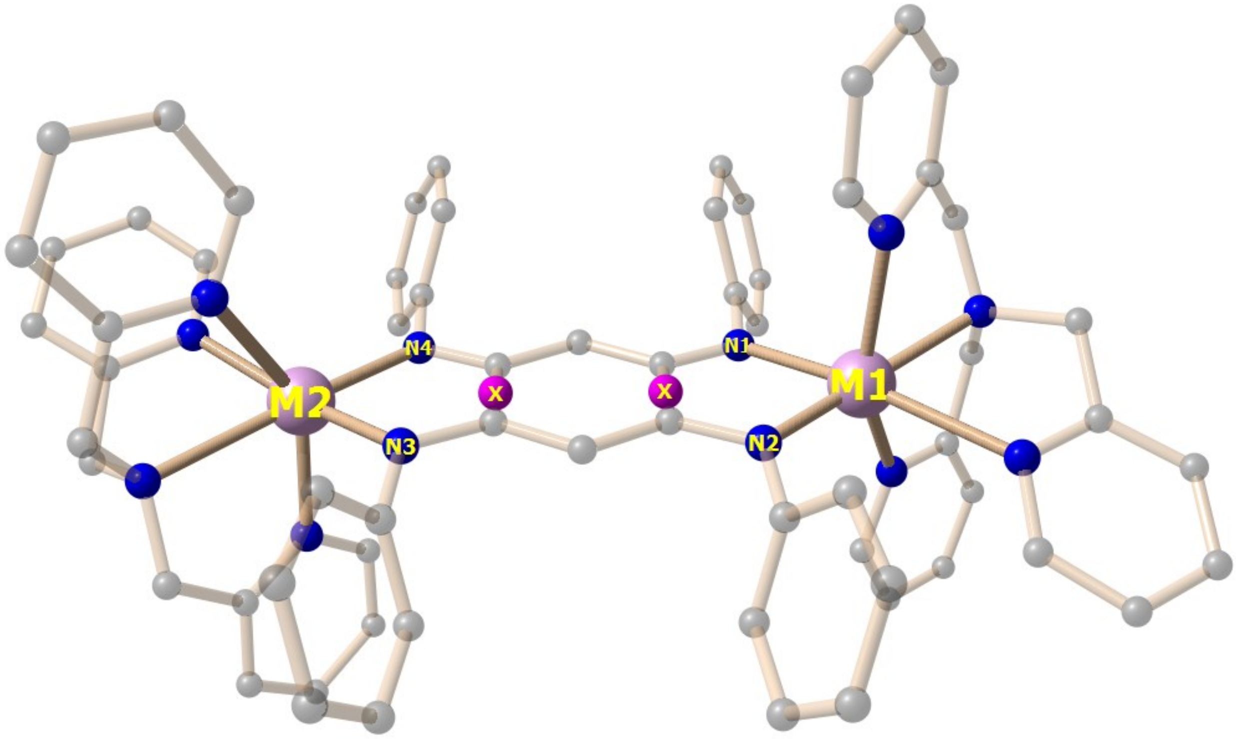
# Probing the Strong Magnetic Exchange Behaviour for Transition Metal-Radical Complexes: A DFT Case Study

**Mukesh Kumar Singh***

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai,

Maharashtra, India-400076.

Email: mklsingh36@gmail.com.



| Complex | M-N(1,3)<br>Å | M-N(2,4)<br>Å | Avg(M-N(1-4))<br>Å | Avg. M-X-X (°) |
|---|---|---|---|---|
| **1 ($Cr^{III}$)** | 2.009 | 1.998 | 2.004 | 174.5 |
| **2 ($Mn^{II}$)** | 2.120 | 2.109 | 2.115 | 176.9 |
| **3 ($Fe^{II}$)** | 2.096 | 2.077 | 2.089 | 177.1 |
| **4 ($Co^{II}$)** | 2.049 | 2.078 | 2.064 | 174.3 |
| **5 ($Fe^{II}$)** | 2.096 | 2.062 | 2.079 | 177.5 |
| **$5_{XRD}$ ($Fe^{II}$)** | 2.103 | 2.042 | 2.073 | 173.0 |

**Figure S1**. Representative DFT optimized structures for complexes **1-5** and experimental structure for complex **5** (**5**$_{XRD}$) with selected structural parameters. Here, A and B are metal-radical distance (Å) and C is Metal-X-X angle/plane (°).

