Electronic Supplementary Information for:

Theoretical Insights into the Origin of Magnetic Exchange and Magnetic Anisotropy in {Re^{IV}-M^{II}} (M=Mn, Fe, Co, Ni and Cu) Single Chain Magnets

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Table ST1: Overlap integral values corresponding to complex **1**

Re/Mn	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
d_{xy}	-0.0052	-0.0948	-0.0576	-0.0184	-0.0134
d_{xz}	0.0027	0.0968	0.0167	-0.0199	0.0483
d_{yz}	-0.0143	-0.0505	-0.1305	0.0093	0.0234
$d_{x^2-y^2}$	0.0007	0.0295	-0.0002	0.0260	-0.0326
d_{z^2}	0.0012	-0.0277	0.0035	-0.0347	0.0604

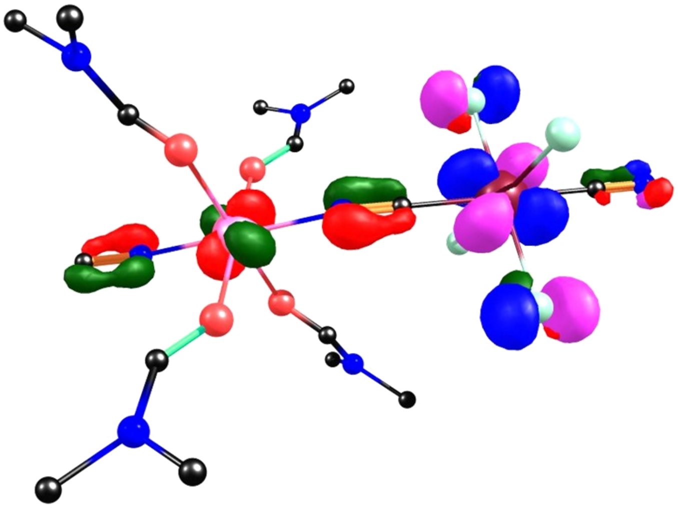


Figure SF1: overlap between d_{yz} -d_{yz}orbitals corresponding to complex **1.**

Table ST2: Overlap integral values corresponding to complex **2**

Re/Fe	d_{xz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}
d_{xy}	0.0213	0.0736	0.0397	-0.0355
d_{xz}	0.0530	0.0878	-0.0357	0.0249
d_{yz}	-0.0326	-0.0164	-0.0486	-0.0198
$d_{x^2-y^2}$	0.1223	0.1313	0.0383	0.0032
d_{z^2}	0.0017	0.0507	-0.0997	0.0013

Table ST3: Overlap integral values corresponding to complex **3**

Re/Co	d_{xz}	$d_{x^2-y^2}$	d_{z^2}
d_{xy}	0.0024	0.0621	-0.0123
d_{xz}	0.0127	-0.0642	0.0321
d_{yz}	-0.0014	-0.0446	-0.0744
$d_{x^2-y^2}$	0.0788	0.1438	0.0414
d_{z^2}	0.0013	-0.0814	0.0019

Table ST4: Overlap integral values corresponding to complex **4**

Ni/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0008	0.0010	0.0069	0.0058	-0.0014
d_{z^2}	0.0000	0.0220	0.0022	-0.0039	-0.0478

Table ST5: Overlap integral values corresponding to complex **5**

Cu/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0012	0.0068	-0.0007	-0.0017	0.0125

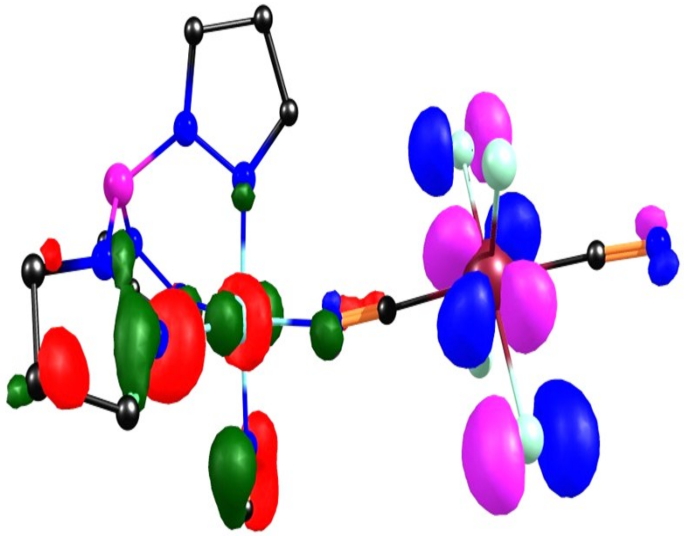


Figure SF2: overlap between d_{z^2} -d_{xz} orbitals corresponding to complex **5.**

Table ST6. DFT computed spin densities of {ReMn} complex in HS and BS states.

