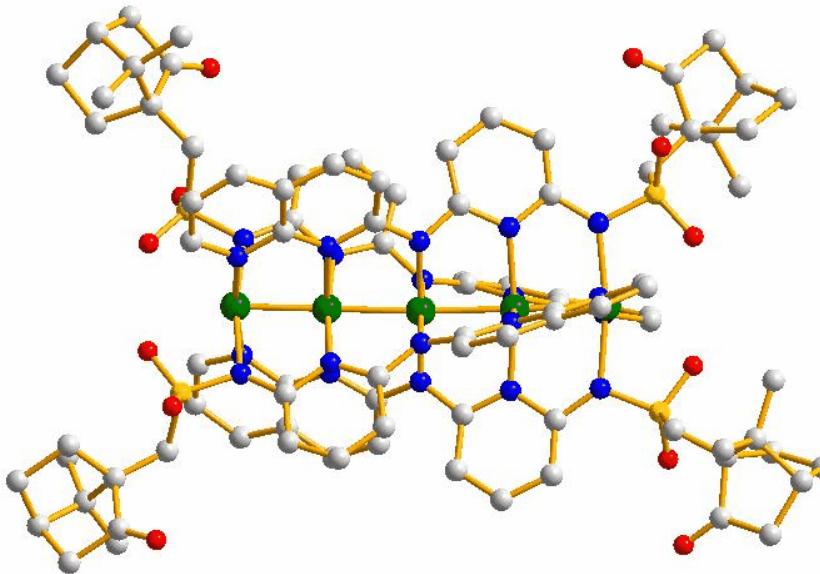
2,2-trans



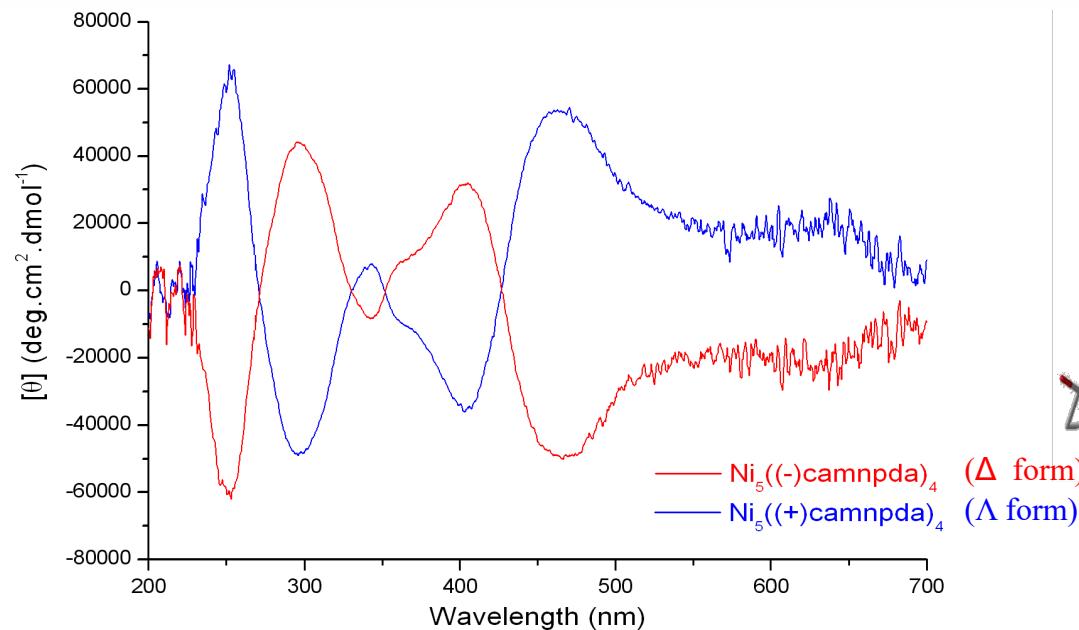
Λ form

# Chirality Control of The Quadruple Helixes of The Metal Strings

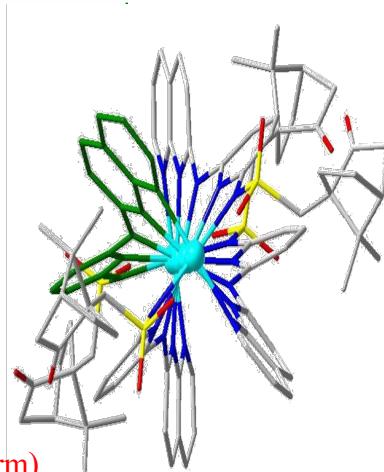
Chem. Asian J. 2014, 9, 3111-3115



$\Delta$  form

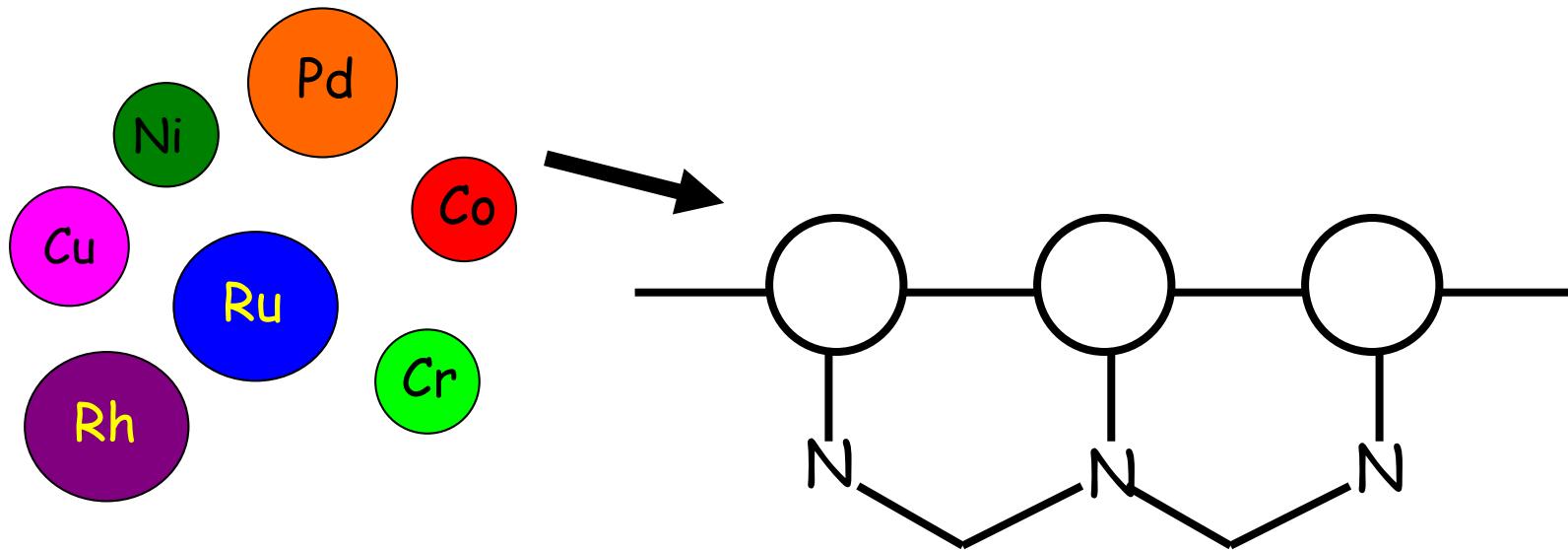


Wavelength (nm)



$\Lambda$  form

# Heteronuclear Metal String Complexes (HMSCs)



Tuning the Physical & Chemical Properties of EMACs

Metal strings



Hetero metal strings

Pure metals



Metal alloy



Cover Picture / Microreview

Chun-hsien Chen, Shie-Ming Peng et al.  
From Homonuclear to Heteronuclear Metal String Complexes

A Journal of



# Syntheses and Characterizations of HMSCs

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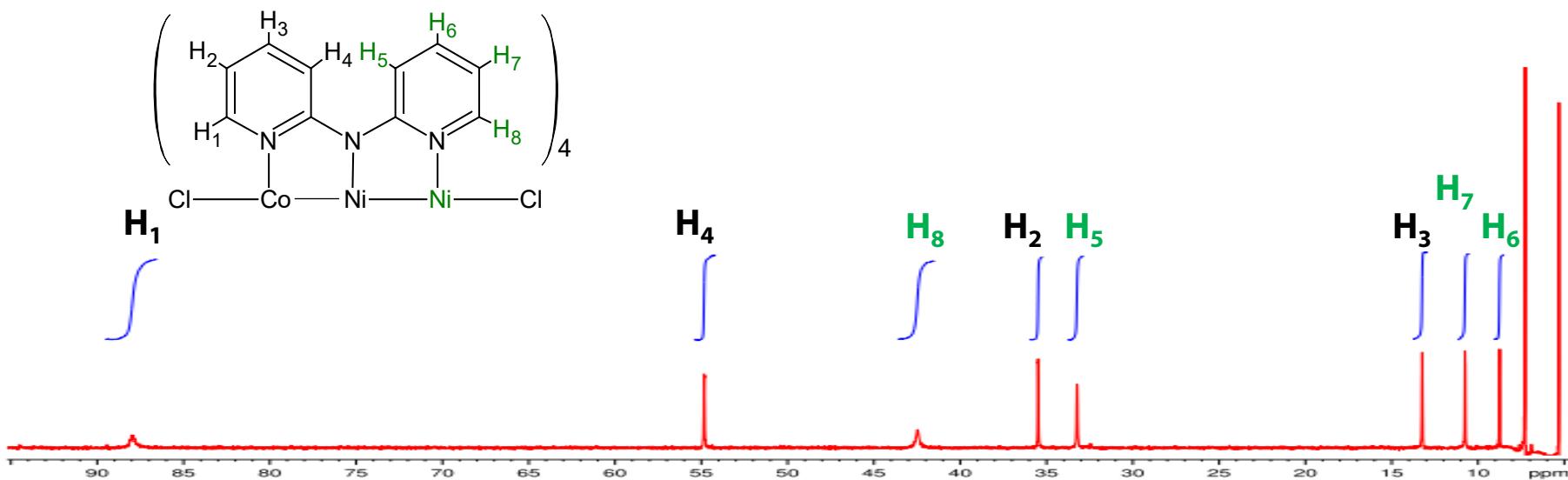
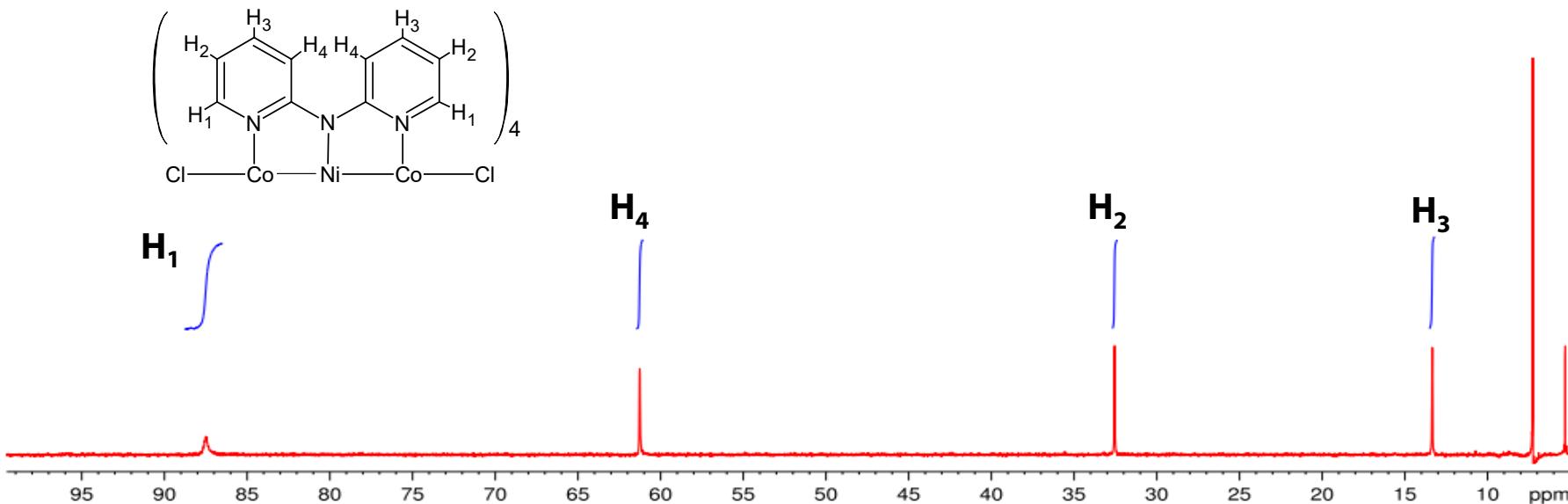
## Synthetic strategies

- (1) Self-Assembly of Metal-Chains  
(Theromodynamic Control)
- (2) Sequential Addition of Different Metal Ions /  
Stepwise formation of Metal-Chain (Kinetic Control)
- (3) Separation  
(Column Chromatography / Chemical Treatments)

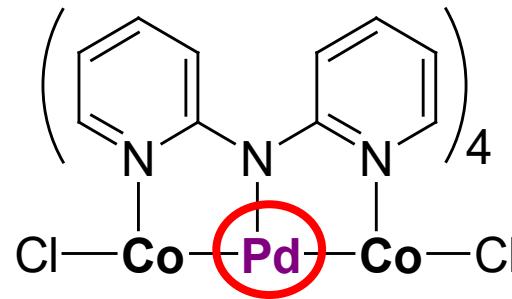
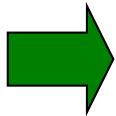
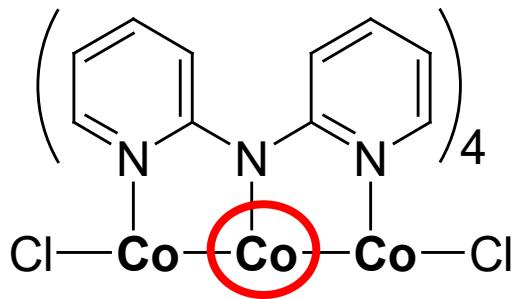
## Characterizations

- (1) Single Crystal Structure Analyses  
(X-ray or Neutron)
- (2) Mass Spectroscopy
- (3) NMR Spectroscopy
- (4) Magnetic properties (SQUID)