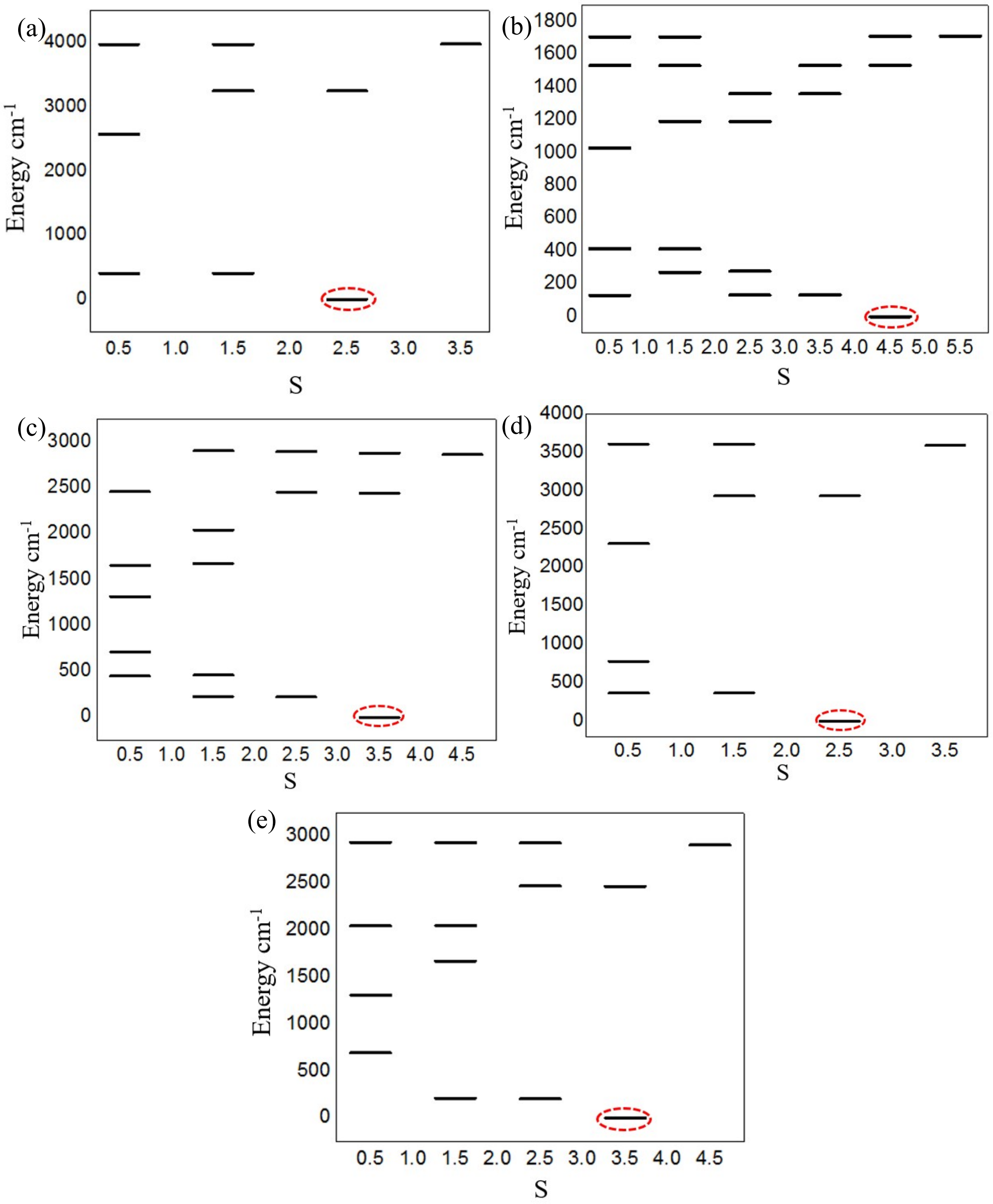

(a)
Energy cm$^{-1}$
0
1000
2000
3000
4000
S
0.5
1.0
1.5
2.0
2.5
3.0
3.5
(b)
Energy cm$^{-1}$
0
200
400
600
800
1000
1200
1400
1600
1800
S
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
(c)
Energy cm$^{-1}$
0
500
1000
1500
2000
2500
3000
S
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
(d)
Energy cm$^{-1}$
0
500
1000
1500
2000
2500
3000
3500
4000
S
0.5
1.0
1.5
2.0
2.5
3.0
3.5
(e)
Energy cm$^{-1}$
0
500
1000
1500
2000
2500
3000
S
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5

**Figure S2**. Energies of various computed spin-states against different S values. The red circles indicate the ground $S_T$ value in each case for complexes (a-e) **1-5** respectively.