	HS	**BS**
Mn	4.8142	4.8124
Re	2.4391	-2.4366
Cl	0.12-0.15	-(0.12-0.15)
C in -CN	-0.1	0.1
N in -CN	0.11 & 0.08	-0.08 & -0.11

Table ST7: DFT computed spin densities of {ReFe} complex in HS and BS states.

	HS	**BS**
Fe	3.7958	3.7911
Re	2.4607	-2.4582
Cl	0.11-0.14	-(0.11-0.14)
C in -CN	-0.1&-0.08	0.1&0.08
N in -CN	0.11 & 0.11	-0.07 & -0.11

Table ST8: DFT computed spin densities of {ReCo} complex in HS and BS states.

	HS	**BS**
Co	2.7710	2.7686
Re	2.4692	-2.4656
Cl	0.12-0.14	-(0.12-0.14)
C in -CN	-0.1&-0.07	0.1&0.07
N in -CN	0.11 &0.12	-0.05 & -0.11

Table ST9: DFT computed spin densities of {ReNi} complex in HS and BS states.

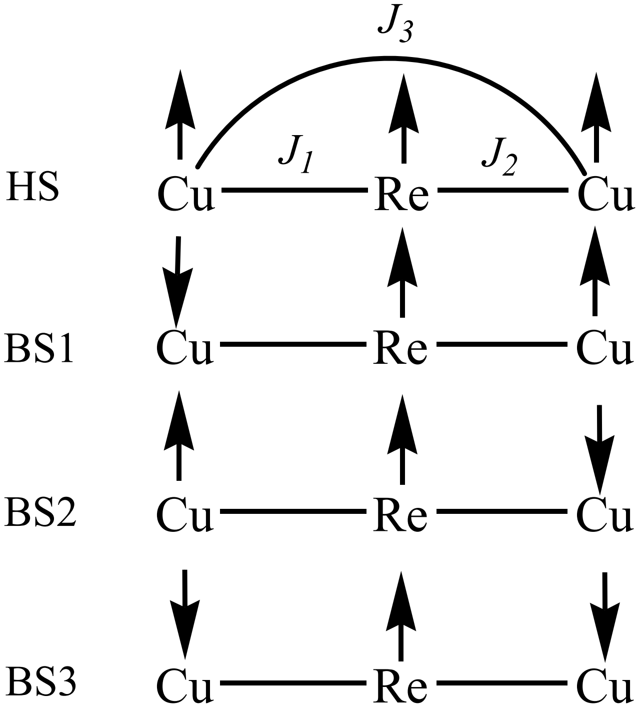
	HS	**BS**
Ni	1.736925	-1.736700
Re	2.4694	2.467349
Cl	0.11-0.14	0.11-0.14
C in -CN	-0.1&-0.08	0.1&0.08
N in -CN	0.11&0.12	-0.07 & -0.11

Table ST10: DFT computed spin densities of {ReCu} complex in HS and BS states.

	HS	**BS**
Cu	0.6442	-0.6456
Re	2.4455	2.4426
Cl	0.12-0.14	0.12-0.14
B	0.00007	-0.00007
C in -CN	-0.1	-0.1 & -0.07
N in -CN	0.11 & 0.18	0.11 & 0.01

Table ST11: DFT computed vs. expected spin contamination values for selected states with their corresponding spin density values and the exchange (*J*) values for trinuclear complex **5b**.

	Energies (Hatrees)	Calculated $<S^2>$	*J* values (cm^{-1})	Spin density on M_1	Spin density on Re	Spin density on M_2
Complex **5a** (Cu-Re-Cu)						
HS	-6976.630012	8.770		0.6453	2.4059	0.6490
BS1	-6976.629672	4.7683	$J_1 = 19.01$	-0.6460	2.4019	0.6489
BS2	-6976.629681	4.7680	$J_2 = 18.52$	0.6452	2.4013	-0.6499
BS2	-6976.629328	2.7665	$J_3 = -0.70$	-0.6461	2.3974	-0.6499



Scheme S1. Trinuclear complex **5b** possessing three different exchange interactions and chosen spin states to extract the *J* values.

Table ST12: Exponential function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for Re-C bond lengths.

