Electronic Supplementary Material (ESI) for Dalton Transactions.

Magnetically Stabilized $Fe_8(\mu_4\text{-}S_6)S_8$ Clusters in $Ba_6Fe_{25}S_{27}$

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Supporting Information

0.1 Density Functional Theory Calculations

For all Density Functional Theory calculations, the Vienna Ab initio Simulation Package (VASP)[1–4] was employed, using Generalized Gradient Approximation and Projector Augmented Wave potentials. These calculations include geometrical optimization of crystal structures, band energies, and density of states (DOS) distributions. For the pentlandite calculations (M_9S_8, where M=Fe,Co,Ni), all crystal structures underwent geometrical optimization before static calculations to discern the band structures and DOS distributions of each compound. Geometrical optimization was performed in a two step process: (1) optimization of the atomic placement, and then (2) optimization of all structural parameters. K-point meshes and energy cutoffs for these calculations are provided in Table S1. Projected DOS curves were calculated through using the PAW method, specified by LORBIT=11.

Table S1. Details of DFT calculations.

Stochiometry	Structure type	k-point meshes	Energy cutoff (eV)
Fe_9S_8	pentlandite	9x9x9, 11x11x11, 13x13x13	360
Co_9S_8	pentlandite	9x9x9, 11x11x11, 13x13x13	360
Ni_9S_8	pentlandite	9x9x9, 11x11x11, 13x13x13	360
$Ba_6Fe_{25}S_{27}$	djfisherite	5x5x5	280
$Ba_6Fe_{25}S_{27}$	djfisherite	5x5x5	280
$Ba_6Fe_{25}S_{27}$	djfisherite	5x5x5	280
BaS	CsCl-type	9x9x9	280

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0.2 Hückel Theory Calculations

All Hückel calculations performed in this Article employed the YAeHMOP package.[5] Each input file specified keywords DIAGWO and NONWEIGHTED, which engages the simple Hückel form of the calculation and turns off the use of counterintuitive orbital mixing correction, respectively.[6] To obtain Hückel parameters that are reflective of the GGA-DFT result, Hückel band energies and projected DOS distributions were refined against a single point energy GGA-DFT calculation. This process was accomplished using *eHtuner*,[7] which uses a Nelder-Mead optimization of the parameters for a least squared fitting of both the band energies and the projected DOS curves (up to 1 eV above the Fermi energy). The resulting parameters are listed in Table S2.

Table S2. DFT-calibrated Hückel parameters.

Compound, RMS deviation*	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
$Ba_6Fe_{25}S_{27}$, 0.070978 eV	Ba	Ba 5*s*	-33.789		3.9288		
		Ba 5*p*	-18.937		3.3029		
		Ba 5*d*	-4.507	1.7838	3.1779	0.5192	1.2459
	Fe	Fe 4*s*	-0.237		2.0286		
		Fe 4*p*	1.039		1.9126		
		Fe 3*d*	-7.978	0.5680	5.4336	0.7164	2.1525
	S	S 3*s*	-16.267		2.3651		
		S 3*p*	-8.491		1.8969		
$Ba_6Co_{25}S_{27}$, 0.079546 eV	Ba	Ba 5*s*	-34.140		3.7086		
		Ba 5*p*	-19.066		2.9853		
		Ba 5*d*	-4.830	0.9612	3.0421	1.0774	1.6980
	Co	Co 4*s*	-1.630		1.8717		
		Co 4*p*	-0.607		1.8432		
		Co 3*d*	-8.303	0.5680	6.5101	0.3895	1.9300
	S	S 3*s*	-17.002		3.1935		
		S 3*p*	-8.053		2.0242		
$Ba_6Ni_{25}S_{27}$, 0.080607 eV	Ba	Ba 5*s*	-33.786		3.7234		
		Ba 5*p*	-18.952		3.1493		

Parameter table continued on next page

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*RMS deviation: root-mean-squared deviation between the GGA-DFT and Hückel energies fit to DFT results, considering all occupied valence bands up to the Fermi energy (E_F plus some additional low-lying unoccupied bands (usually up to 1 eV above E_F).

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
		Ba 5*d*	-6.105	1.4911	2.9805	0.9693	1.5244
	Ni	Ni 4*s*	-1.186		2.1489		
		Ni 4*p*	-0.401		1.9329		
		Ni 3*d*	-8.924	0.5680	5.3907	0.4221	2.1385
	S	S 3*s*	-15.641		2.4180		
		S 3*p*	-8.120		1.9558		
Fe_9S_8, 0.150080 eV	Fe	Fe 4*s*	-0.716		1.9988		
		Fe 4*p*	0.758		1.9603		
		Fe 3*d*	-8.701	0.5680	5.3964	0.3959	1.8499
	S	S 3*s*	-15.189		2.3919		
		S 3*p*	-7.540		1.9144		
Co_9S_8, 0.088563 eV	Co	Co 4*s*	-2.566		1.9344		
		Co 4*p*	-1.942		2.0057		
		Co 3*d*	-8.604	0.5680	6.1447	0.3950	1.8939
	S	S 3*s*	-15.515		3.0517		
		S 3*p*	-7.559		2.1107		
Ni_9S_8, 0.079158 eV	Ni	Ni 4*s*	-2.015		1.9293		
		Ni 4*p*	-1.364		2.0598		
		Ni 3*d*	-8.893	0.5680	6.5810	0.4429	2.0936
	S	S 3*s*	-17.107		3.3679		
		S 3*p*	-7.451		1.9866		
Ba_1S_1, 0.101675 eV	Ba	Ba 5*s*	-34.228		4.1800		
		Ba 5*p*	-19.464		2.8570		
		Ba 5*d*	-6.735	0.1911	2.5236	0.0049	0.4779
	S	S 3*s*	-18.249		2.5494		
		S 3*p*	-8.856		2.2070		

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