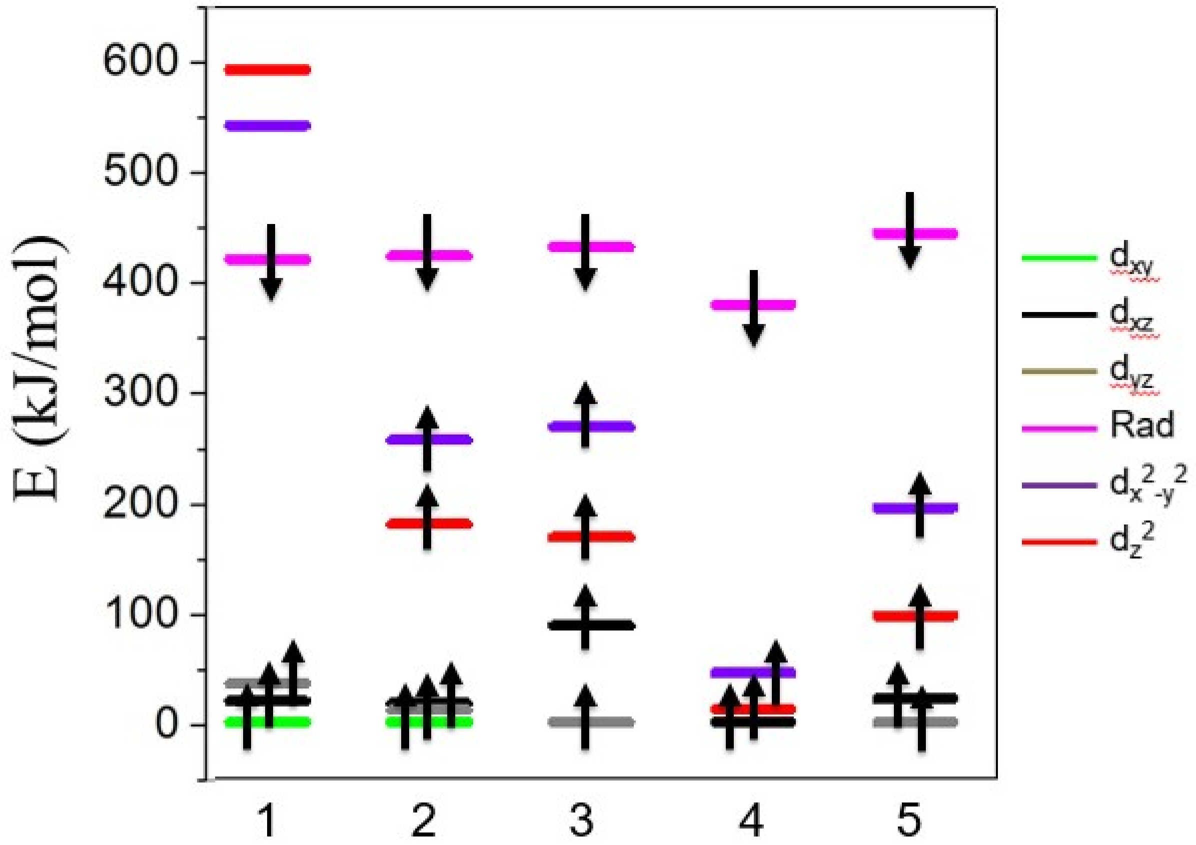


**Figure S3**. Magnetic orbital energies for complexes **1-5**.