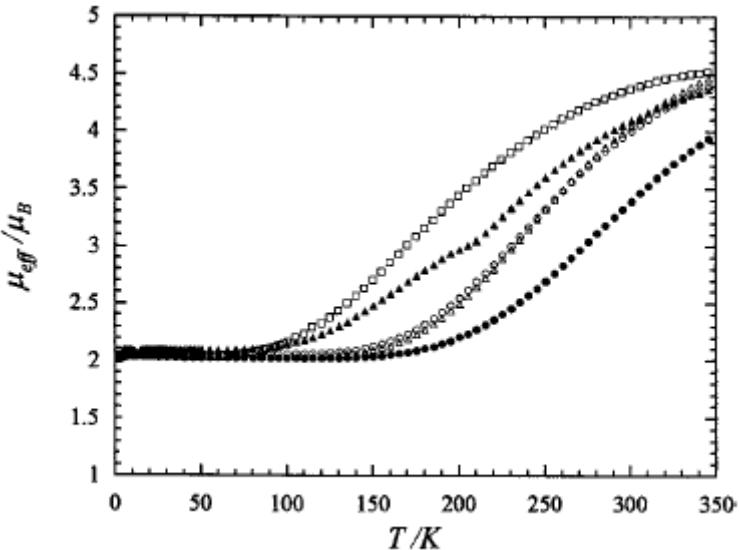
# <sup>1</sup>H NMR Identification of Arrangement of Metal Ions



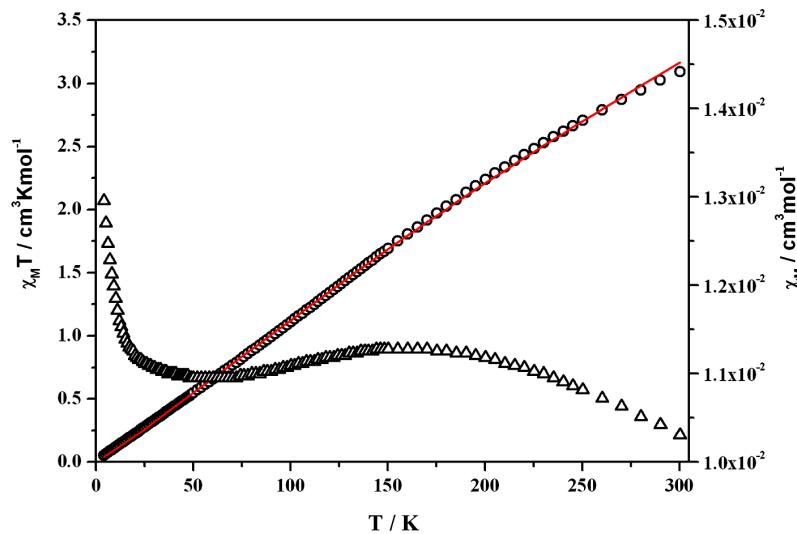
# The First Heterotrinuclear Metal String Complex: [CoPdCo(dpa)<sub>4</sub>Cl<sub>2</sub>]



spin-crossover



strong antiferromagnetic



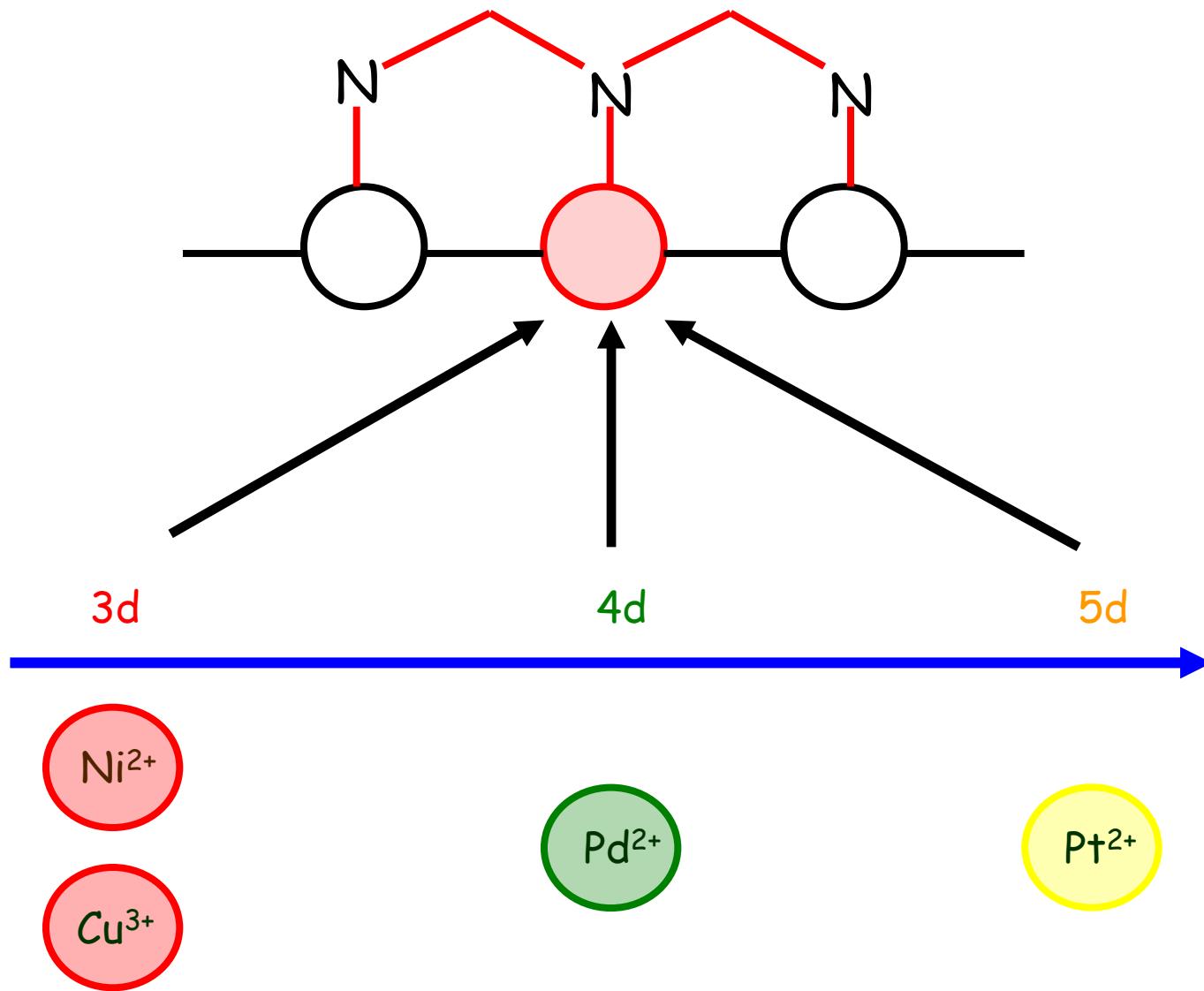
Chem. Commun. 1994, 2377

Cotton, et al., Inorg. Chem. 2001, 40, 1256

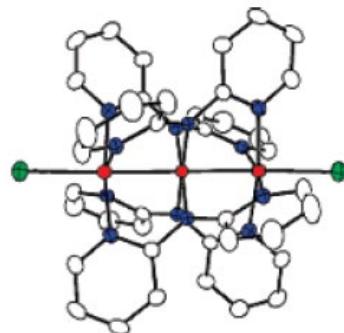
Angew. Chem. Int. Ed. 2007, 46, 3533

# Manipulation of Magnetic Interaction by Substituting the Central d<sup>8</sup> Atom and terminal metal ions (from d<sup>5</sup> to d<sup>10</sup>)

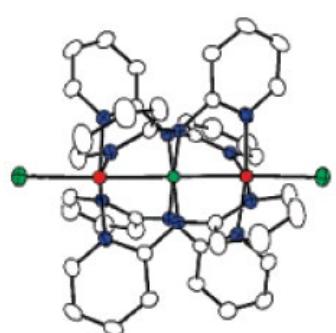
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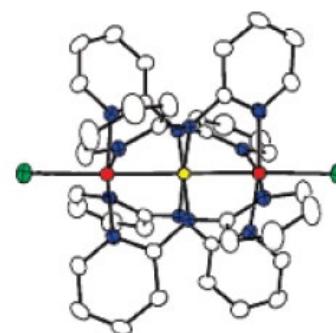
## [Cu<sub>3</sub>Cu(dpa)<sub>4</sub>Cl<sub>2</sub>] (M = Pd & Pt)



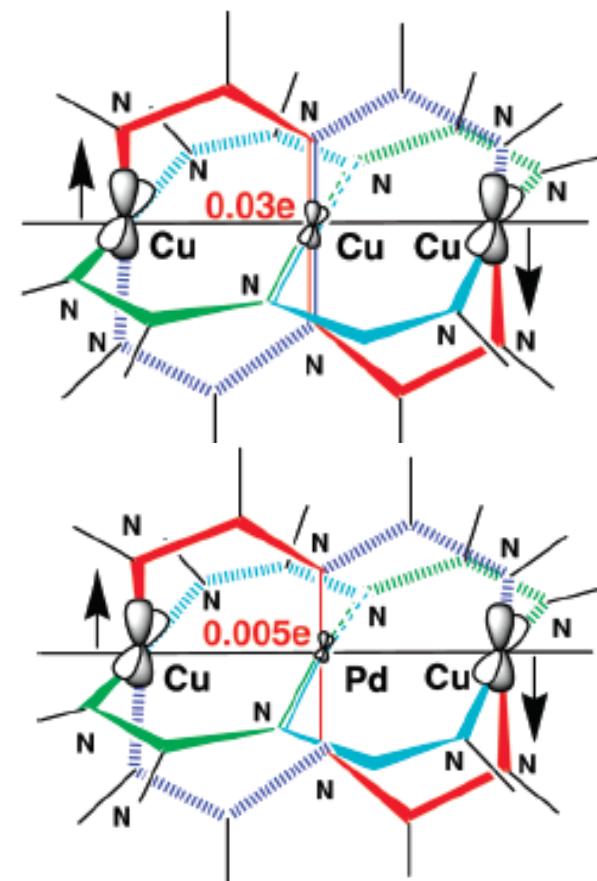
[Cu<sub>3</sub>(dpa)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>  
-2J = 34 cm<sup>-1</sup>



Cu<sub>2</sub>Pd(dpa)<sub>4</sub>Cl<sub>2</sub>  
-2J = 7.45 cm<sup>-1</sup>



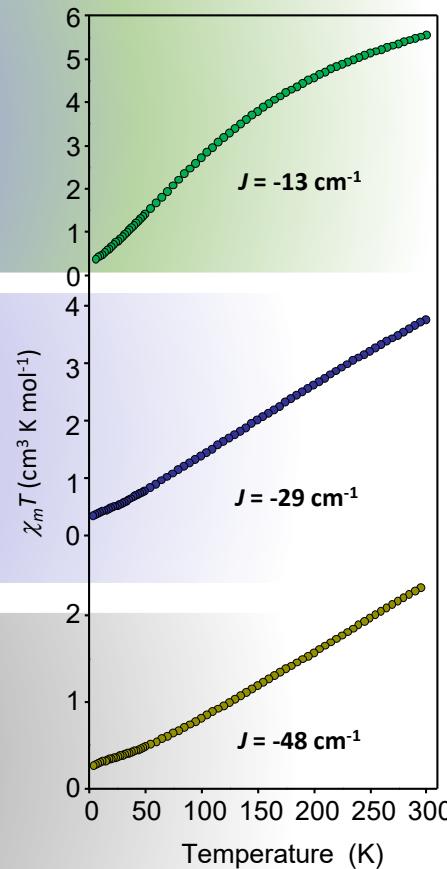
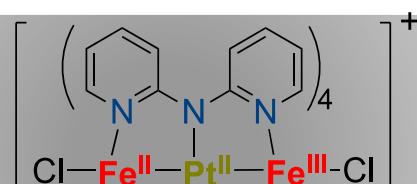
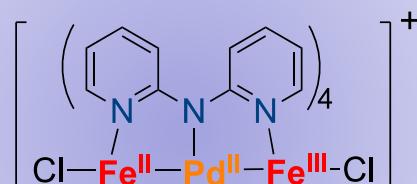
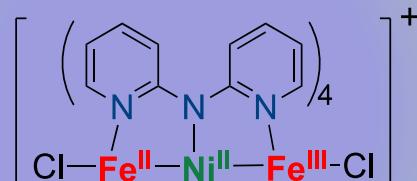
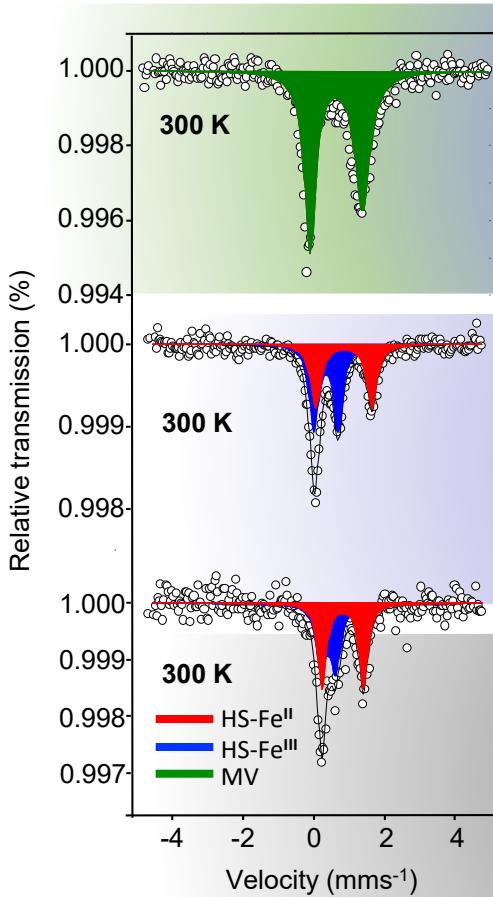
Cu<sub>2</sub>Pt(dpa)<sub>4</sub>Cl<sub>2</sub>  
-2J = 0.77 cm<sup>-1</sup>



The exchange interaction between two terminal Cu(II) ions could be fine-tuned by replacing the central diamagnetic d<sup>8</sup> metal ions. (Cu<sup>III</sup>, Pd<sup>II</sup>, Pt<sup>II</sup>)

The difference of the J values is attributed to the energy gap between two b<sub>2</sub> symmetry orbitals and the variances of the spin density at the central crossing point metal ion.

