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Electron Supporting Information

Fractional Transfer of a Free Unpaired Electron to Overcome Energy Barriers in the Formation of Fe^{4+} from Fe^{3+} during Core Contraction of Macrocycles: Implication for Heme Distortion

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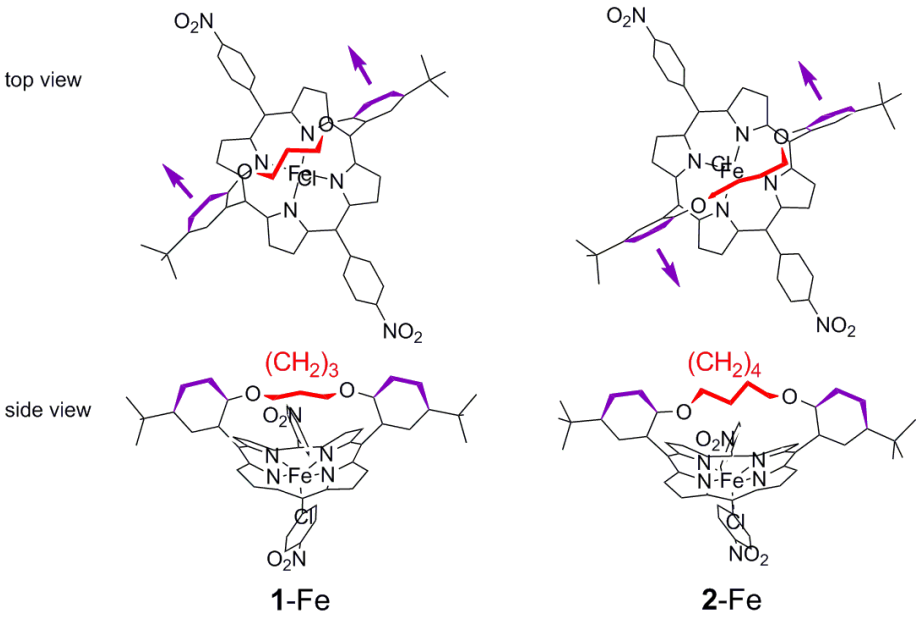
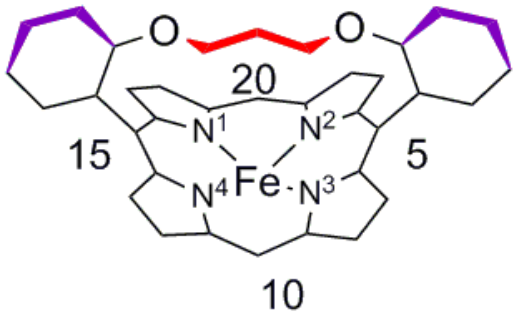
Contents

1. Comments to core diameters of model compounds

The structure feature (take compound **1**-Fe and **2**-Fe as samples)





$A_{CMC}1$ is the bond angle of central iron atom to two of 5,15-*meso*-C atoms,
$A_{CMC}2$ is that of central iron atom to two of 10,20-*meso*-C atoms,
$L_{NN}1$ is the averaged distance of two N atoms, N_1N_2 or N_3N_4,
$L_{NN}2$ is the averaged distance of two N atoms, N_1N_4 or N_2N_3
$rA_{CMC} = A_{CMC}1/A_{CMC}2$
$rL_{NN} = L_{NN}1/L_{NN}2$
All of these structural parameters are showed in Table 1.

Figure 1

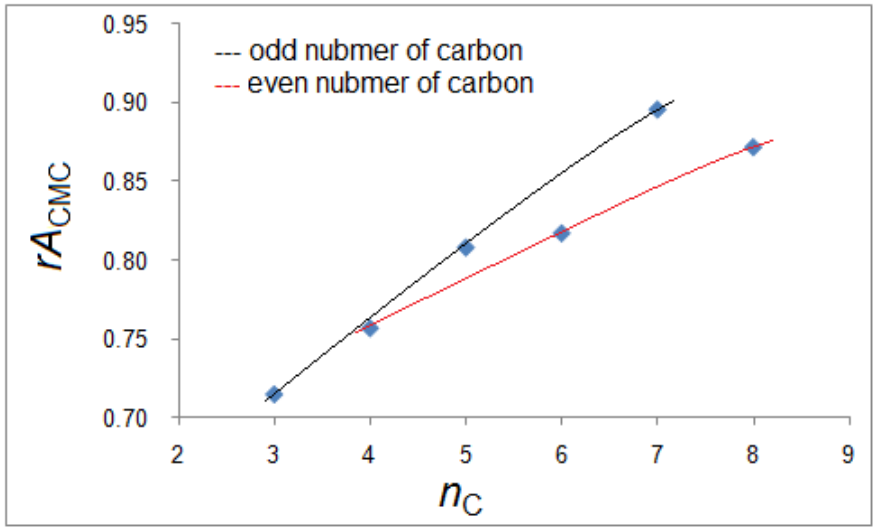
For model compounds with odd number of carbon atoms in strap, the two phenyl groups linked the strap slope to the macrocycle at the same side (e.g. **1**-Fe); while for those with even number of ones, the two groups slope to the macrocycle at the opposite directions (e.g. **2**-Fe).