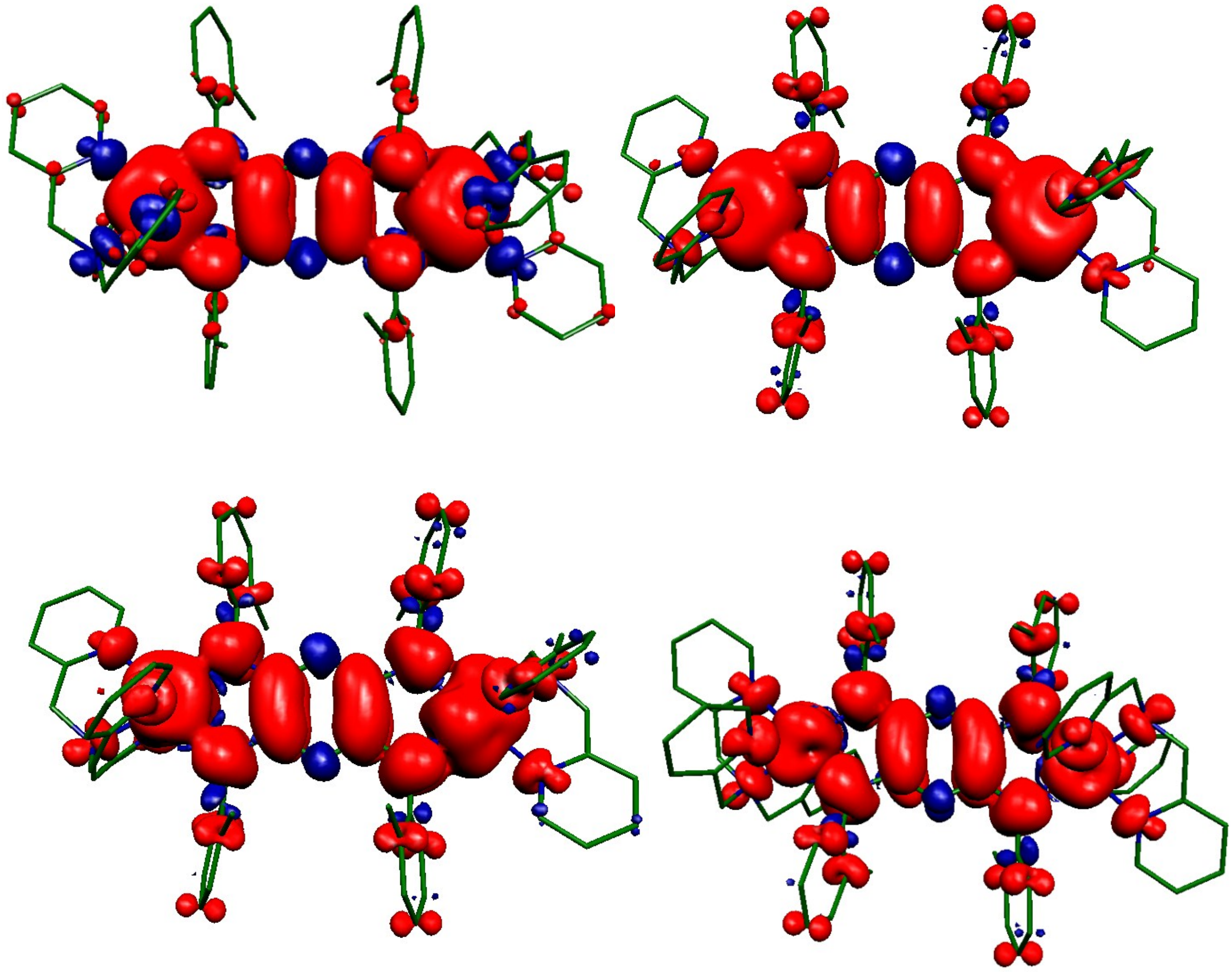
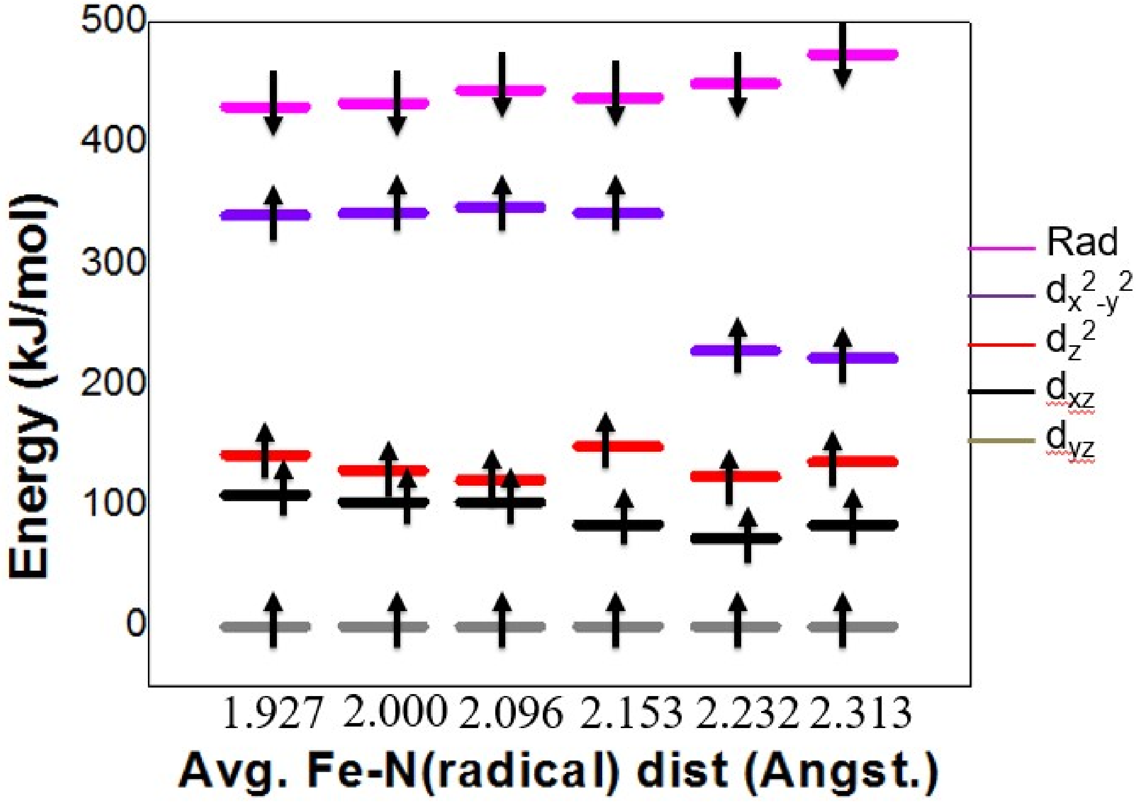