# Mediating the Electron Delocalization and Antiferromagnetic Coupling of MV Diiron Sites in $[\text{FeMFe}(\text{dpa})_4\text{Cl}_2]^+$ (M = Ni, Pd, Pt) Complexes



Electron Delocalization

Antiferromagnetic Coupling

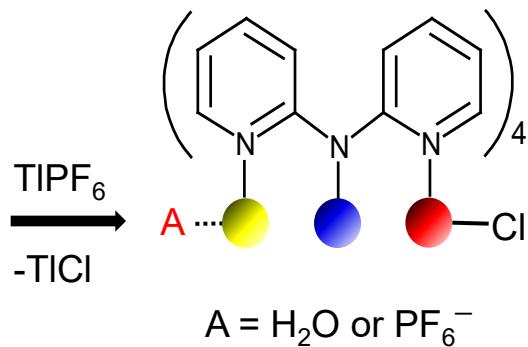
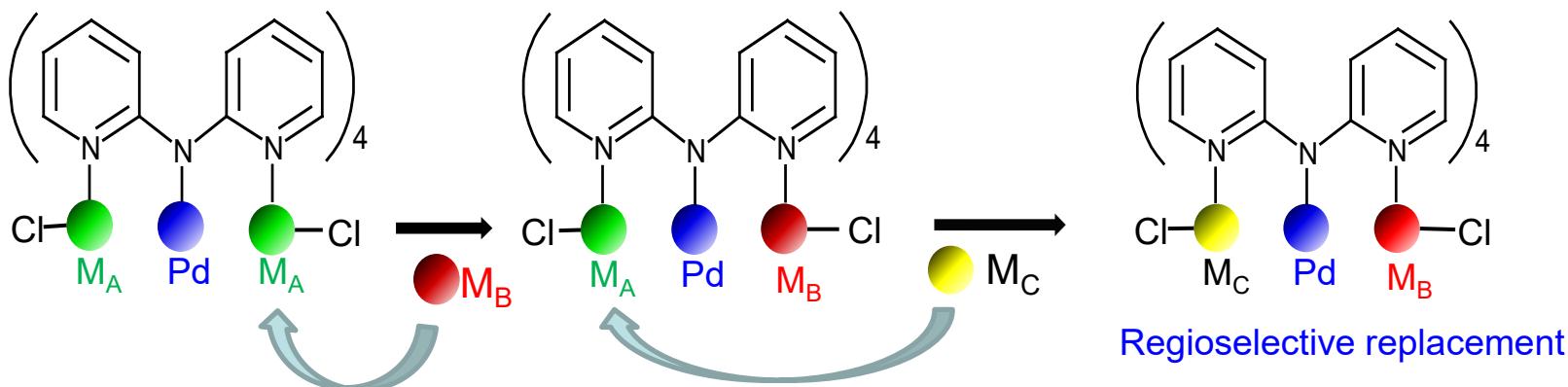
# Heterotrimetallic Complexes: $[\text{MPdM}'(\text{dpa})_4\text{Cl}_2]$

**M / M' = Ni, Co, Fe, Mn, Cd, Cu (M ≠ M')**

Substitution sequence:

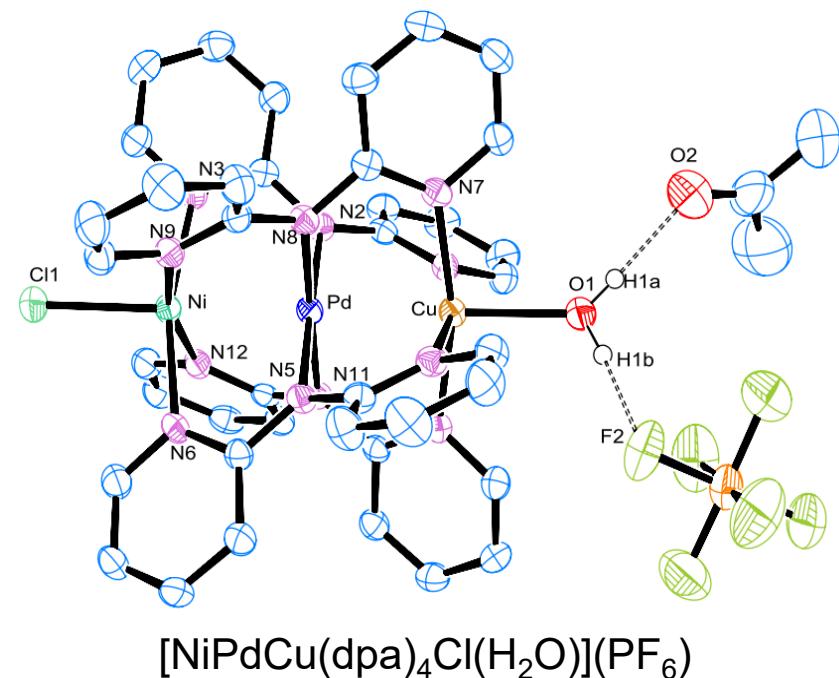
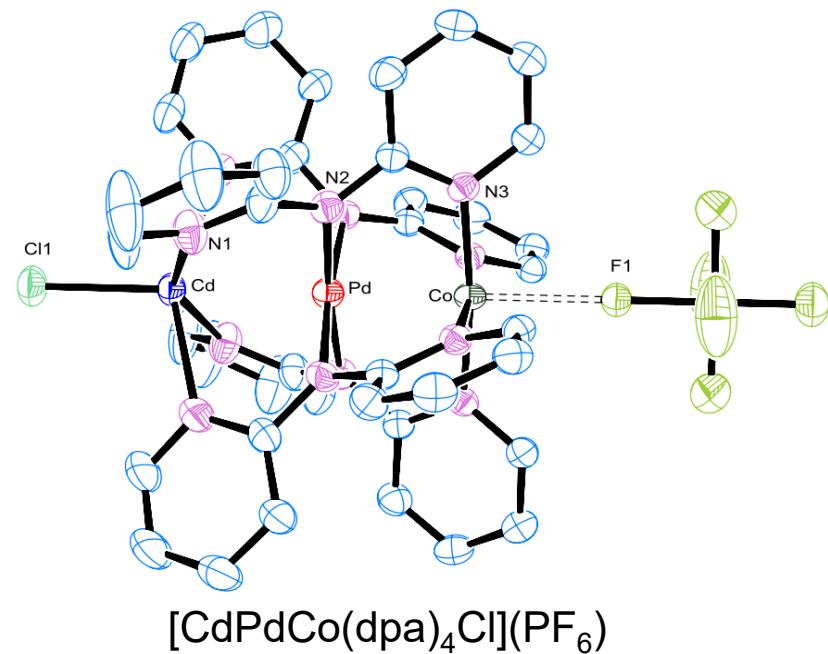
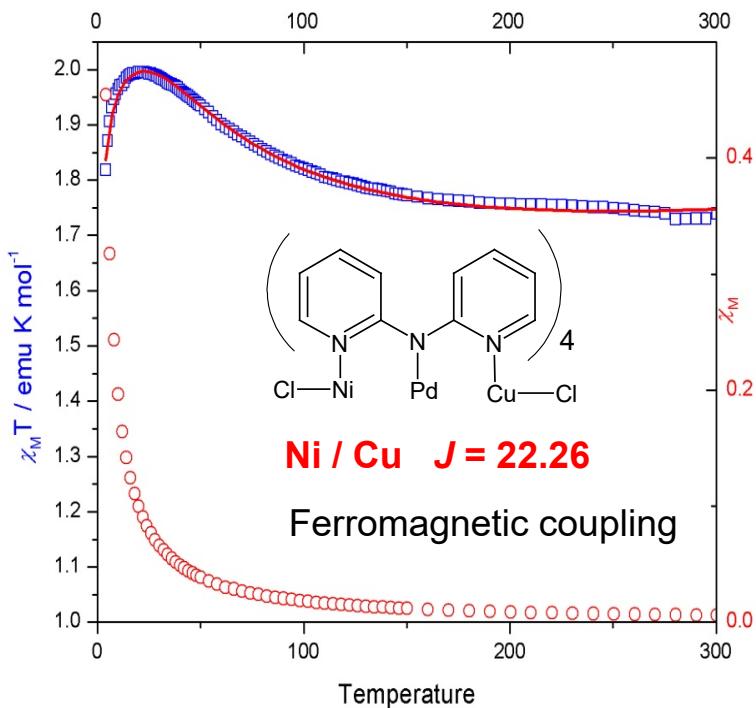
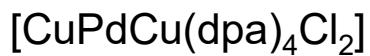


Irving-Williams series :  $\text{Zn}^{2+} < \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$

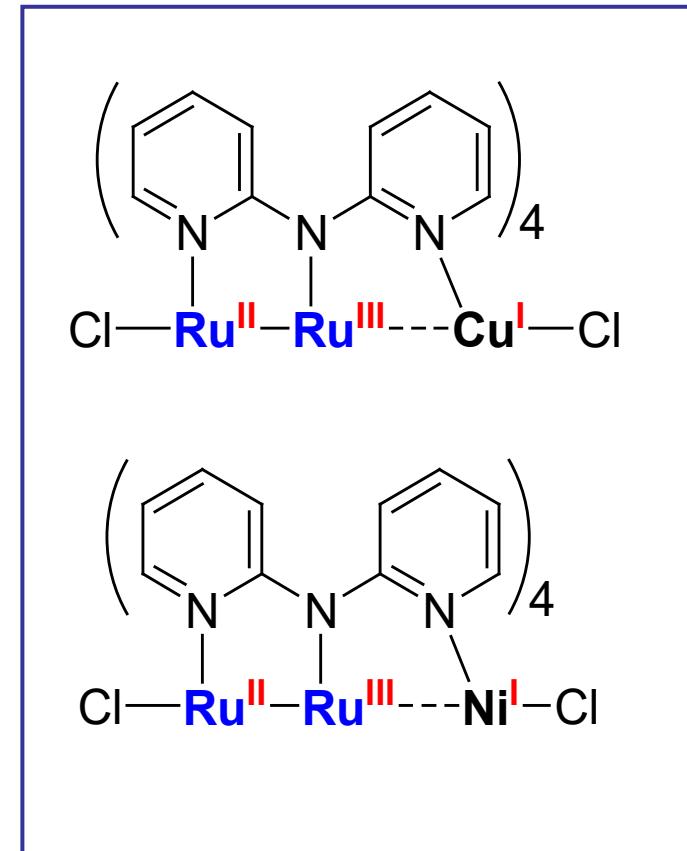
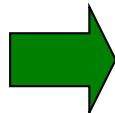
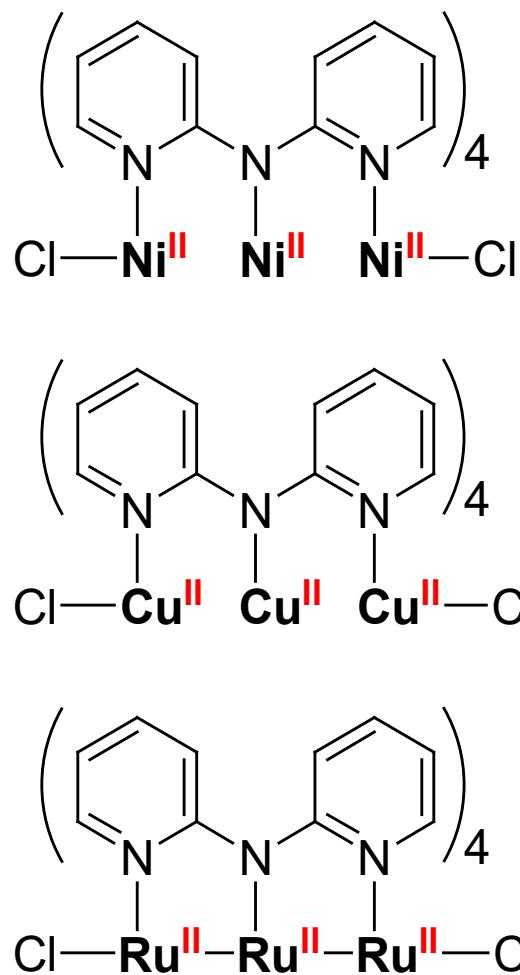


Unsymmetrical axial

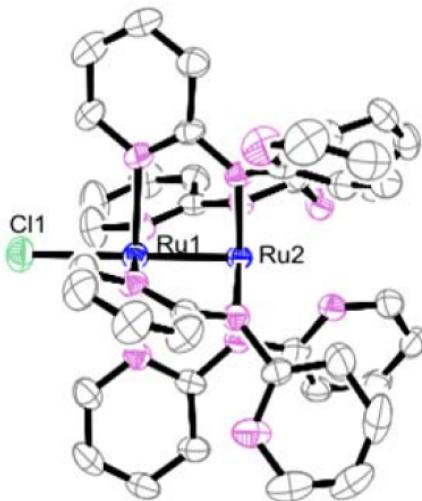
Solved crystallographic disorder



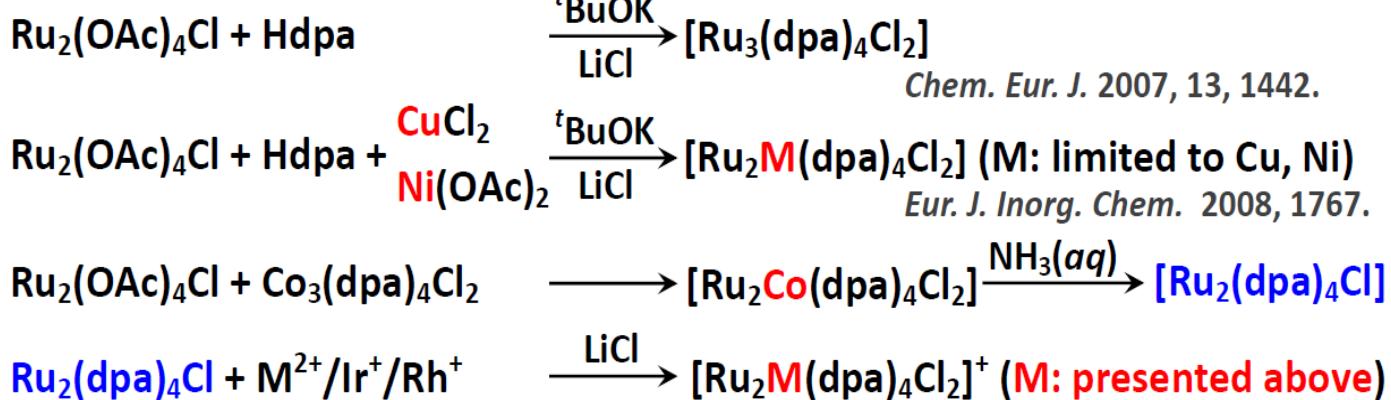
# Manipulation of Heterotrinucler Metal String with MMM' (M=Ru, Rh, W, Mo)



# $[\text{Ru}_2(\text{dpa})_4\text{Cl}_2]$ as tetra-dentate chelating ligand



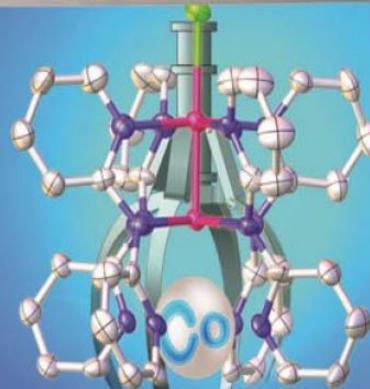
25 Mn $[\text{Ar}]4s^23d^5$ manganese 54.94	26 Fe $[\text{Ar}]4s^23d^6$ iron 55.85	27 Co $[\text{Ar}]4s^23d^7$ cobalt 58.93	28 Ni $[\text{Ar}]4s^23d^8$ nickel 58.69	29 Cu $[\text{Ar}]3s^13d^10$ copper 63.55	30 Zn $[\text{Ar}]4s^23d^{10}$ zinc 65.39
44 Ru $[\text{Ar}]5s^14d^7$ ruthenium 101.1	45 Rh $[\text{Ar}]5s^14d^8$ rhodium 102.9	46 Pd $[\text{Ar}]4d^10$ palladium 106.4	47 Ag $[\text{Ar}]5s^14d^10$ silver 107.9	48 Cd $[\text{Ar}]5s^24d^{10}$ cadmium 112.4	
77 Ir $[\text{Ar}]5s^24f^145d^5$ iridium 192.2					



# Dalton Transactions

*Cover Picture*

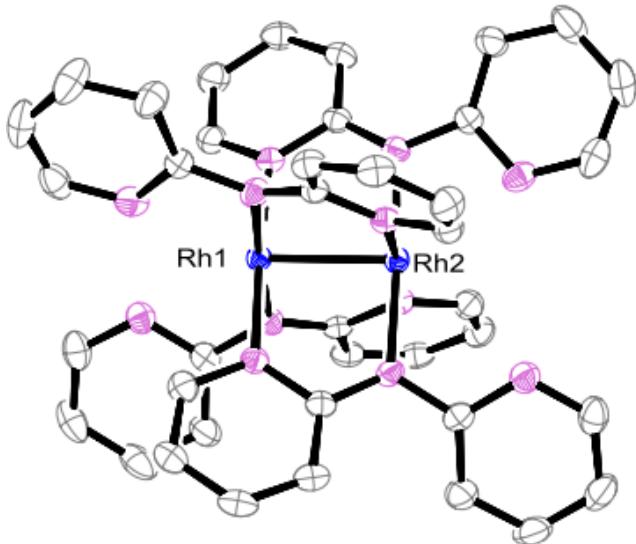
## Metal Crane



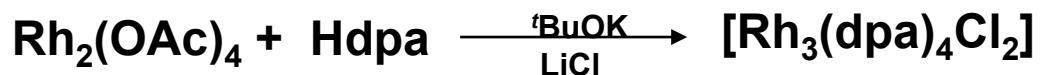
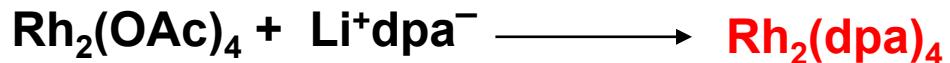
*Dalton Trans.* 2018,  
47, 1422–1434.