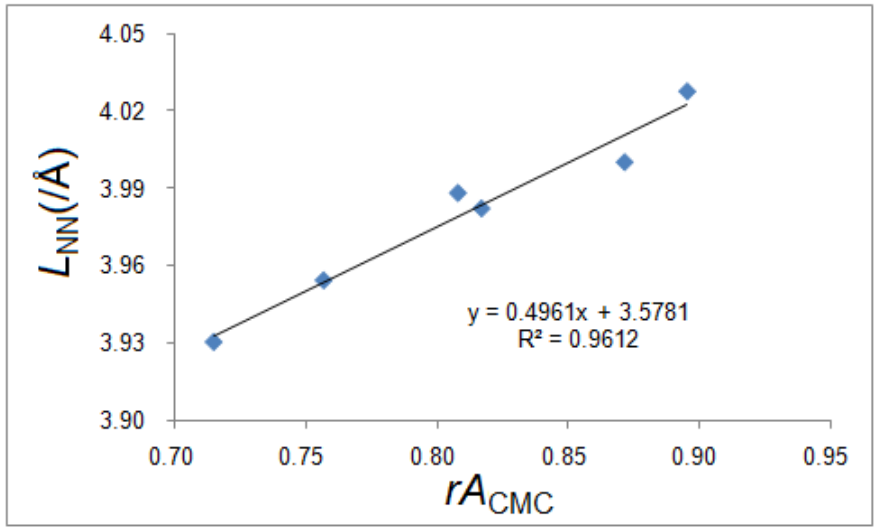
The macrocyclic deformations take on slight difference in two types of models, this difference can be reflected in the ratio of bond angle rA_{CMC} and the shape of N4 unit. These parameters, rA_{CMC} and rL_{NN}, implies that the N4 unit is slightly different deformed rectangle in those macrocycles with odd and even number of carbon atoms in strap.

Table 1. The structural parameters of 6 strapped iron model complexes

Parameters \ Compounds	**1**-Fe	**2**-Fe	**3**-Fe(a)	**3**-Fe(b)	**4**-Fe	**5**-Fe	**6**-Fe
$L_{NN(/Å)}$	3.930	3.954	3.993	3.982	3.982	4.028	4.000
rA_{CMC}	0.715	0.757	0.815	0.801	0.817	0.896	0.872
$A_{CMC}1(/^{o})$	126.1	133.8	142.1	139.7	142.0	151.7	148.7
$A_{CMC}2(/^{o})$	176.4	176.8	174.3	174.4	173.8	169.4	170.6
rL_{NN}	1.042	1.035	1.014	1.012	1.014	1.019	1.006
$L_{NN}h(/Å)$	2.721	2.747	2.804	2.799	2.796	2.821	2.821
$L_{NN}v(/Å)$	2.835	2.844	2.844	2.833	2.836	2.874	2.837

Three of above parameters L_{NN}, rA_{CMC} and rL_{NN}, in some degree, take on two isolated trends based on the odd and even number in straps. The parameters L_{NN}, rA_{CMC} show good correlation. (In below Figure 2)