**Figure S4**. (a-d) Lowedin spin density plots for complexes **1**-**4** respectively, suggesting strong metal-radical magnetic interactions and are in excellent agreement to the Mulliken spin population. The isodensity surface represented corresponds to a value 0.001 e/bohr$^3$.


500
400
300
200
100
0
Energy (kJ/mol)
1.927
2.000
2.096
2.153
2.232
2.313
Avg. Fe-N(radical) dist (Angst.)
Rad
$d_{x^2-y^2}$
$d_{z^2}$
$d_{xz}$
$d_{yz}$

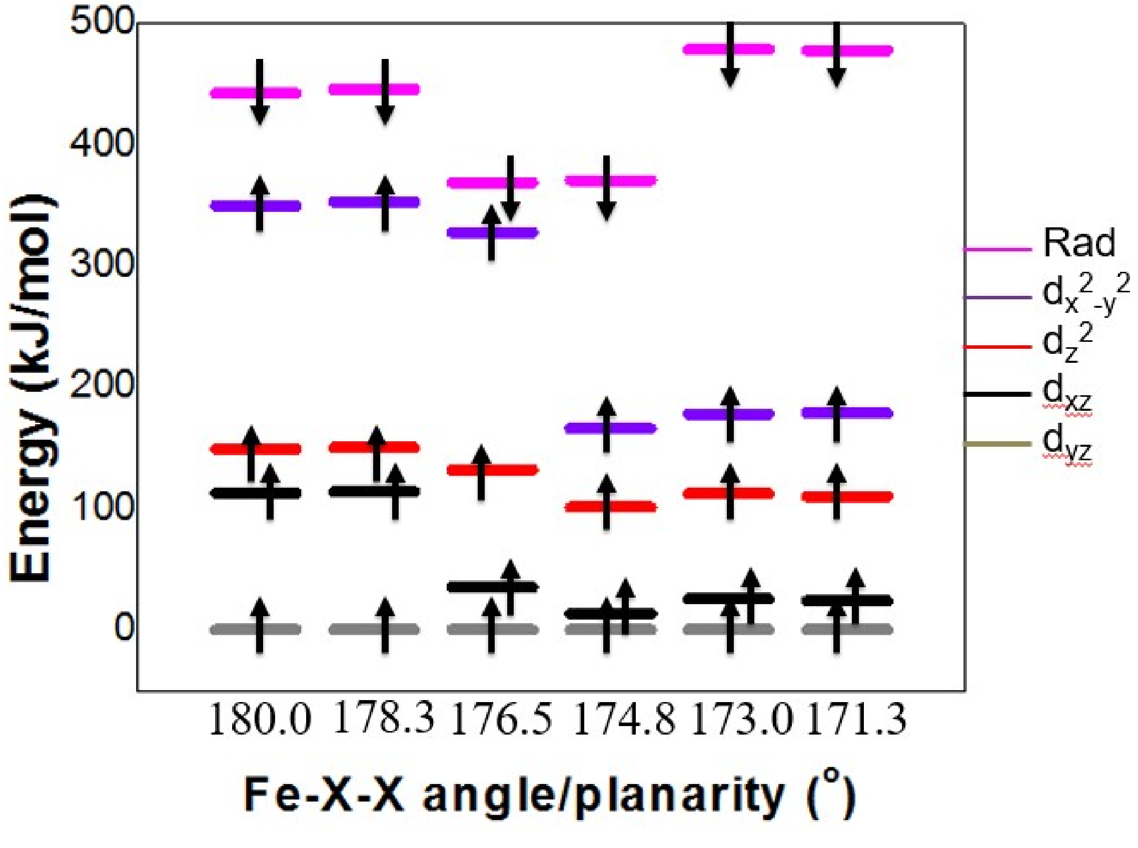

500
400
300
200
100
0
Energy (kJ/mol)
180.0
178.3
176.5
174.8
173.0
171.3
Fe-X-X angle/planarity (°)
Rad
$d_{x^2-y^2}$
$d_{z^2}$
$d_{xz}$
$d_{yz}$

**Figure S5**. Magnetic orbital energies for the magneto-structural models.

**Table S1**. Spin configurations used for all five complexes to estimate $J_1$ and $J_2$.

| Spin Configurations | S value for complexes **1**, **2**, **3**, **4**, **5** respectively with respect to corresponding spin configurations | Spin orientation | | |
|---|---|---|---|---|
| | | M1 | Radical | M2 |
| 1 | 7/2, 11/2, 9/2, 7/2, 9/2 | α | α | α |
| 2 | 1/2, 1/2, 1/2. 1/2, 1/2 | β | α | α |
| 3 | 1/2, 1/2, 1/2. 1/2, 1/2 | α | α | β |
| 4 | 5/2, 9/2, 7/2, 5/2, 7/2 | α | β | α |

**Table S2**. SHAPE analysis performed on all complexes. SHAPE analysis suggests coordination environment around metals close to octahedral.

| | | | |
|---|---|---|---|