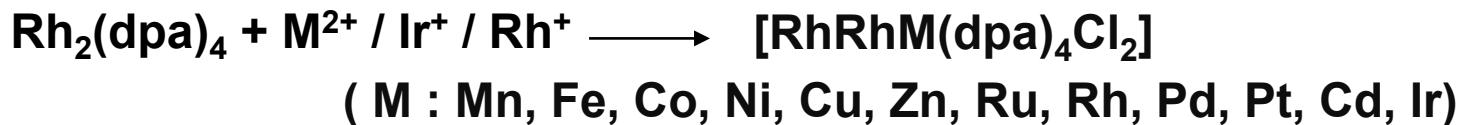
# $[\text{Rh}_2(\text{dpa})_4]$ is also as Metal Crane

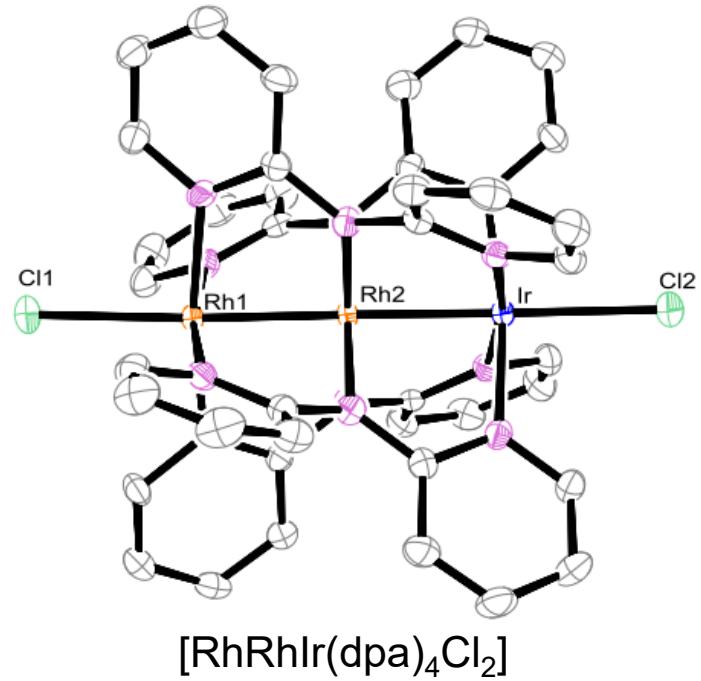
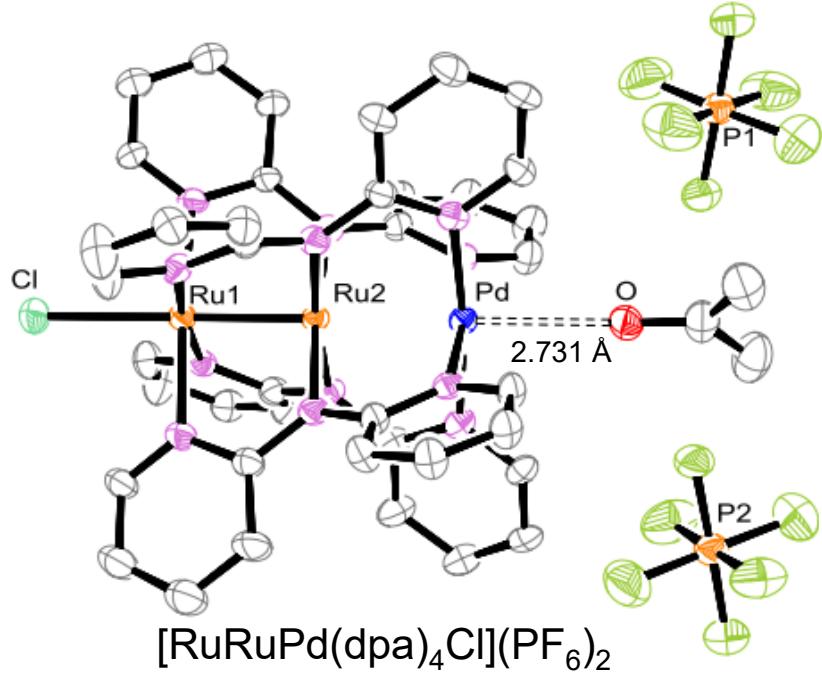


25 <b>Mn</b> [Ar]4s <sup>2</sup> 3d <sup>5</sup> manganese 54.94	26 <b>Fe</b> [Ar]4s <sup>2</sup> 3d <sup>6</sup> iron 55.85	27 <b>Co</b> [Ar]4s <sup>2</sup> 3d <sup>7</sup> cobalt 58.93	28 <b>Ni</b> [Ar]4s <sup>2</sup> 3d <sup>8</sup> nickel 58.69	29 <b>Cu</b> [Ar]4s <sup>1</sup> 3d <sup>10</sup> copper 63.55	30 <b>Zn</b> [Ar]4s <sup>2</sup> 3d <sup>10</sup> zinc 65.39
44 <b>Ru</b> [Kr]5s <sup>1</sup> 4d <sup>7</sup> ruthenium 101.1	45 <b>Rh</b> [Kr]5s <sup>1</sup> 4d <sup>8</sup> rhodium 102.9	46 <b>Pd</b> [Kr]4d <sup>10</sup> palladium 106.4	47 <b>Ag</b> [Kr]5s <sup>1</sup> 4d <sup>10</sup> silver 107.9	77 <b>Ir</b> [Kr]6s <sup>2</sup> 4f <sup>5</sup> 5d <sup>7</sup> iridium 192.2	78 <b>Pt</b> [Kr]6s <sup>1</sup> 4f <sup>1</sup> 5d <sup>9</sup> platinum 195.1