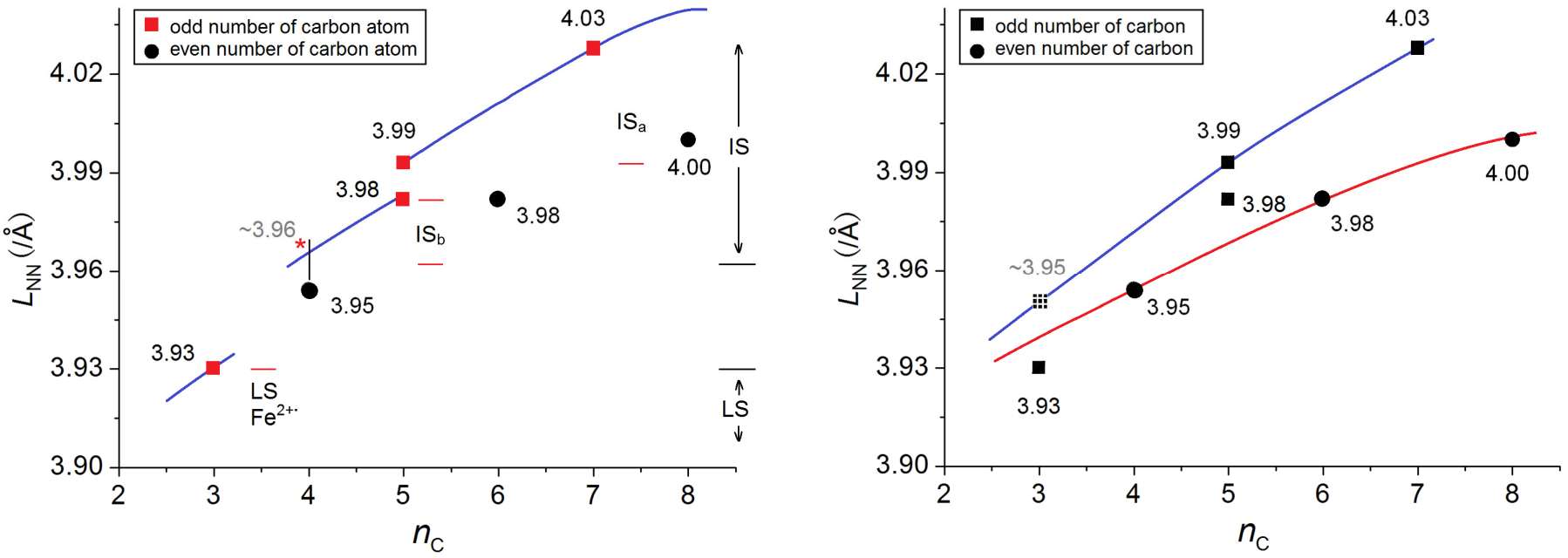
Note: The parameters of compound **3**-Fe are extracted from the average value of those in its isomers in current correlation analysis.

Figure 2. Correlation analysis

Concluded that:

This difference from the macrocyclic deformations covers up that from the change of electron structure in central metallic ions.

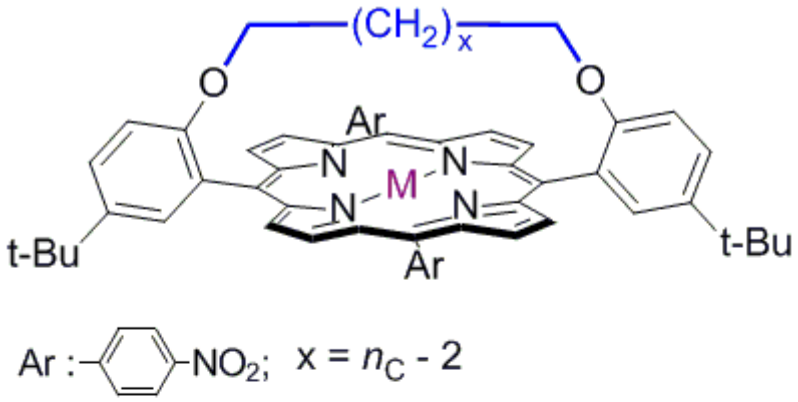
Therefore, the data from those compounds with odd number of carbon atoms were selected to differentiate the change of electronic structure in metal ions in this paper for eliminating thus disturbance of above deformation difference (Figure 3 left).



Core size in diameters, **2**-Fe, **4**-Fe and **6**-Fe with even number carbon atoms in straps is smaller than those with odd number carbon atoms.

