Support Information

Exploring the Effect of Axial Ligands, Solvation, and Redox on Structure and Inter-Metal Communication in Fe_3-EMACs

Mohammed Obies

Structure and electronic properties of $[Fe_3L_3]$ complex

To obtain optimized structure parameters that are comparable to experimental data, in another word to find a symmetrical structure with equal Fe-Fe bond distances, a range of hybrid functionals with varying Hartree-Fock percentages, including TPSSH (10%HF), B3LYP with 10-50%HF, and BHandHLYP (50%HF), were employed for optimization. All the applied exchange-correlation functionals produced a symmetrical structure of the $[Fe_3L_3]$ complex. The Fe-Fe bond lengths were found to be within ±0.01Å with the TPSSH (10%HF) and B3LYP with 10% and 15% compared to the experimental value, while the B3LYP with 20-50%HF, and BHandHLYP (50%HF) overestimated the bond distances. All the functionals predicted a Fe_2-Fe_1-Fe_3 bond angles within about 1.0 ° of the X-ray value. The Mulliken spin density computed with all functionals show similar trend of that computed with BP86 with less spin density on the central Fe ion, nevertheless, the spin density increased with increase the Hartree-Fock percentages going from 10% to 50%.

Table SI1: Comparison of computed structure parameters of $[Fe_3L_3]$ with different density functionals, bond lengths in Å, bond angles in °, and ρ is Mulliken spin density.

	Fe_1-Fe_3	Fe_1-Fe_2	Fe_2-Fe_1-Fe_3	ρFe_1	ρFe_2	ρFe_3
BP86	2.39	2.42	177.3	3.46	3.57	3.56
BLYP	2.39	2.42	177.7	3.44	3.48	3.48
TPSS	2.40	2.43	178.7	3.50	3.58	3.56
TPSSH (10%HF)	2.45	2.45	178.9	3.56	3.65	3.64
B3LYP (10%HF)	2.43	2.43	178.2	3.48	3.57	3.57
B3LYP (15%HF)	2.45	2.45	178.2	3.52	3.63	3.63
B3LYP (20%HF)	2.48	2.48	178.2	3.57	3.65	3.65
B3LYP (25%HF)	2.50	2.50	178.2	3.62	3.68	3.68
B3LYP (50%HF)	2.58	2.58	177.8	3.78	3.80	3.80
BHandHLYP (50%HF)	2.56	2.56	177.9	3.76	3.78	3.78
X-ray	2.4416(5)	2.4416(5)	179.27(4)	-----	-----	-----

Ground state investigation of $[Fe_3L_3]$ complex

Table SI2: Relative energies (eV) along structural parameters of different spin multiplicities computed with BP86 functional. bond lengths in Å, bond angles in °, and ρ is Mulliken spin density.

	R.E.	Fe_1-Fe_3	Fe_1-Fe_2	Fe_2-Fe_1-Fe_3	ρFe_1	ρFe_2	ρFe_3
S=1	+1.77	2.04	2.04	173.0	0.00	0.00	0.00
S=3	+0.43	2.09	2.45	179.2	-3.01	0.80	3.48
S=5	+0.10	2.50	2.31	175.9	3.50	-3.40	3.53
S=7	+0.39	2.21	2.21	175.7	2.44	1.58	1.57
S=9	+0.25	2.15	2.33	169.1	2.43	1.55	3.30
S=11	+0.13	2.24	2.22	176.0	2.37	3.22	3.18
S=13	0.00	2.39	2.42	177.3	3.46	3.57	3.56

Solvation effect on the structure of $[Fe_3L_3X_2]$ complexes

Table SI3: Computed structure parameters optimized with BP86 functional of $[Fe_3L_3CN_2]$ and $[Fe_3L_3NCS_2]$ in gas phase and with different solvents.

	Fe_1-Fe_3	Fe_1-Fe_2	Fe_2-Fe_1-Fe_3	ρFe_1	ρFe_2	ρFe_3
$[Fe_3L_3CN_2]$-gas phase	2.50	2.49	179.8	3.49	3.69	3.69
$[Fe_3L_3CN_2]$-benzene	2.50	2.49	179.8	3.50	3.68	3.68
$[Fe_3L_3CN_2]$-toluene	2.50	2.49	179.8	3.50	3.68	3.68
$[Fe_3L_3(NCS)_2]$-gas phase	2.47	2.46	179.8	3.43	3.69	3.70
$[Fe_3L_3(NCS)_2]$-benzene	2.47	2.46	179.8	3.43	3.69	3.70
$[Fe_3L_3(NCS)_2]$-toluene	2.47	2.46	179.8	3.43	3.69	3.70