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Theoretical Calculations on Fe_3CuS_4 Clusters

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Abstract

Fe_3CuS_4 clusters exhibit promising applications in bioenzyme mimics and photocatalytic H_2 evolution. We systematically investigated their spin-state properties across the oxidation states ranging from $[Fe_3CuS_4]^{1-}$ to $[Fe_3CuS_4]^{5-}$.

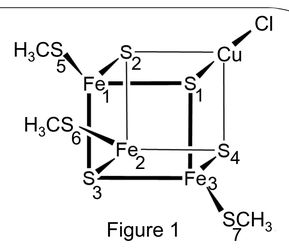

Figure 1

Computational Methods

- **Density Functional Theory (DFT)**

Structural optimization, spin-state energies, and reduction potentials clusters were calculated using BP/B3LYP functionals with two basis sets.

(**A**) C def-SV(P); S def-SV(P); H def-SV(P); Fe ecp-10-mdf; Cl def-SV(P); Cu ecp-10-mdf. ECP: Fe ecp-10-mdf; Cu ecp-10-mdf.

(**B**) C def2-TZVP; S def2-TZVP; H def2-TZVP; Fe ecp-10-mdf-f; Cl def2-TZVP; Cu ecp-10-mdf _VTZ-PP-f. ECP: Fe ecp-10-mdf; Cu ecp-10-mdf. Dispersion correction: BJ .

- **Broken Symmetry (BS) Approach**

Local high-spin / overall low-spin configurations were constructed to characterize Fe-Cu magnetic coupling, enabling the determination of stable ground spin states in each oxidation state.

- **Mulliken Charge Analysis**

Charge distributions of Fe, Cu, and S were quantified, revealing charge-transfer pathways during redox processes.

- **Conductor-like Screening Model (COSMO)**

Solvent effects were modeled at ε = 78.39 to evaluate solvation energies and solvent effects on spin state energies.

- **The calculation process of $\Delta G_{EA}(aq)$**

Theoretical calculations of redox potentials $\Delta G_{EA}(g)$ utilize a free-energy-type cycle similar to the one shown in Figure 2. $\Delta G_{EA}(aq)$ is the electron affinity in gas phase, ΔG_s and $\Delta G_s'$ are the solvation Gibbs energies of the structurally and electronically optimized $[Fe_3CuS_4(SCH_3)_3Cl]^{n-}$(n=1-5) complexes. The standard reduction potential E^o can be expressed as: $E^0_{\mathrm{rel},SHE} = -\frac{\Delta G^0_{EA}(aq)}{F} - E^0_H$, F is the Faraday constant (96.485 kJ/mol·V) and E^0_H denotes the absolute standard potential of the standard hydrogen electrode (SHE) in aqueous solution (reference values range from 4.05 to 4.44 V).

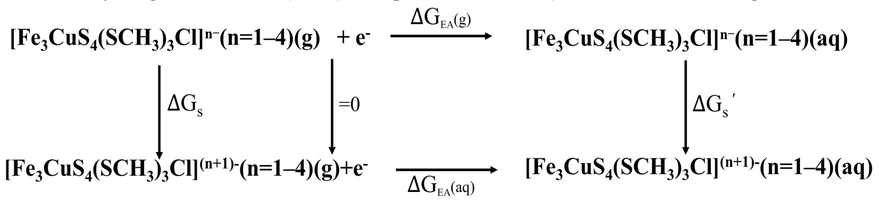

Figure 2

Table 1 Calculated energies (a.u.) of the ground spin states for Fe_3CuS_4

	BP, B			B3LYP, B		
Q	**S_{th}**	**E**	**S_{ac}^2**	**S_{th}**	**E**	**S_{ac}^2**
-5	2	-3938.6621	10.39	2	-3937.9778	11.71
-4	3/2	-3938.5959	8.64	5/2	-3937.9001	13.52
-3	2	-3938.5114	10.02	2	-3937.7868	10.72
-2	3/2	-3938.3723	7.73	5/2	-3937.6453	13.39
-1	1	-3938.2066	5.70	1	-3937.4512	7.82

S_{th}: theoretical value of spin
S_{ac}: actual value of spin(under the influence of spin contamination)

Table 2 Calculated bond length (Å) of Fe_3CuS_4 Cluster

	BP, B					B3LYP, B				
Q	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
Fe-S_b	2.22	2.26	2.29	2.29	2.28	2.29	2.31	2.33	2.36	2.32
Fe- S_l	2.18	2.25	2.32	2.28	2.27	2.23	2.29	2.36	2.37	2.36
Cu-Cl	2.16	2.22	2.29	2.28	2.27	2.16	2.25	2.29	2.32	2.34
Cu-S_b	2.37	2.38	2.40	2.40	2.39	2.46	2.45	2.78	2.40	2.49

S_b: bridged S, i.e., S_1-S_4
S_l: ligand S, i.e., S_5-S_7

Table 3 Calculated bond angle (deg) of Fe_3CuS_4 Cluster

	BP, B					B3LYP, B				
Q	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
S_l-Fe-S_b	114	117	114	115	115	116	116	113	118	114
S_b-Fe-S_b	107	105	105	105	104	103	104	103	100	104
S_b-Cu-S_b	100	100	101	99	98	100	100	105	97	98
Fe-S_b-Fe	74	74	74	74	74	74	77	75	75	76
Fe-S_b-Cu	74	76	74	76	77	79	75	72	82	76
S_b-Cu-Cl	122	121	119	120	121	127	120	127	122	121