Figure 3. Comparison of the treatment of core diameter data in this paper to that in the previous report. (Org. Lett. 2013, 15, 606)

2. Accounts of isomer phenomena



x \ M	MnCl	FeCl	Co	Ni
1	**1**-Mn	**1**-Fe	**1**-Co	**1**-Ni
2	**2**-Mn	**2**-Fe	**2**-Co	**2**-Ni
3	**3**-Mn	**3**-Fe	**3**-Co	**3**-Ni
4	**4**-Mn	**4**-Fe	**4**-Co	**4**-Ni
5	**5**-Mn	**5**-Fe	**5**-Co	**5**-Ni
6	**6**-Mn	**6**-Fe	**6**-Co	**6**-Ni

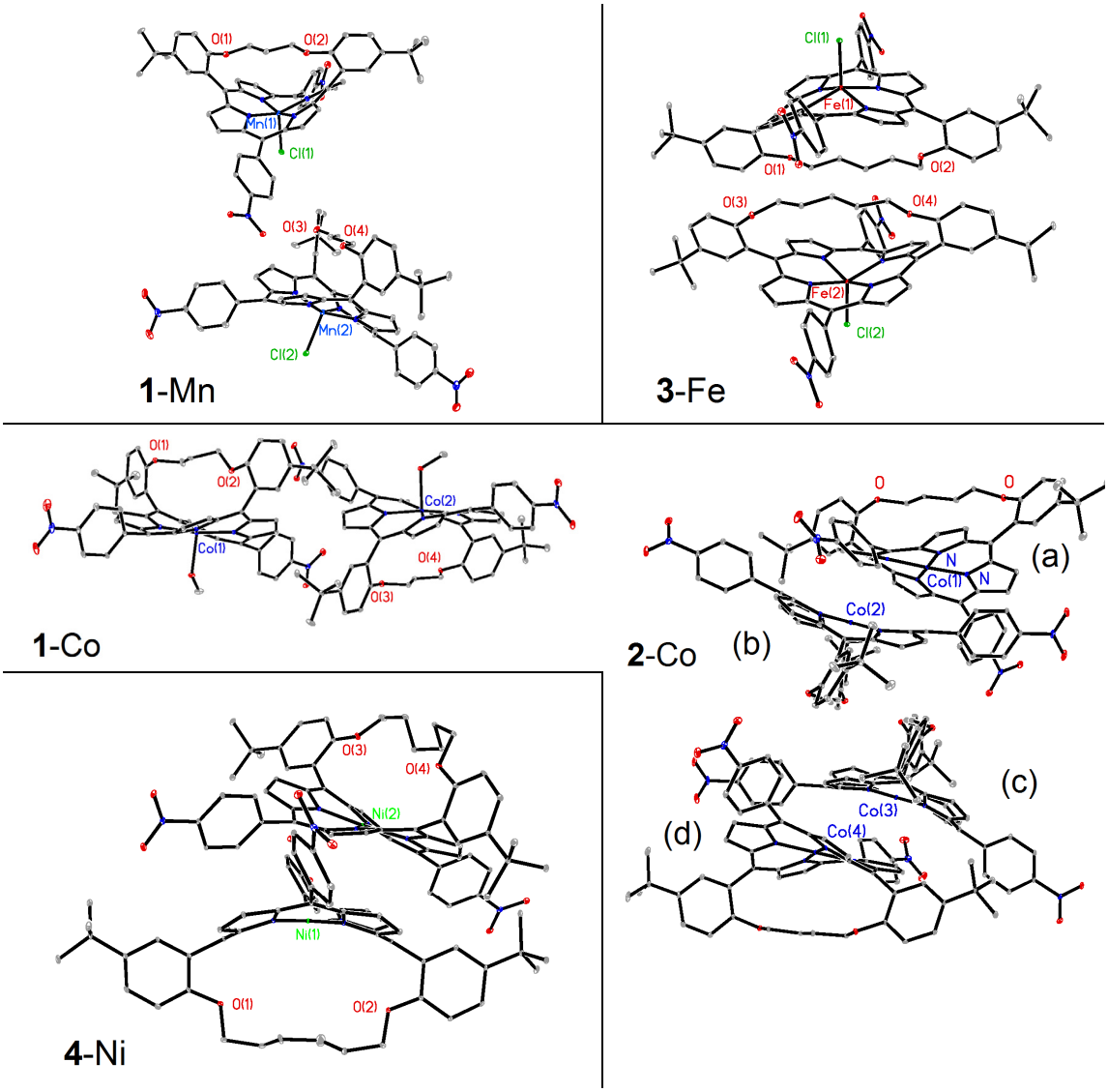
Figure 4. Model compounds

Crystal results show that:

- The isomer phenomena occur in each series of metallic models containing Mn, Fe, Co or Ni;
- And the occurrence of these phenomena is closely related to core size in each series (red labyled), which also indicates the phenomena isn't occassional.
- It is interesting that the difference of core diameter (L_{NN}) of in each couple of isomers is about 0.01 Å (Table 2, the first row labyled red) for above 4 samples.