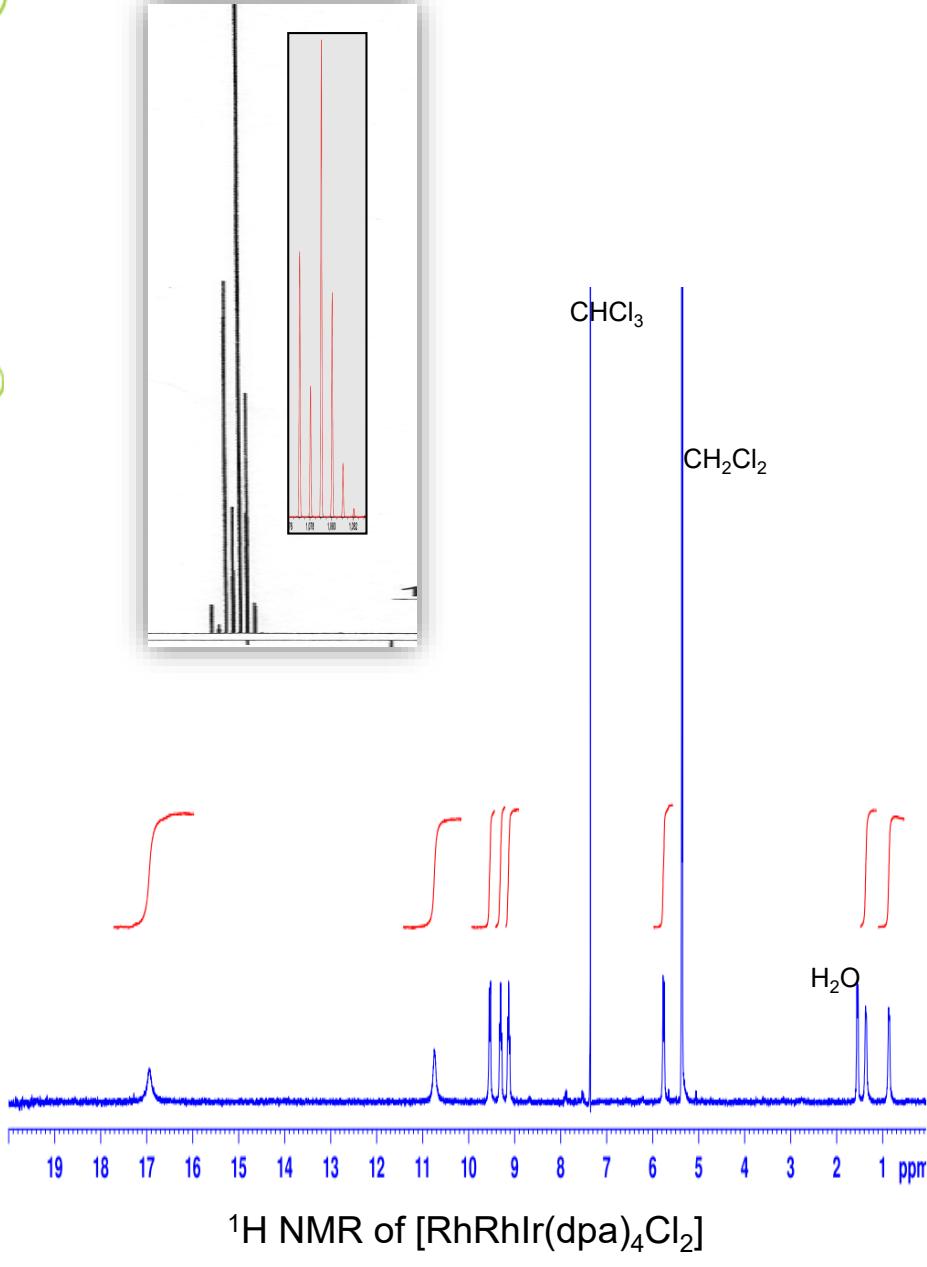


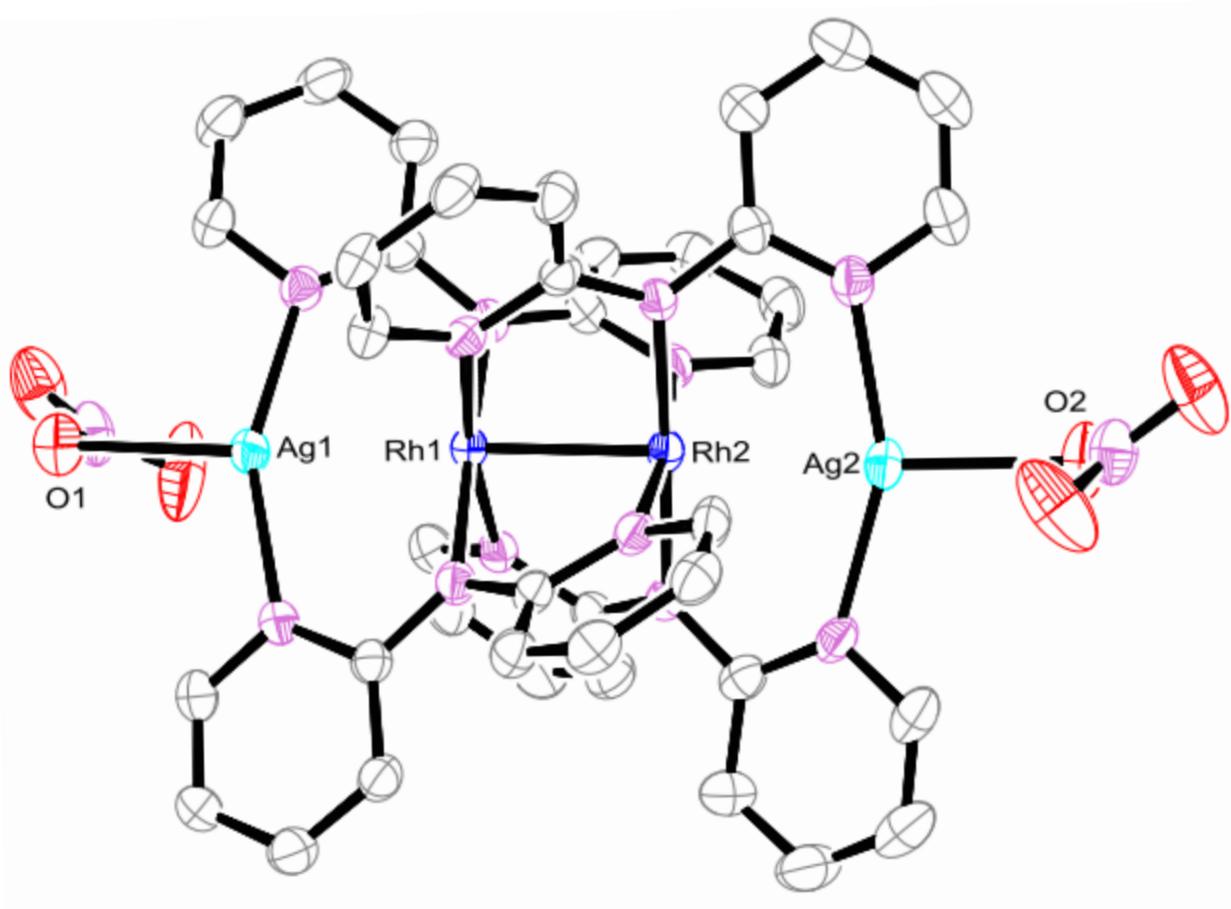
Dalton. Trans., 2009, 2623-2629





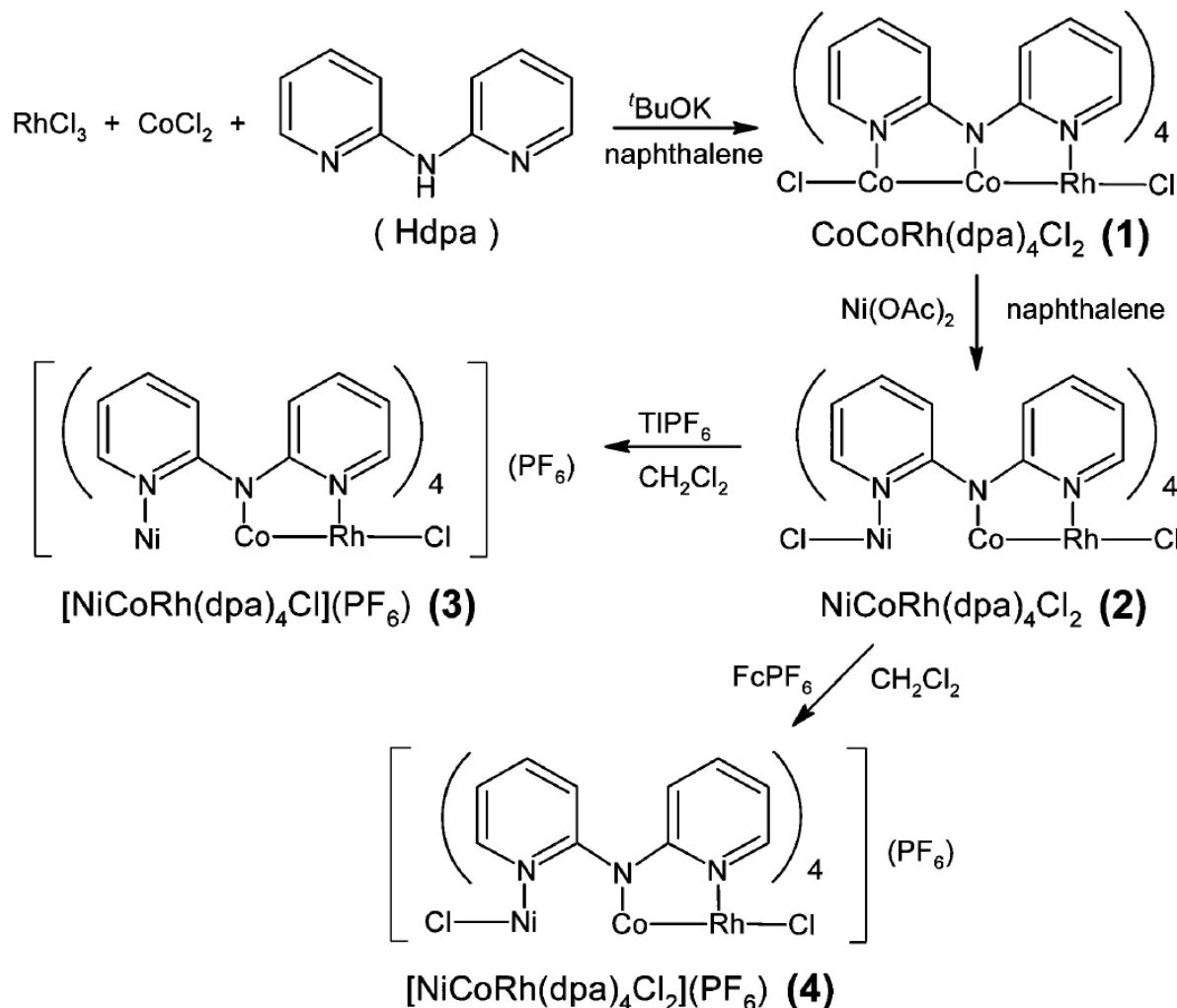
$[\text{RhRhIr}(\text{dpa})_4]^+$





[AgRhRhAg(dpa)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]

# Facile synthesis of heterotrimetallic metal-string complex $[\text{NiCoRh}(\text{dpa})_4\text{Cl}_2]$ through direct metal replacement

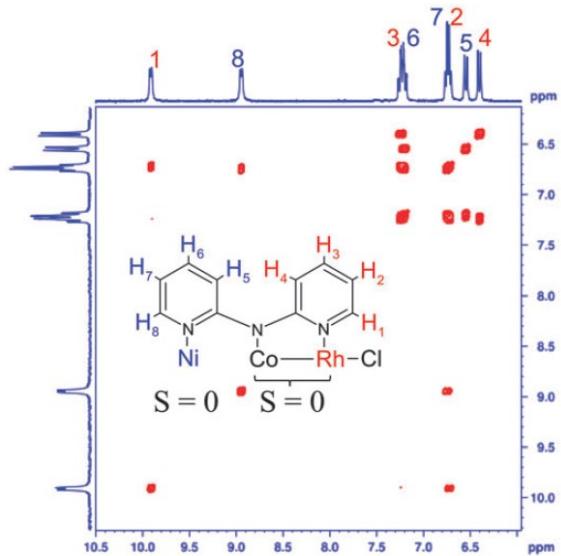
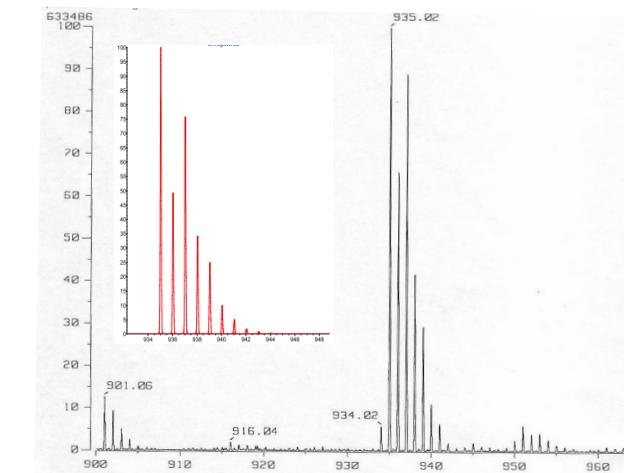


**Scheme 1** Synthesis of compounds **1**, **2**, **3** and **4**.

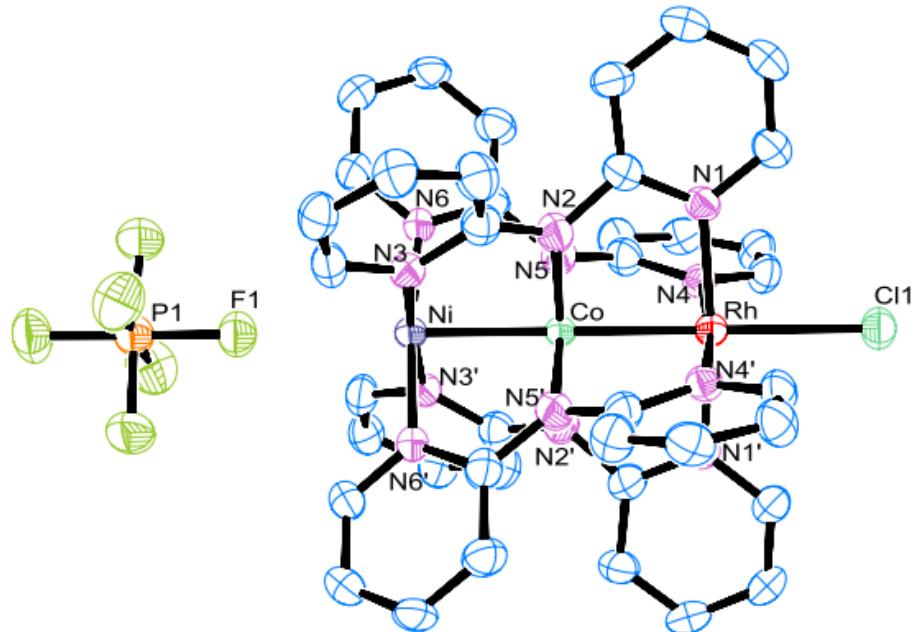
*Chem. Commun.*, 2013, 7938-7940

# Stepwise formation of M<sub>A</sub>-M<sub>B</sub>-M<sub>C</sub> Type of HMSC

[NiCoRh(dpa)<sub>4</sub>Cl](PF<sub>6</sub>)

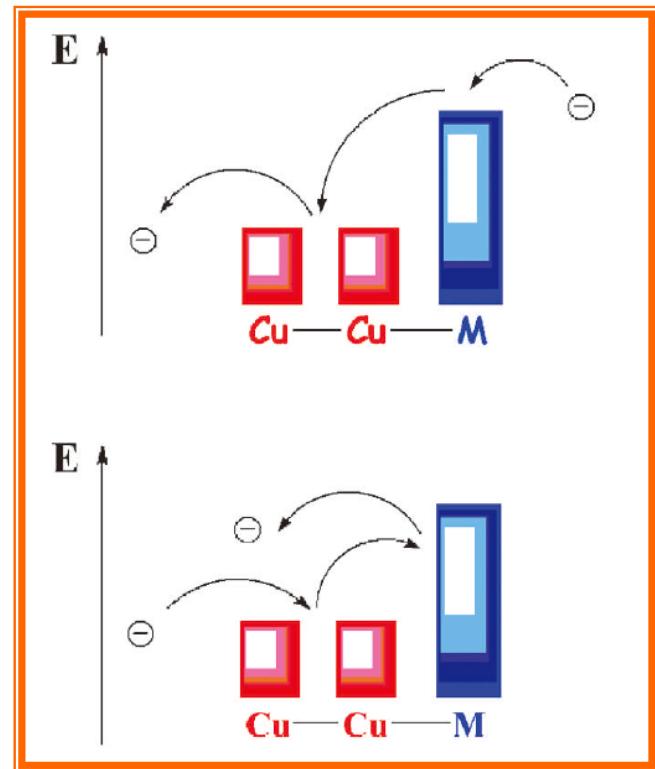
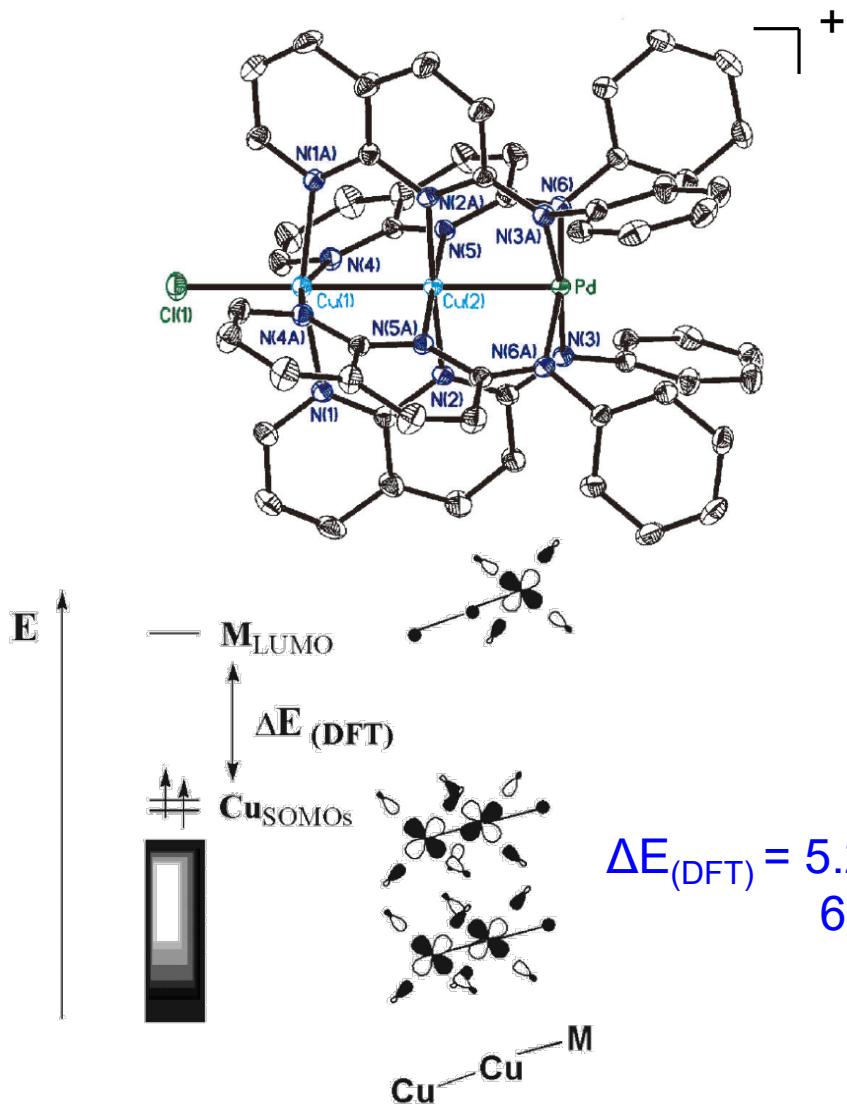


$^1\text{H}-^1\text{H}$  2D COSY spectrum of [NiCoRh(dpa)<sub>4</sub>Cl](PF<sub>6</sub>) (**3**) in acetone-d<sub>6</sub>.

