

The magnetic coupling in manganese-based dinuclear superhalogens and their analogues. A theoretical characterization from combined DFT and BS study

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Table S1 Lowest frequencies of normal modes of clusters under study (in cm⁻¹) 2

Table S2 Relative energies of various HS and BS states of [Fe₂Cl₅]⁺ (in K cal mol⁻¹) 3

Table S3 Relative energies of various HS and BS states of MnFeCl₅ (in K cal mol⁻¹) 4

Table S1 Lowest frequencies of normal modes of clusters under study (in cm^{-1})^a

		B3LYP	O3LYP	MPW1	BLYP	OLYP	PW91
DB-[Mn ₂ Cl ₅] ⁻	DZ	18.90/17.68	16.32/15.81	16.55/14.91	18.97/16.42	19.02/17.21	16.97/11.28
	TZ	15.13/13.67	13.91/12.83	12.45/10.06	15.22/10.84	15.94/13.17	11.95/-6.54
	QZ	15.76/14.32	15.48/14.79	13.30/11.13	16.18/12.58	17.30/14.67	13.77/5.56
TB-[Mn ₂ Cl ₅] ⁻	DZ	50.28/51.40	51.88/52.29	50.17/51.04	47.67/50.10	51.44/52.49	46.21/48.70
	TZ	50.42/51.40	53.50/53.64	49.95/50.72	48.01/50.03	51.32/52.07	46.15/48.22
	QZ	50.46/51.75	52.30/52.88	50.64/51.68	47.95/50.10	51.44/52.49	46.21/48.70
DB-[Fe ₂ Cl ₅] ⁺	DZ	19.06/18.14	22.67/22.12	20.09/20.15	-15.33/-107.45	18.25/-5.15	-4.70/-69.11
	TZ	19.52/19.19	27.77/21.34	19.27/19.64	13.90/13.97	18.27/11.75	15.68/-66.92
	QZ	18.97/18.48	22.24/21.63	19.40/19.60	8.92/14.24	18.70/9.67	14.83/-82.31
TB-[Fe ₂ Cl ₅] ⁺	DZ	45.64/53.73	47.41/51.42	45.54/52.25	45.22/53.71	44.02/51.91	40.27/52.94
	TZ	45.26/53.27	46.81/51.14	44.32/52.18	41.98/53.75	42.84/51.64	39.69/53.01
	QZ	48.25/55.39	50.06/54.12	47.55/54.21	44.57/55.14	47.09/54.09	42.92/54.42
DB-MnFeCl ₅	DZ	17.70/19.73	16.42/17.14	17.73/18.75	15.06/21.29	15.49/19.53	15.63/20.15
	TZ	17.25/19.05	14.39/14.86	17.21/18.44	14.31/20.99	13.61/19.11	14.24/19.88
	QZ	16.47/18.38	15.33/15.77	16.96/18.04	13.36/21.52	14.13/19.98	14.96/21.89
TB-MnFeCl ₅	DZ	44.25/50.01	49.41/51.60	45.01/49.36	38.81/48.78	45.70/50.36	37.45/47.68
	TZ	44.42/49.86	47.36/51.66	44.73/49.31	37.93/48.53	44.80/49.92	36.29/47.48
	QZ	44.26/50.36	45.66/51.82	45.30/50.24	37.65/49.71	45.19/51.59	37.68/49.40

^a results from calculations on optimized structures of HS states are at the left side of “/”, results from calculations on optimized structures of BS states are at the right side of “/”.

Table S2 Relative energies of various HS and BS states of $[\text{Fe}_2\text{Cl}_5]^+$ (in K cal mol⁻¹)

		B3LYP	O3LYP	MPW1	BLYP	OLYP	PW91
DZ	DB-HS ^a	10.36	3.78	12.86	12.87	10.34	17.02
	DB-BS ^b	9.00	3.13	11.62	9.05	8.18	12.40
	TB-HS ^c	3.57	2.06	3.14	8.18	5.43	9.25
	TB-BS ^d	0.00	0.00	0.00	0.00	0.00	0.00
TZ	DB-HS	8.96	2.20	11.55	11.41	9.22	15.83
	DB-BS	7.58	1.53	10.24	7.51	6.99	11.19
	TB-HS	3.71	2.28	3.38	8.66	5.81	9.46
	TB-BS	0.00	0.00	0.00	0.00	0.00	0.00
QZ	DB-HS	9.08	2.24	11.75	11.15	9.20	15.57
	DB-BS	7.72	1.54	10.49	7.28	7.02	11.10
	TB-HS	3.74	2.40	3.37	8.08	5.82	9.25
	TB-BS	0.00	0.00	0.00	0.00	0.00	0.00

^a HS state of double-bridged structure. ^b BS state of double-bridged structure. ^c HS state of triple-bridged structure. ^d BS state of triple-bridged structure.

Table S3 Relative energies of various HS and BS states of MnFeCl₅ (in K cal mol⁻¹)

		B3LYP	O3LYP	MPW1	BLYP	OLYP	PW91
DZ	DB-HS ^a	2.70	-0.62	3.86	7.08	4.70	9.92
	DB-BS ^b	1.07	-1.60	2.50	2.12	1.71	4.24
	TB-HS ^c	3.78	2.51	3.32	8.64	5.89	9.44
	TB-BS ^d	0.00	0.00	0.00	0.00	0.00	0.00
TZ	DB-HS	1.69	-1.58	2.92	5.83	3.76	8.89
	DB-BS	0.04	-2.58	1.48	0.76	0.55	2.89
	TB-HS	3.73	2.48	3.38	8.35	6.01	9.42
	TB-BS	0.00	0.00	0.00	0.00	0.00	0.00
QZ	DB-HS	1.50	-1.96	2.78	5.46	3.51	8.53
	DB-BS	-0.14	-2.97	1.39	0.43	0.31	2.67
	TB-HS	3.78	2.60	3.43	8.34	6.15	9.40
	TB-BS	0.00	0.00	0.00	0.00	0.00	0.00

^a HS state of double-bridged structure. ^b BS state of double-bridged structure. ^c HS state of triple-bridged structure. ^d BS state of triple-bridged structure.