| JPPY-6 | 5 | C5v | Johnson pentagonal pyramid J2 |
| TPR-6 | 4 | D3h | Trigonal prism |
| OC-6 | 3 | Oh | Octahedron |
| PPY-6 | 2 | C5v | Pentagonal pyramid |
| HP-6 | 1 | D6h | Hexagon |

| Structure [ML6} | JPPY-6 | TPR-6 | OC-6 | PPY-6 | HP-6 |
|---|---|---|---|---|---|
| **1** (Cr1) | 26.677, | 9.751, | 2.291, | 22.708, | 28.958 |
| **1** (Cr2) | 26.675, | 9.742, | 2.292, | 22.704, | 28.954 |
| **2** (Mn1) | 24.153, | 9.218, | 4.189, | 20.704, | 29.154 |
| **2** (Mn2) | 24.155, | 9.220, | 4.188, | 20.707, | 29.152 |
| **3** (Fe1) | 24.460, | 9.033, | 3.687, | 20.846, | 29.031 |
| **3** (Fe2) | 24.457, | 9.029, | 3.688, | 20.842, | 29.033 |
| **4** (Co1) | 24.948, | 9.419, | 3.271, | 21.240, | 29.528 |
| **4** (Co2) | 24.951, | 9.421, | 3.270, | 21.243, | 29.527 |
| **5** (Fe1) | 23.947, | 8.491, | 3.760, | 20.628, | 28.035 |
| **5** (Fe2) | 23.947, | 8.491, | 3.760, | 20.628, | 28.035 |
| **5*** (Fe1) | 23.517, | 10.184, | 2.978, | 20.570, | 26.909 |
| **5*** (Fe2) | 23.517, | 10.185, | 2.978, | 20.571, | 26.910 |

**Table S3**. DFT computed overlap values for complex **1-5**. Larger overlap contributes to antiferromagnetic interaction, whereas orthogonality of the magnetic orbitals contributes to ferromagnetic interaction. Here, the values in bracket are the overlap integral values for complex **5** X-ray structure ($\mathbf{5}_{\mathrm{XRD}}$).