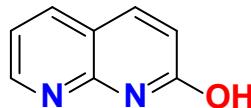
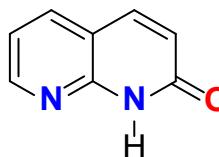


Monoclinic,  $C_2/c$   $Z=4$   
 $R_1 = 0.0518$ ,  $wR_2 = 0.1364$ ,  
 $\text{Co-Ni} = 2.3259(10)$   
 $\text{Co-Rh} = 2.3371(8)$   
 $\text{Co-N}_{\text{av}} = 1.923(4)$   
 $\text{Rh-N}_{\text{av}} = 2.091(4)$   
 $\text{Ni-N}_{\text{av}} = 1.921(4)$   
 $\text{Rh-Cl} = 2.5767(16)$   
 $\text{Ni}\cdots\text{F1} = 2.712$

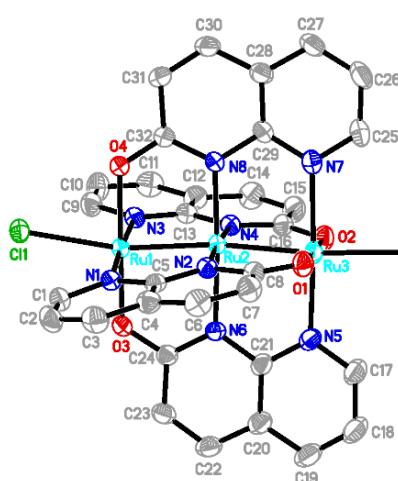
# Asymmetric Ligand Backbone of HMSC (4,0)-[Cu<sub>2</sub>M(np<sub>4</sub>)<sub>4</sub>Cl]<sup>+</sup> (M = Pd & Pt)



# Symmetric & Asymmetric HMSC of Naphthyridonate ligand



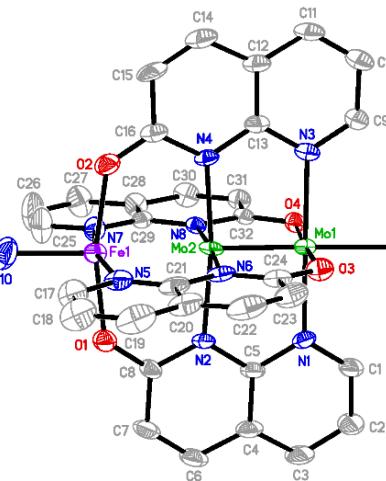
(Naphthyridonate, npo<sup>-</sup>)



(2,2)  $[\text{Ru}_3(\text{npo})_4\text{Cl}_2]^+$

Ru — Ru — Ru

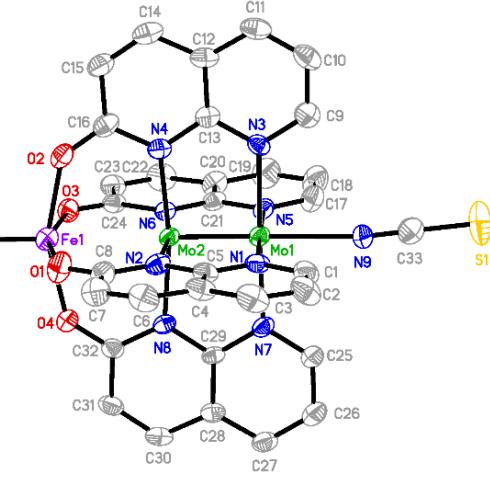
2.3238(4) 2.3287(4)



(2,2)  $[\text{Mo}_2\text{Fe}(\text{npo})_4(\text{NCS})_2]$

Mo ≡ Mo      Fe

2.151(7)    2.653(9) (disordered)



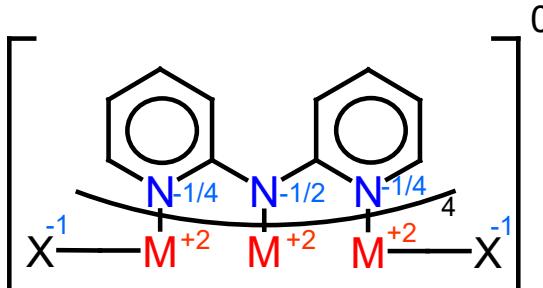
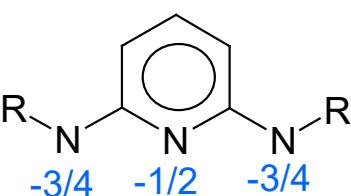
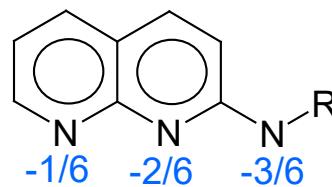
(4,0)  $[\text{Mo}_2\text{Fe}(\text{npo})_4(\text{NCS})_2]$

Mo ≡ Mo      Fe

2.0994(5)    2.8534(8)

They exhibit high conductance amount trinuclear strings

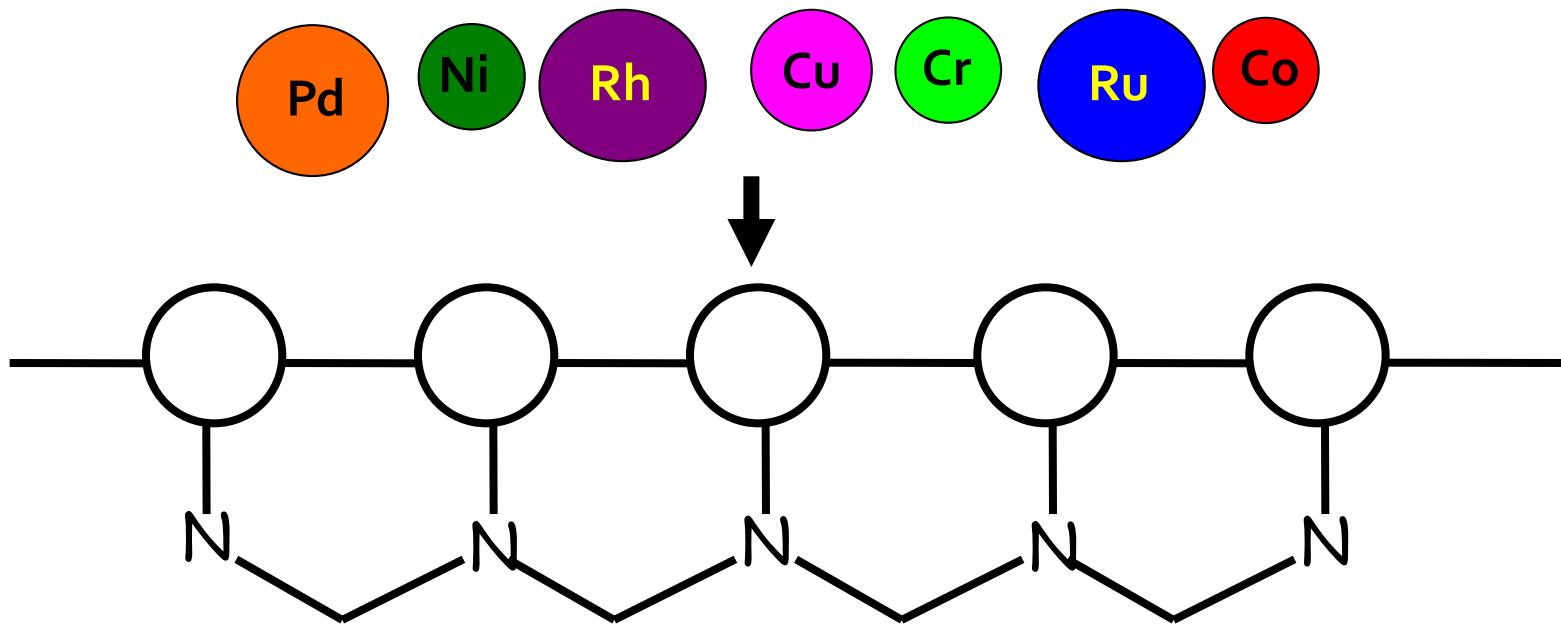
# Charge Distribution Among Various Ligands

# of resonance forms	probability	negative charge on nitrogen
2X2	4/8	1/2
2	2/8	1/4
2	2/8	1/4
		
		

# Pentanuclear HMSCs

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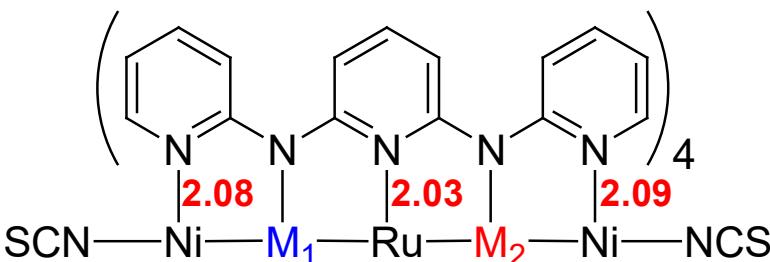
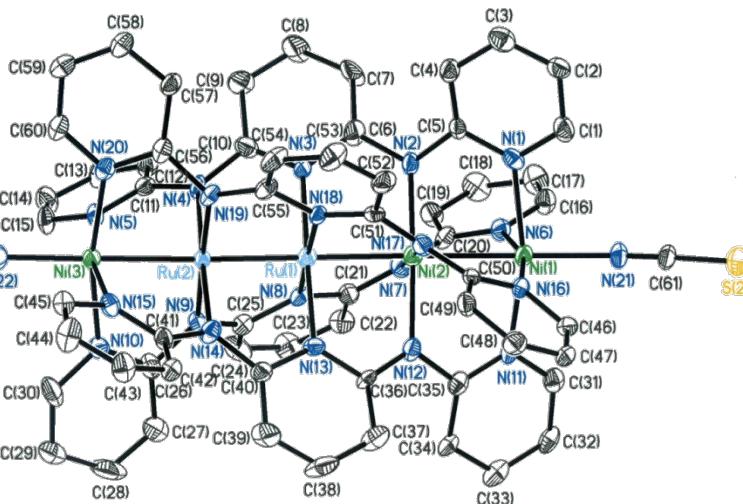


## Challenges:

- Lack of suitable reaction precursors
- Poor reactivity of 2<sup>nd</sup>-row transition metals
- Homo-nuclear EMACs as reaction concomitants

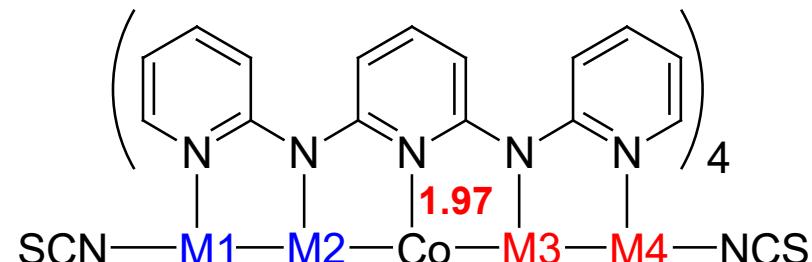
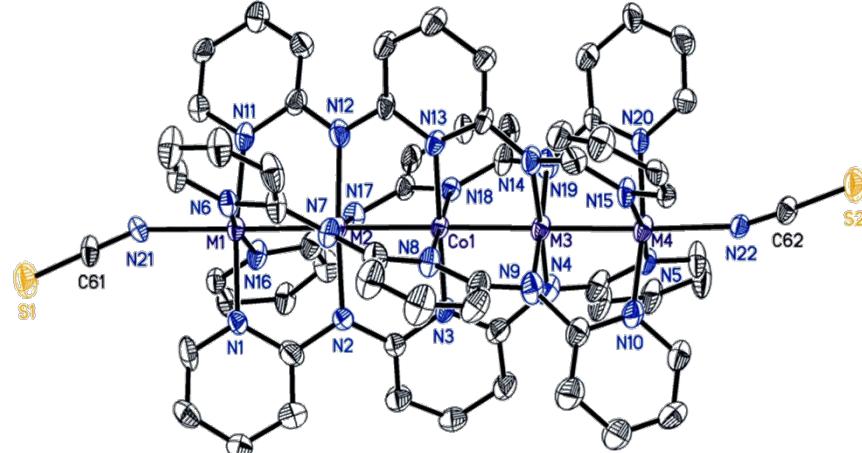
# Characterization of $[\text{Ru}_2\text{M}_3(\text{tpda})_4(\text{NCS})_2]$ HMSCs: Crystal Structure Analysis

## $[\text{NiRu}_2\text{Ni}_2(\text{tpda})_4(\text{NCS})_2]$



M<sub>1</sub> = M<sub>2</sub> = 50% Ru + 50% Ni

## $[\text{Ru}_2\text{Co}_3(\text{tpda})_4(\text{NCS})_2]$



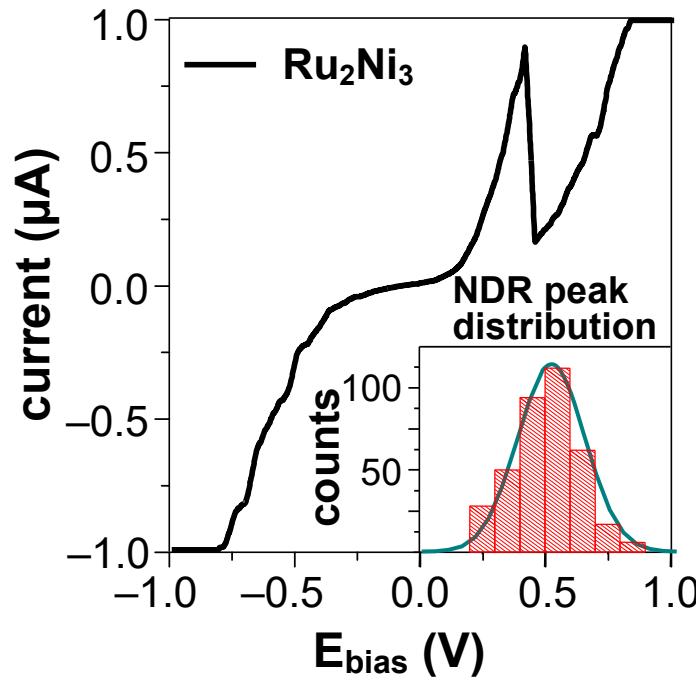
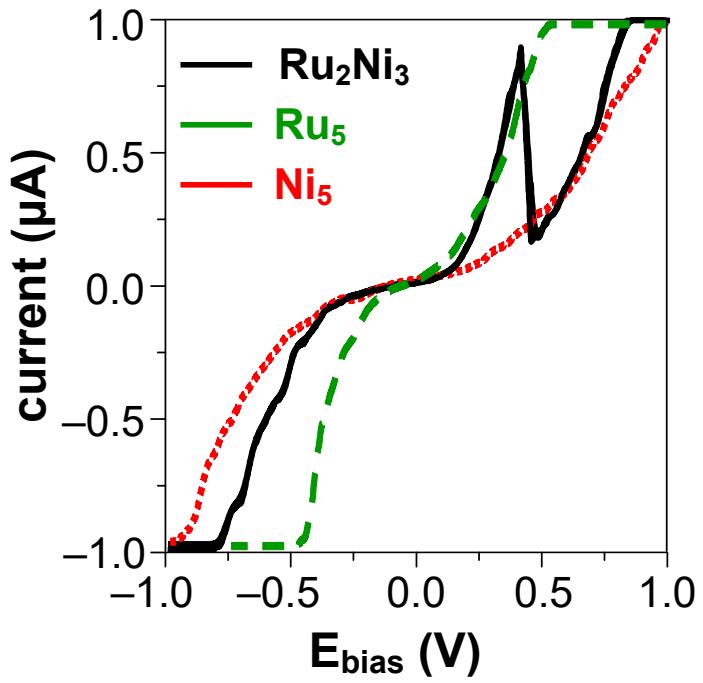
M<sub>1</sub> = M<sub>2</sub> = 66% Ru + 33% Co  
 M<sub>3</sub> = M<sub>4</sub> = 66% Co + 33% Ru