The crystal structures* of isomers for compounds **1**-Mn, **3**-Fe, **1**-Co, **2**-Co and **4**-Ni are showed in below.

* The crystal structures of isomers for compounds **1**-Mn, **1**-Co, **2**-Co and **4**-Ni are not published.



Note: Maintain the relative positions of each double of isomers.

Figure 5. Crystal structures of 4 strapped complexes containing isomers.

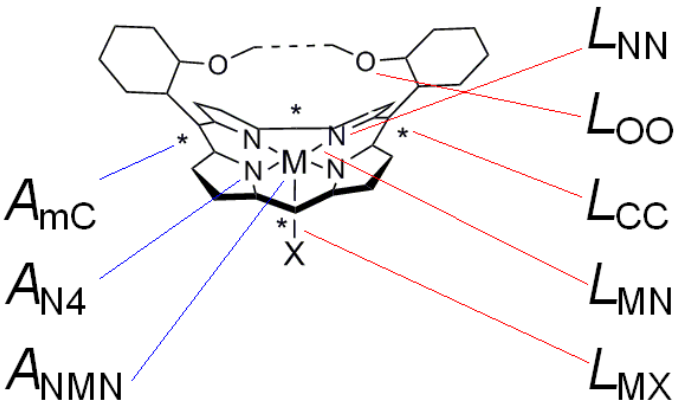


Figure 6. Types and definition of structural parameters

Table 2. The structural parameters of 4 strapped metallic complexes containing isomer

Compd. / Parameters	**1**-Mn		**3**-Fe		**1**-Co		**2-Co**		**4**-Ni		
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(c)	(a)	(b)	
L_{NN}(/Å) [a]	3.872	3.856	3.993	3.982	3.850	3.842	3.835	3.854	3.819	3.810	ΔL_{NN} ~0.01 Å
L_{OO}(/Å) [b]	4.759	4.759	7.227	6.570	4.750	4.698	6.103	6.103	6.387	6.858	
L_{CC}(/Å) [c]	6.173	6.117	6.612	6.558	6.245	6.233	6.407	6.422	6.502	6.496	
L_{MN}(/Å) [d]	1.969	1.961	2.059	2.057	1.930	1.926	1.919	1.928	1.910	1.905	
L_{MX}(/Å) [e]	2.347	2.387	2.215	2.220	2.219	2.215	-	-	-	-	
A_{mC}(/°) [f]	38.3	39.0	22.6	24.2	33.0	35.0	32.3	30.4	29.5	32.7	
A_{N4}(/°) [g]	1.5	1.3	1.0	0.7	2.3	0.1	3.5	0.4	4.9	2.5	
A_{NMN}(/°) [h]	159.0	159.0	151.8	151.0	172.1	172.2	174.7	177.0	176.6	178.3	

a. L_{NN} is core diameters represented by the average length of the diagonal N atoms in core; b. L_{OO} is the distance of two ether O atoms in straps;
c. L_{CC} is the distance of two *meso*-carbon atoms at 5,15 positions; d. L_{MN} is the bond length of M-N in core;
e. L_{MX} is the bond length of M-X in axial position; f. A_{mC} is the dihedral angle of 4 *meso*-carbon atoms;
g. A_{N4} is the dihedral angle of 4 nitrigen atoms; h. A_{NMN} is the bond angle of central iron atom to two diagonal N atoms.

3. Ionic radii in Shannon effective ionic radii table

For iron ions, Shannon Effective Ionic Radii that we can obtain is the most complete size data.

Table 3. The Shannon Effective Ionic Radii (r_M) of metal under differential charge number and spin modes.

Ion forms [a]	r_{Fe}/Å	Δr/Å [a]	Δd/Å [b]
Fe^{2+}, HS	0.78		
		0.17	0.34
Fe^{2+}, LS	0.61		
		-0.035	-0.07
Fe^{3+}, HS	0.645		
		0.095	0.19
Fe^{3+}, LS	0.55		
		-0.025	-0.05
Fe^{4+}, HS	0.585		

a. The coordination number of all ions is 6.
b. Δr and Δd denote the difference of metallic radii and diameters in the two adjacent ionic states, and $\Delta d = 2\Delta r$.