	1	**5**
Exponential function	$y = y_0 + A*\exp(R0*x)$	
y_0	2.51452	1.38732
A	-4922.08907	28552.5656
R0	-3.01862	-3.47101

Table ST13: Overlap integral values corresponding to complex **5** when Re-C distance is 2.4 Å.

Cu/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0197	0.0257	0.0020	0.0055	0.0311

Table ST14: Overlap integral values corresponding to complex **5** when Re-C distance is 1.8 Å.

Cu/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0022	0.0116	0.0284	0.0143	0.0185

Table ST15: Exponential function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for M-N bond lengths (M=Mn(**1**) and Cu(**5**)).

	1	**5**
Exponential function	$y = y_0 + A*\exp(R0*x)$	
y_0	-41.2566	-0.26772
A	205.45846	-131579.85855
R0	-0.60825	-4.56458

Table ST16: Exponential function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for Re-C-N bond angle.

	1	**5**
Exponential function	$y = y_0 + A*\exp(R0*x)$	
y_0	-4.92478	20.36184
A	-0.00078	-17096.38802
R0	0.03794	-0.06193

Table ST17: Exponential function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for M-N-C bond angle.

	1	**5**
Exponential function	$y = y_0 + A*\exp(R0*x)$	
y_0	-3.66512	22.70344
A	-1917.19852	-226940.94186
R0	-0.04421	-0.06452

Table ST18: Overlap integral values corresponding to complex **5** when Cu-N-C angle is 130 degree

Cu/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0020	0.1131	0.0188	-0.0016	0.0110

Table ST19: Overlap integral values corresponding to complex **5** when Cu-N-C angle is 180 degree

Cu/Re	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
$d_{x^2-y^2}$	0.0000	-0.0023	0.0040	-0.0307	0.0221

Table ST20:

CASSCF/PT2+RASSI computed energies of lowest spin-free and spin-orbit states along D, |E| and g-tensor (g_{xx}, g_{yy}, g_{zz}) along with experimental observed values (provided in parenthesis)

Atomic Terms	Spin-free states		Spin-orbit states		D_{cal} (D_{exp})	$\lvert E_{cal}\rvert$ ($\lvert E_{exp}\rvert$)	g_{cal} (g_{exp})
	CASSCF	MS-CASPT2	CASSCF	MS-CASPT2			
$^4A_2$	0.0	0.0	0.0	0.0	*MS-CASPT2 values*		
			0.0	0.0	+16.06 cm^{-1}	3.7 cm^{-1}	1.756, 1.751, 1.729
^2E	12445.4	7377.3	43.3	33.9	(+11 cm^{-1})	(3.2 cm^{-1})	(1.89, 1.89, 1.58)
	12470.8	7649.2	43.3	33.9			
			11164.9	6570.5			
$^2T_1$	12517.9	8351.5	11164.9	6570.5			
	12584.6	8419.6	12134.1	7923.0			
	13414.7	8554.3	12134.1	7923.0			
$^2T_2$	20279.4	14439.9	12825.8	8823.2	*CASSCF values*		
	20820.7	15965.5	12825.8	8823.2			
	20967.3	16224.1	13369.2	8990.6	-20.97 cm^{-1}	1.25 cm^{-1}	1.827, 1.825, 1.78
			13369.2	8990.6	(+11 cm^{-1})	(3.2 cm^{-1})	(1.89, 1.89, 1.58)
$^4T_2$	28840.4	30778.3					
	34441.2	36080.6					
	34734.1	36212.4					

The most common approximation is the leading J_{AB} term, because the exchange interaction is quite large ranging from few wave numbers to hundreds of wave numbers in transition metal complexes. In case of strong exchange limit, the zfs of the spin state S can be resulted by vector coupling of two spins S_{Co} and S_{Re} which is given by the following equation,

$$D_{total} = d_{Co} D_{Co} + d_{\mathrm{Re}} D_{\mathrm{Re}} + d_{Co\mathrm{Re}} D_{Co\mathrm{Re}}$$

Where the D_{Co} is the single-ion anisotropy of Co(II) ion, D_{Re} is the single-ion anisotropy of Re(IV) ion, D_{CoRe} is the anisotropy arises due to exchange between these two ions. The d coefficients are d_{Co}=1/5, d_{Re}=1/5 and d_{CoRe}=3/10 (see Bencini, Gatteschi, Dante, Electron Paramagnetic Resonance of Exchange Coupled Systems, Springer 2011).

$$D_{total} = \frac{1}{5} D_{Co} + \frac{1}{5} D_{\mathrm{Re}} + \frac{3}{10} D_{Co\mathrm{Re}}$$