# Single Molecular Conductance of HMSCs

M	Resistance (MΩ)	Conductance (x10 <sup>-3</sup> G <sub>0</sub> )	M	Resistance (MΩ)	Conductance (x10 <sup>-3</sup> G <sub>0</sub> )
Cr <sub>3</sub>	1.1 ± 0.2	11.5 ± 2.1	Cr <sub>5</sub>	3.3 ± 0.7	3.9 ± 0.8
Ru <sub>3</sub>	1.0 ± 0.2	11.7 ± 2.1	Ru <sub>5</sub>	4.2 ± 0.9	3.1 ± 0.7
			Ru <sub>2</sub> Co <sub>3</sub>	5.8 ± 1.3	2.3 ± 0.3
Ru <sub>2</sub> Ni	1.5 ± 0.3	8.6 ± 1.7	NiRu <sub>2</sub> Ni <sub>2</sub>	6.3 ± 1.0	2.0 ± 0.3
Co <sub>3</sub>	2.0 ± 0.3	6.5 ± 0.9	Co <sub>5</sub>	10.5 ± 2.1	1.2 ± 0.2
Ni <sub>3</sub>	3.4 ± 0.5	3.8 ± 0.6	Ni <sub>5</sub>	23.3 ± 4.1	0.6 ± 0.1

# NDR Effect of $[\text{NiRu}_2\text{Ni}_2(\text{tpda})_4(\text{NCS})_2]$

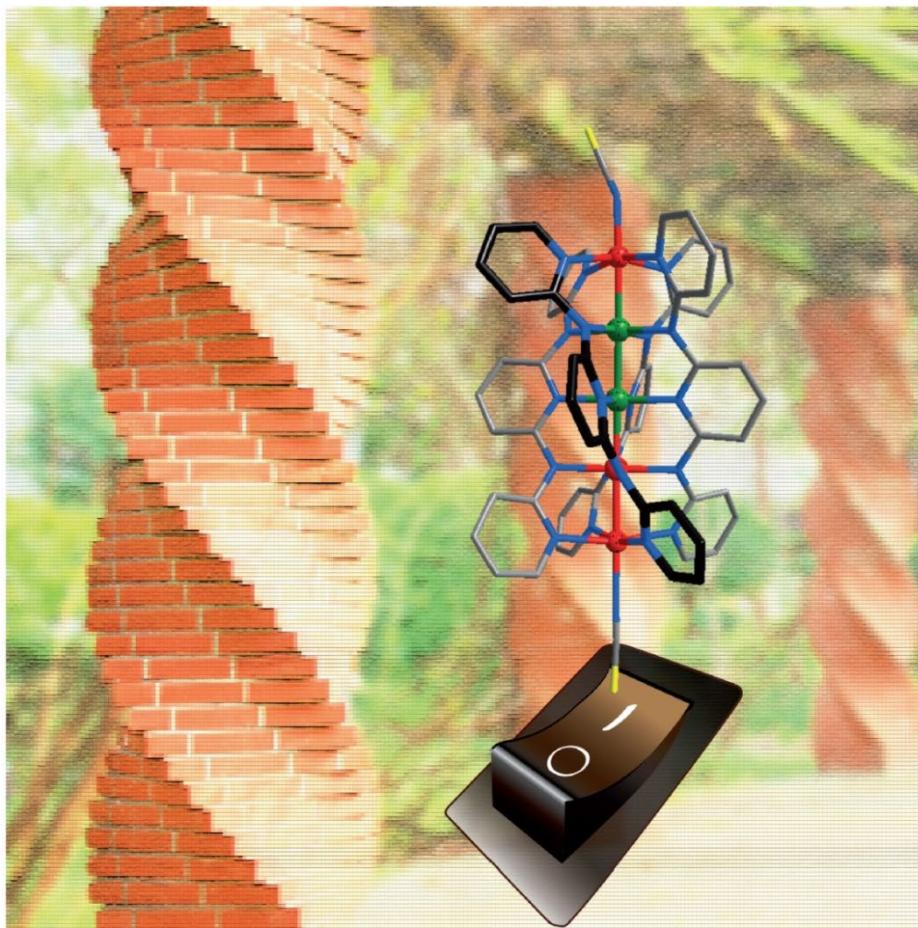
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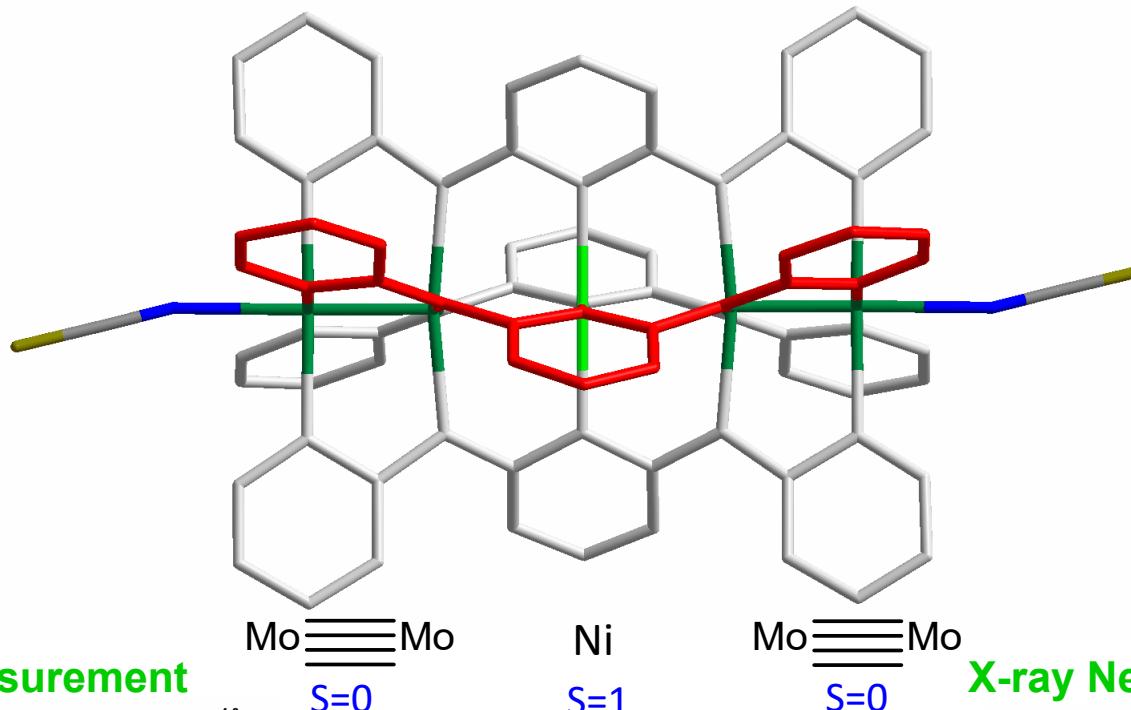
## Metal Chains

**The First Heteropentanuclear Extended Metal-Atom Chain:  
[Ni<sup>+</sup>–Ru<sub>2</sub><sup>5+</sup>–Ni<sup>2+</sup>–Ni<sup>2+</sup>(tripyridylidiamido)<sub>4</sub>(NCS)<sub>2</sub>]**

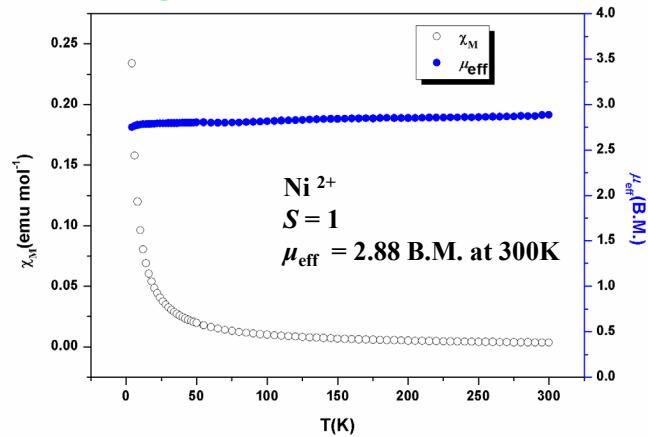
Min-Jie Huang,<sup>[a]</sup> Shao-An Hua,<sup>[a]</sup> Ming-Dung Fu,<sup>[a]</sup> Gin-Chen Huang,<sup>[a]</sup> Caixia Yin,<sup>[b]</sup> Chih-Hung Ko,<sup>[a]</sup> Ching-Kuo Kuo,<sup>[a]</sup> Chia-Hung Hsu,<sup>[a]</sup> Gene-Hsiang Lee,<sup>[a]</sup> Kuan-Yi Ho,<sup>[c]</sup> Chia-Hsin Wang,<sup>[d]</sup> Yaw-Wen Yang,<sup>[d]</sup> I-Chia Chen,<sup>\*[c]</sup> Shie-Ming Peng,<sup>\*[a, e]</sup> and Chun-hsien Chen<sup>\*[a]</sup>



# Pentanuclear Hetero-metallic Metal String

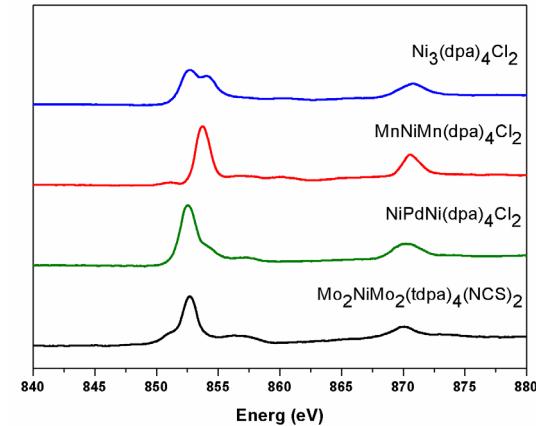


# Magnetic Measurement



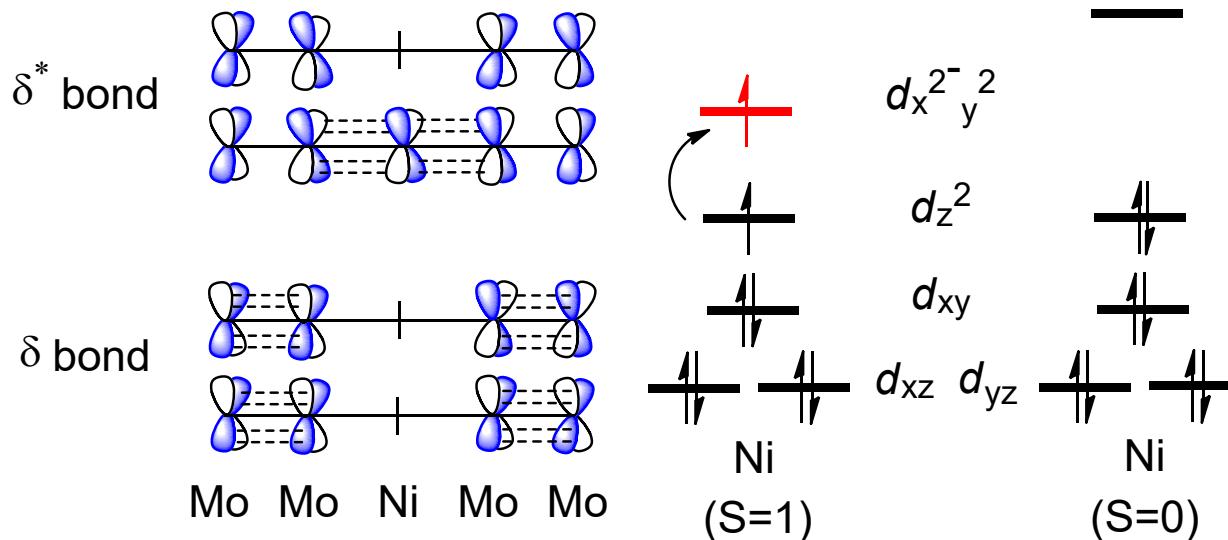
(high spin square planar Ni(II))