S_b: bridged S, i.e., S_1-S_4
S_l: ligand S, i.e., S_5-S_7

Table 4 Calculated dihedral angle (deg) of Fe_3CuS_4 Cluster

	BP, B					B3LYP, B				
Q	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
Fe_3-S_1-Fe_1-S_3	-15	-14	-16	-11	-16	-15	-14	-20	-17	-16
Cu-S_4-Fe_3-S_1	15	12	14	12	11	11	7	14	5	10
Cu-S_2-Fe_1-S_1	-10	-13	-12	-13	-12	-12	-14	-9	-15	-10

Table 5 Calculated relative energies to the ground state (a.u.)

$[Fe_3CuS_4(SCH_3)_3Cl]^{n-}$ (n=1-5)	S	BP, A/B	B3LYP, B
-5	3	16.7959/8.6977	-
	2^c	0/0	0
	1	49.4735/37.4914	-
	0	107.1218/-	-
-4	7/2	71.5223/-	-
	5/2	0/ 283.5118	0
	3/2	29.5091/0	17.16
	1/2	96.0068/57.5544	133.89
-3	3	48.5041/52.4656	-
	$2^{a,b}$	0/0	0
	1	59.9770/68.9301	53.0919
-2	7/2	53.0383/51.6025	-
	5/2	7.1846/6.9372	0
	$3/2^b$	0/0	31.8142
	$1/2^a$	46.9180/43.5121	95.2542
-1	3	35.8067/21.7626	-
	2	29.4138/29.0757	-
	1^b	0/0	0
	0^b	25.3814/33.5223	61.5812

(a) Ground state from experimental data by Staples et al. [2] (b) Ground state calculated by Jensen et al. [3]
We did not perform large-basis-set calculations for spin states that were confirmed to be impossible as ground states using small basis sets.

Table 6 Calculated Reduction Potentials(V)

	BP, B				B3LYP, B				BP, calculated by Jensen et al. [3]	
Q variation	**-5/-4**	**-4/-3**	**-3/-2**	**-2/-1**	**-5/-4**	**-4/-3**	**-3/-2**	**-2/-1**	**-3/-2**	**-2/-1**
$\triangle G^o_{EA}$/kJ/mol	-181.19	-215.46	-372.61	-434.71	-201.40	-305.02	-376.59	-513.55	-317.44	-383.05
E^o/V (E_H^0= 4.43 V)	-2.55	-2.20	-0.57	0.08	-2.34	-1.26	-0.53	0.89	-1.14	-0.46

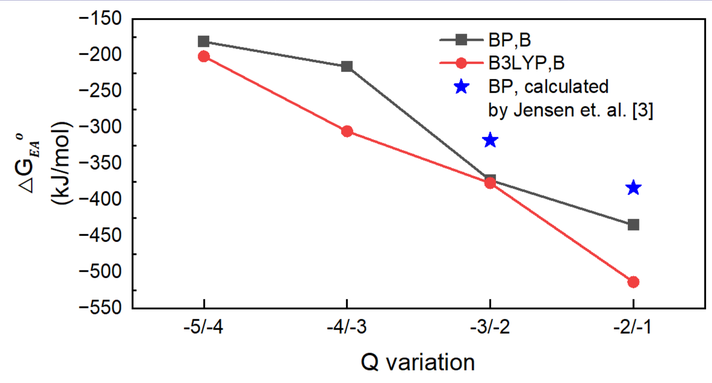

Figure 3 Calculated $\triangle G^o_{EA}$ (kJ/mol)

Conclusion

1. The calculated ground spin states are generally consistent with previous theoretical results and available experimental data, except for the case of Q = −2, where the computed results are in agreement with earlier theoretical findings but deviate from the experimental data. The BP and B3LYP functionals predict different ground spin states at Q = −2 and Q = −4. For Q = −4, the S = 5/2 state is predicted to have a relatively high energy under the BP functional, which is speculated to be attributed to the fact that although the geometry optimization satisfied the convergence criteria, it did not converge to the lowest-energy structure.
2. Both BP and B3LYP produced the similar geometry, except for R(Cu-S_b) at Q = −3 , in which the difference is 0.38 Å. For other structures, at different charges, bond length differences are below 0.2 Å, bond angle differences below 7°, and dihedral angle differences below 7°. We may conjecture that the change in charge has little effect on the geometry.
3. Among all redox pairs, significant reduction potential differences are observed between the calculated values from the BP and B3LYP functionals, indicating that the choice of DFT functional exerts a substantial influence on the computational results. For the -3/-2 and -2/-1 redox pairs, the BP values differ from those reported by Jensen et al. [3], which suggests discrepancies between the present computational system and the previously reported one. Specifically, we employed Cl instead of CH_3 as the ligand for Cu in our calculations, and smaller basis sets such as 6-31G(d) were used in the previous study.

Acknowledgements

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[3] Jensen, K. P., Ooi, B. L., Christensen, H. E. M. Computational Chemistry of Modified [MFe_3S_4] and [$M_2Fe_2S_4$] Clusters: Assessment of Trends in Electronic Structure and Properties. J. Phys. Chem. A, 2008, 112, 12829-12841.