| Complex **1** | Radical orbital |
|---|---|
| Cr $d_{yz}$ | 0.553 |
| Cr $d_{xz}$ | 0.046 |
| Cr $d_{xy}$ | 0.092 |

| Complex **2** | Radical orbital |
|---|---|
| Mn $d_{x^2-y^2}$ | 0.007 |
| Mn $d_{z^2}$ | 0.000 |
| Mn $d_{xz}$ | 0.000 |
| Mn $d_{yz}$ | 0.232 |
| Mn $d_{xy}$ | 0.053 |

| Complex **3** | Radical orbital |
|---|---|
| Fe $d_{x^2-y^2}$ | 0.014 |
| Fe $d_{z^2}$ | 0.000 |
| Fe $d_{xz}$ | 0.009 |
| Fe $d_{yz}$ | 0.283 |

| Complex **4** | Radical orbital |
|---|---|
| Co $d_{x^2-y^2}$ | 0.161 |
| Co $d_{z^2}$ | 0.052 |
| Co $d_{xz}$ | 0.078 |

| Complex **5 (5*)** | Radical orbital |
|---|---|
| Fe $d_{x^2-y^2}$ | 0.013 (0.011) |
| Fe $d_{z^2}$ | 0.001 (0.001) |
| Fe $d_{xz}$ | 0.034 (0.005) |
| Fe $d_{yz}$ | 0.277 (0.214) |

**Table S4.** DFT calculated Mulliken spin density values for complexes **1-5**. The values given in the brackets are DFT computed Lowedin spin density values for complexes **1-4** using Orca suite of program employing the UB3LYP functional using the Alhrichs def2-TZVP basis set for the metal ions and nitrogen atoms. While for the remaining atoms we have used the def2-SVP basis set with an auxiliary def2/J columbic fitting basis set for all atoms. Increased integration grids (Grid 5 in ORCA) along with tight SCF convergence were used.

| Complex | M1 spin | Radical | M2 spin | L1+L1 |
|---|---|---|---|---|
| **1** | 3.081 (2.936) | 1.019 (1.128) | 3.081 (2.936) | -0.181 (0.000) |
| **2** | 4.778 (4.691) | 1.261 (1.320) | 4.778 (4.691) | 0.184 (0.299) |
| **3** | 3.778 (3.662) | 1.316 (1.344) | 3.778 (3.709) | 0.127 (0.285) |
| **4** | 2.718 (2.669) | 1.333 (1.363) | 2.718 (2.669) | 0.231 (0.298) |
| **5** | 3.734 | 1.313 | 3.734 | 0.219 |
| **$5_{XRD}$ (Fe$^{II}$)** | 3.767 | 1.308 | 3.767 | 0.159 |

**Table S5.** Bond critical point (BCP) properties for X-ray and optimized structures of complexes **1**-**5**. AIM analysis was performed at the same computational level as used for single point calculations. [a]The electron density at the bond critical density (BCP). [b]The Laplacian of the electron density at the BCP. [c]The electronic kinetic energy density [d]The total energy density at the BCP.