## X-ray Near-Edge Absorption

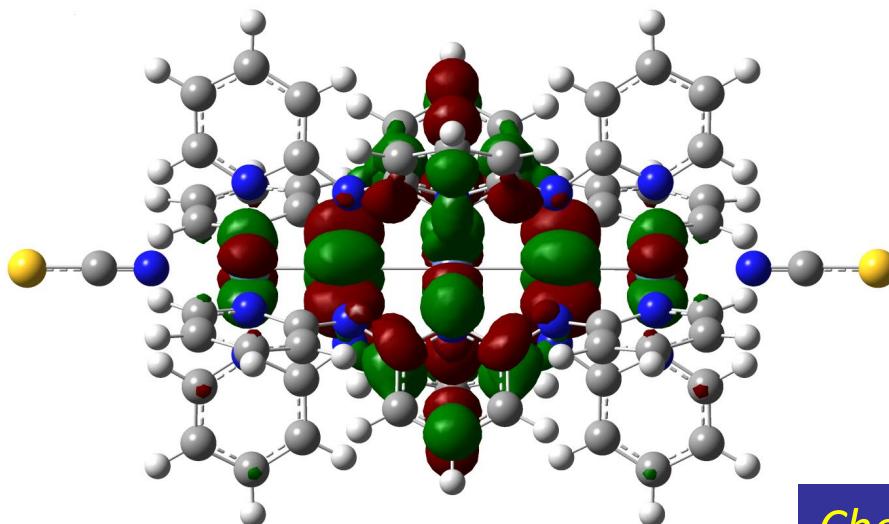


# V shape of the ligands, Meso metal string

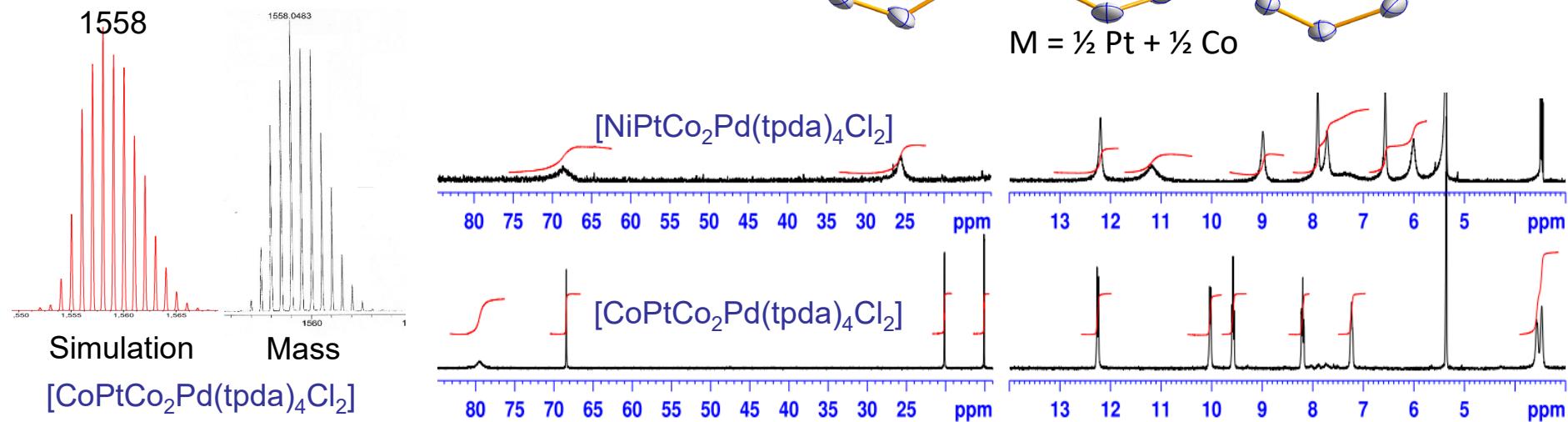
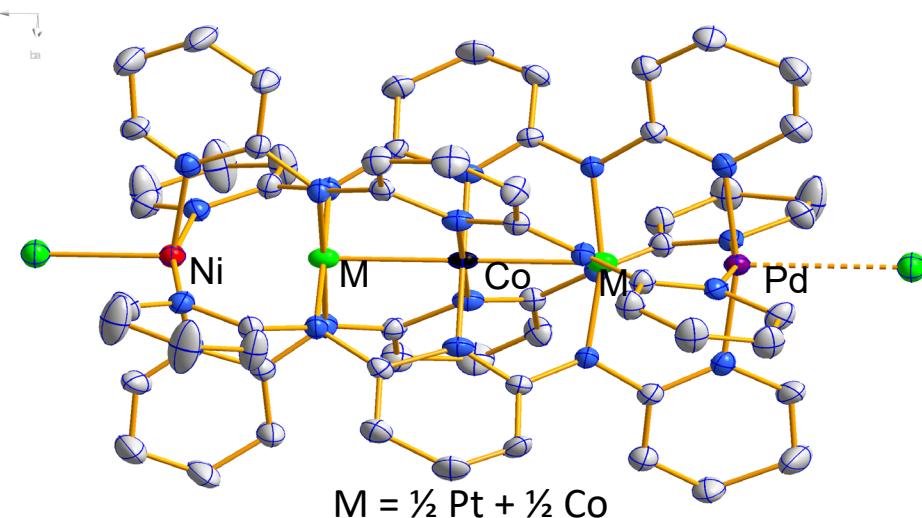
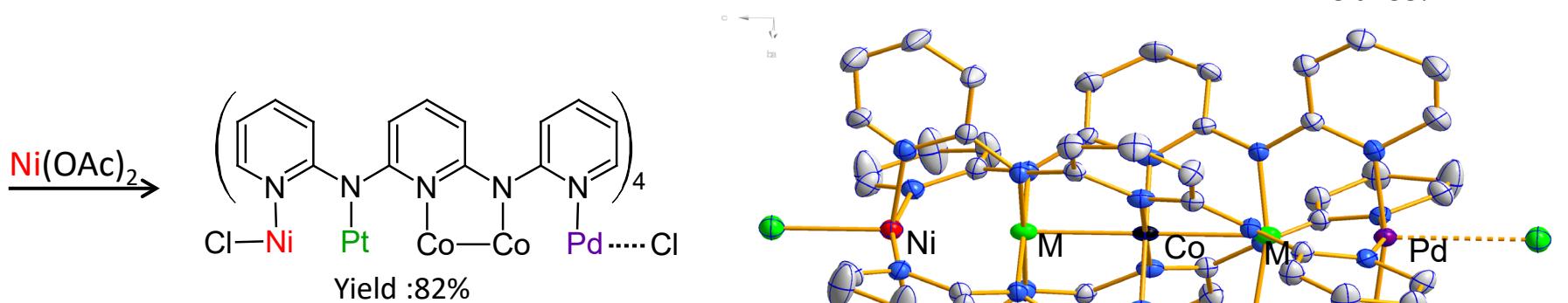
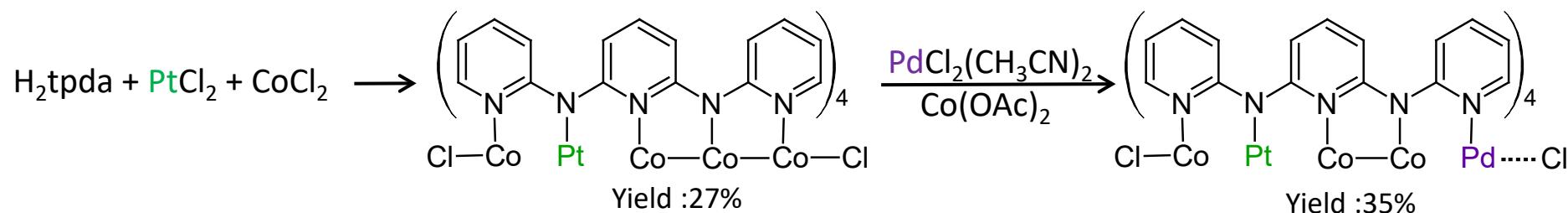
# Mo-Mo Delta Bond Orbital Influence



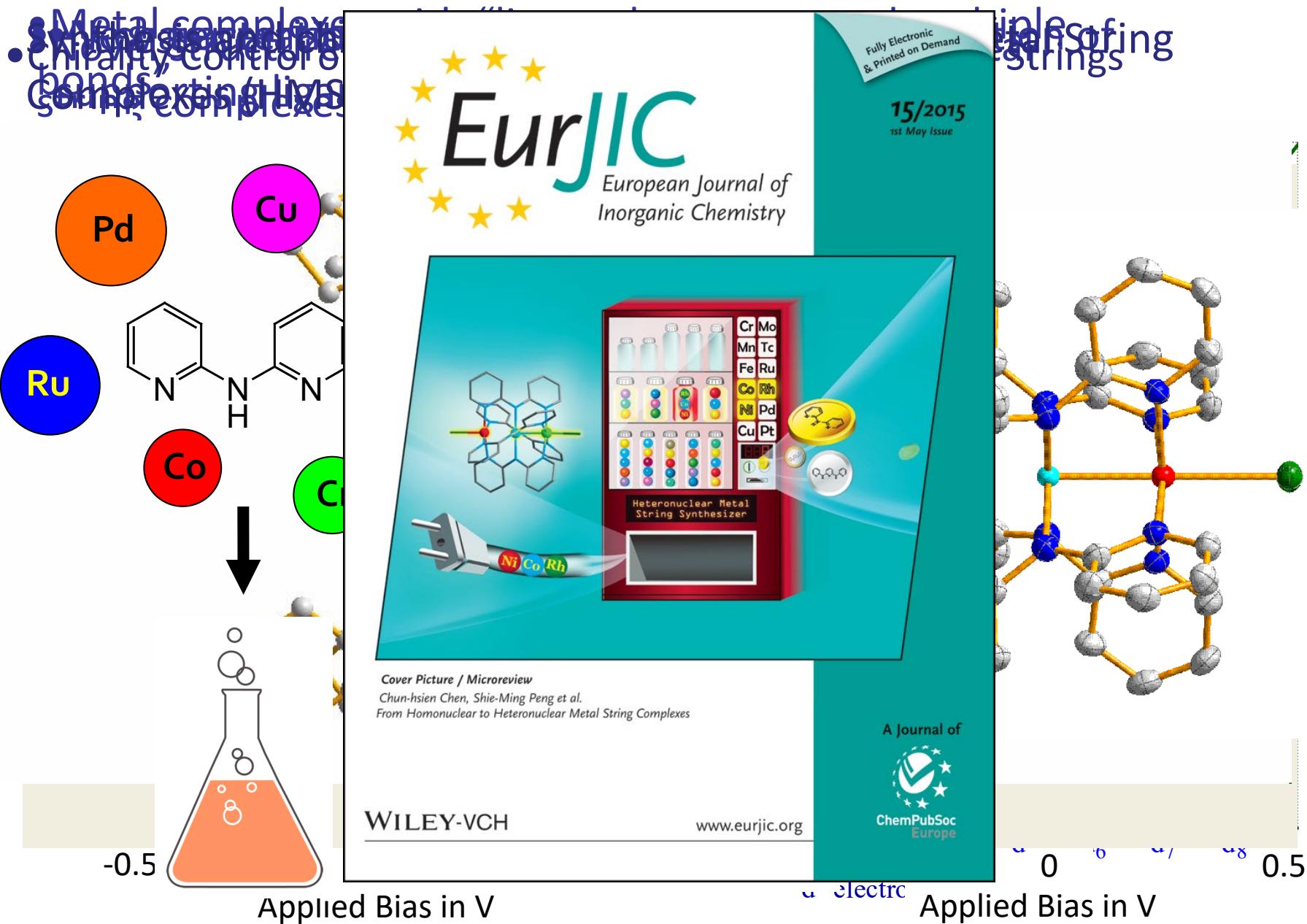
Low spin state without  
the interaction!



# **Pentanuclear Hetero-trimetallic and Hetero-tetrametallic Metal String : $[\text{CoPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$ and $[\text{NiPtCo}_2\text{Pd}(\text{tpda})_4\text{Cl}_2]$**



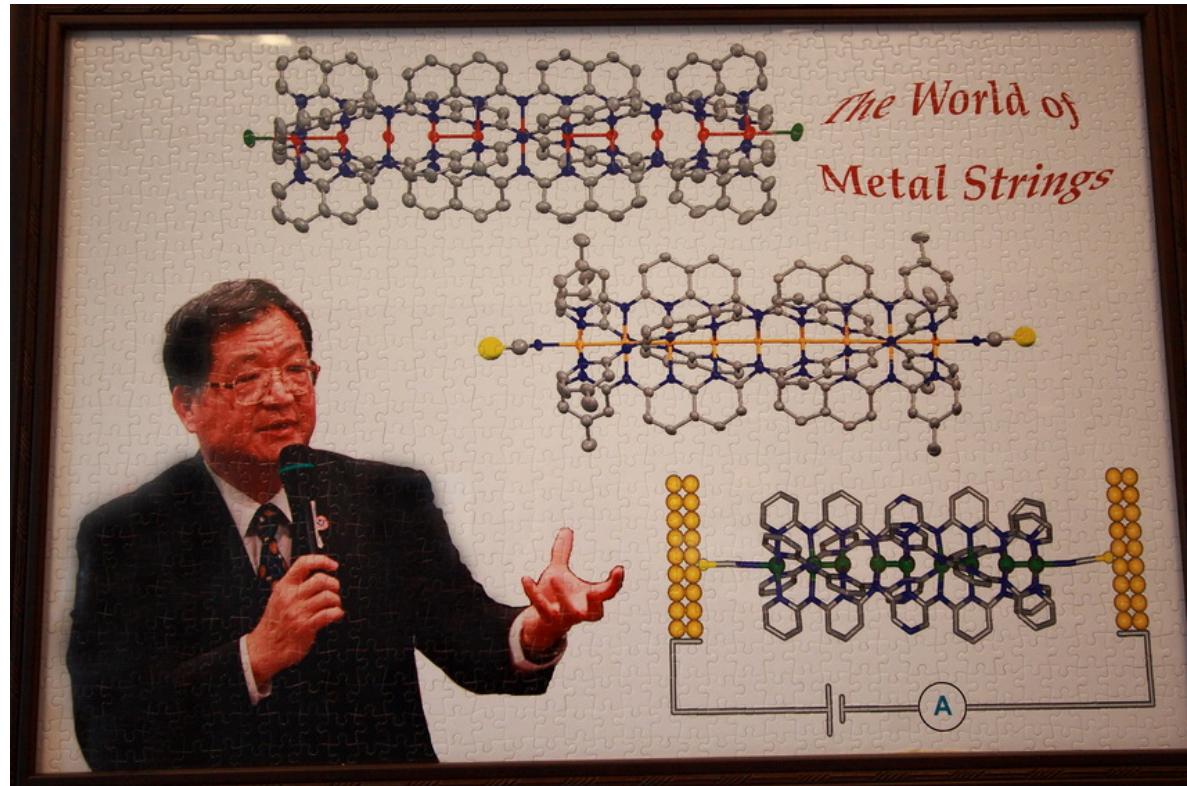
# Conclusions



# 總結

- 合成世界最細之金屬線，即一維單原子金屬線，並量測他們相對之導電度。

Conductance !!!!!



# **Acknowledgement**

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NTU ( National Taiwan University )

MOE ( Ministry of Education, Taiwan )

AS ( Academia Sinica )

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Prof. P.T. Chou (周必泰)----- Fluorescence Spectroscopy

Prof. C.Y. Mou (牟中原)----- Molecular Simulation

Prof. B.Y. Jin (金必耀)----- Theoretical Studies on Conductivity

Prof. C.H. Chen (陳俊顯)----- Conductivity Measurements

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Prof. C.Y. Yeh (葉鎮宇)----- Electrochemistry

### ***Université Louis Pasteur, Strasbourg, France :***

Prof. M. Bénard and M.-M. Rohmer---- DFT Calculations



# Firework of Dragon at New Year Eve, 2011







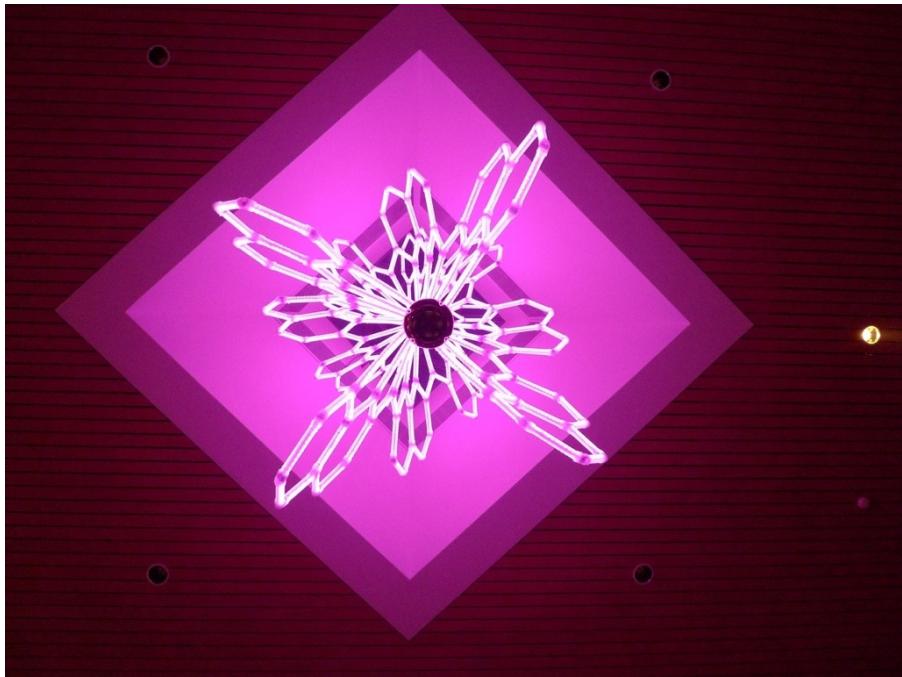
積學館



精勤館

# New Chemistry Building, NTU

台大化學系 積學館



[Ni<sub>11</sub>(tentra)<sub>4</sub>Cl<sub>2</sub>]<sup>4+</sup>  
tetrakis-tetranaphthyridyltriamido  
dichloro undecanickel ion





# 感謝各位的聆聽

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