| | | $\rho^a$ | λ1 | λ2 | λ3 | $\nabla^2\rho^b$ | *G* | 1/4(∇2ρ) | *H* |
|---|---|---|---|---|---|---|---|---|---|
| Complex **1** | | | | | | | | | |
| **Cr1** | **N1** | 0.0942 | -0.1274 | -0.1127 | 0.6000 | 0.3599 | 0.1040 | 0.0900 | -0.0140 |
| **Cr1** | **N2** | 0.0958 | -0.1303 | -0.1123 | 0.6234 | 0.3808 | 0.1096 | 0.0952 | -0.0144 |
| **Cr2** | **N3** | 0.0958 | -0.1303 | -0.1124 | 0.6234 | 0.3808 | 0.1096 | 0.0952 | -0.0144 |
| **Cr2** | **N4** | 0.0941 | -0.1274 | -0.1126 | 0.5999 | 0.3598 | 0.1040 | 0.0900 | -0.0140 |
| Complex **2** | | | | | | | | | |
| **Mn1** | **N1** | 0.0734 | -0.0988 | -0.0861 | 0.4639 | 0.2790 | 0.0839 | 0.0697 | -0.0142 |
| **Mn1** | **N2** | 0.0732 | -0.0987 | -0.0887 | 0.4627 | 0.2753 | 0.0830 | 0.0688 | -0.0142 |
| **Mn2** | **N3** | 0.0732 | -0.0987 | -0.0888 | 0.4628 | 0.2753 | 0.0831 | 0.0688 | -0.0142 |
| **Mn2** | **N4** | 0.0734 | -0.0988 | -0.0861 | 0.4639 | 0.2790 | 0.0839 | 0.0697 | -0.0142 |
| Complex **3** | | | | | | | | | |
| **Fe1** | **N1** | 0.0749 | -0.0925 | -0.0708 | 0.5018 | 0.3384 | 0.0970 | 0.0846 | -0.0124 |
| **Fe1** | **N2** | 0.0722 | -0.0934 | -0.0707 | 0.4794 | 0.3153 | 0.0905 | 0.0788 | -0.0116 |
| **Fe2** | **N3** | 0.0727 | -0.1052 | -0.0654 | 0.4797 | 0.3091 | 0.0891 | 0.0773 | -0.0119 |
| **Fe2** | **N4** | 0.0769 | -0.1137 | -0.0966 | 0.5040 | 0.2938 | 0.0871 | 0.0734 | -0.0137 |
| Complex **4** | | | | | | | | | |
| **Co1** | **N1** | 0.0794 | -0.1057 | -0.0787 | 0.5011 | 0.3167 | 0.0966 | 0.0792 | -0.0174 |
| **Co1** | **N2** | 0.0794 | -0.1057 | -0.0787 | 0.5010 | 0.3167 | 0.0965 | 0.0792 | -0.0174 |
| **Co2** | **N3** | 0.0733 | -0.0911 | -0.0726 | 0.5169 | 0.3533 | 0.1062 | 0.0883 | -0.0178 |
| **Co2** | **N4** | 0.0733 | -0.0911 | -0.0726 | 0.5169 | 0.3533 | 0.1062 | 0.0883 | -0.0178 |
| Complex **5** | | | | | | | | | |
| **Fe1** | **N1** | 0.0726 | -0.0916 | -0.0691 | 0.4591 | 0.2985 | 0.0886 | 0.0746 | -0.0139 |
| **Fe1** | **N2** | 0.0780 | -0.0962 | -0.0755 | 0.5035 | 0.3318 | 0.0990 | 0.0830 | -0.0160 |
| **Fe2** | **N3** | 0.0726 | -0.0916 | -0.0691 | 0.4591 | 0.2985 | 0.0886 | 0.0746 | -0.0139 |
| **Fe2** | **N4** | 0.0780 | -0.0962 | -0.0755 | 0.5035 | 0.3318 | 0.0990 | 0.0830 | -0.0160 |

**Table S6.** Magneto-structural studies performed on model **5a**/**5b** with respect to metal-radical distance and metal-radical planarity. Here, A and B parameters are metal-radical distances in Å and C parameter is metal-radical planarity (angle Fe-X-X, X is the dummy atom placed between center of two carbon atoms of phenyl ring)

| **Magneto-structural Models** | **A** | **B** | **Avg(AB)** | **C** | $J$ **cm$^{-1}$** | **Fe$^{II}$** | **Rad** | **L** |
|---|---|---|---|---|---|---|---|---|
| D-1 | 1.998 | 1.856 | 1.927 | 177.3 | -20.5 | 3.795 | 1.136 | 0.069 |
| D-2 | 2.071 | 1.929 | 2.000 | 177.3 | -110.1 | 3.794 | 1.149 | 0.057 |
| D-3 | 2.167 | 2.024 | 2.096 | 177.3 | -164.2 | 3.797 | 1.151 | 0.052 |
| D-4 | 2.224 | 2.081 | 2.153 | 177.3 | -174.7 | 3.800 | 1.145 | 0.054 |
| D-5 | 2.304 | 2.160 | 2.232 | 177.3 | -176.1 | 3.806 | 1.134 | 0.060 |
| D-6 | 2.385 | 2.241 | 2.313 | 177.3 | -172.2 | 3.810 | 1.123 | 0.067 |
| | | | | | | | | |
| P-1 | 2.100 | 2.090 | 2.095 | 180.0 | -151.9 | 3.809 | 1.133 | 0.057 |
| P-2 | 2.113 | 2.078 | 2.096 | 178.3 | -153.7 | 3.812 | 1.129 | 0.058 |
| P-3 | 2.138 | 2.058 | 2.098 | 176.5 | -163.4 | 3.735 | 1.137 | 0.128 |
| P-4 | 2.163 | 2.039 | 2.101 | 174.8 | -184.6 | 3.816 | 1.124 | 0.060 |
| P-5 | 2.189 | 2.022 | 2.106 | 173.0 | -209.6 | 3.817 | 1.123 | 0.060 |
| P-6 | 2.217 | 2.006 | 2.112 | 171.3 | -235.5 | 3.813 | 1.126 | 0.061 |