

Supporting Information

Pseudo-polymorphism in layered FeS intercalates: A competition between charged and neutral guest species

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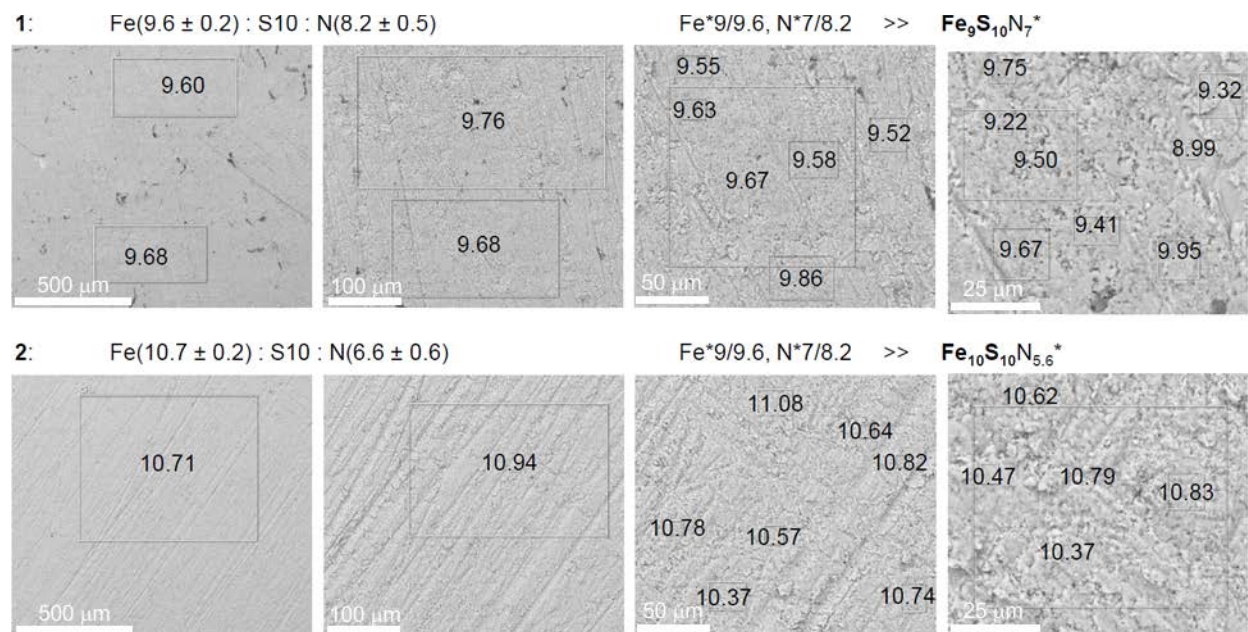


Figure S1. EDS-SEM images from pellets of **1** (top) and **2** (bottom) at magnification levels from left to right of 100, 300, 600, 1500 respectively. The Fe content normalized to 10 S atoms is given at each collection area. EDS systematically overestimates the Fe content. To account for this, compositions were recalculated. * indicates the corrected compositions using [Fe₈S₁₀]Fe(en)₃·en_{0.5} as a reference. Sample **2** was subjected to magnetic treatment to remove majority of elemental Fe impurity.

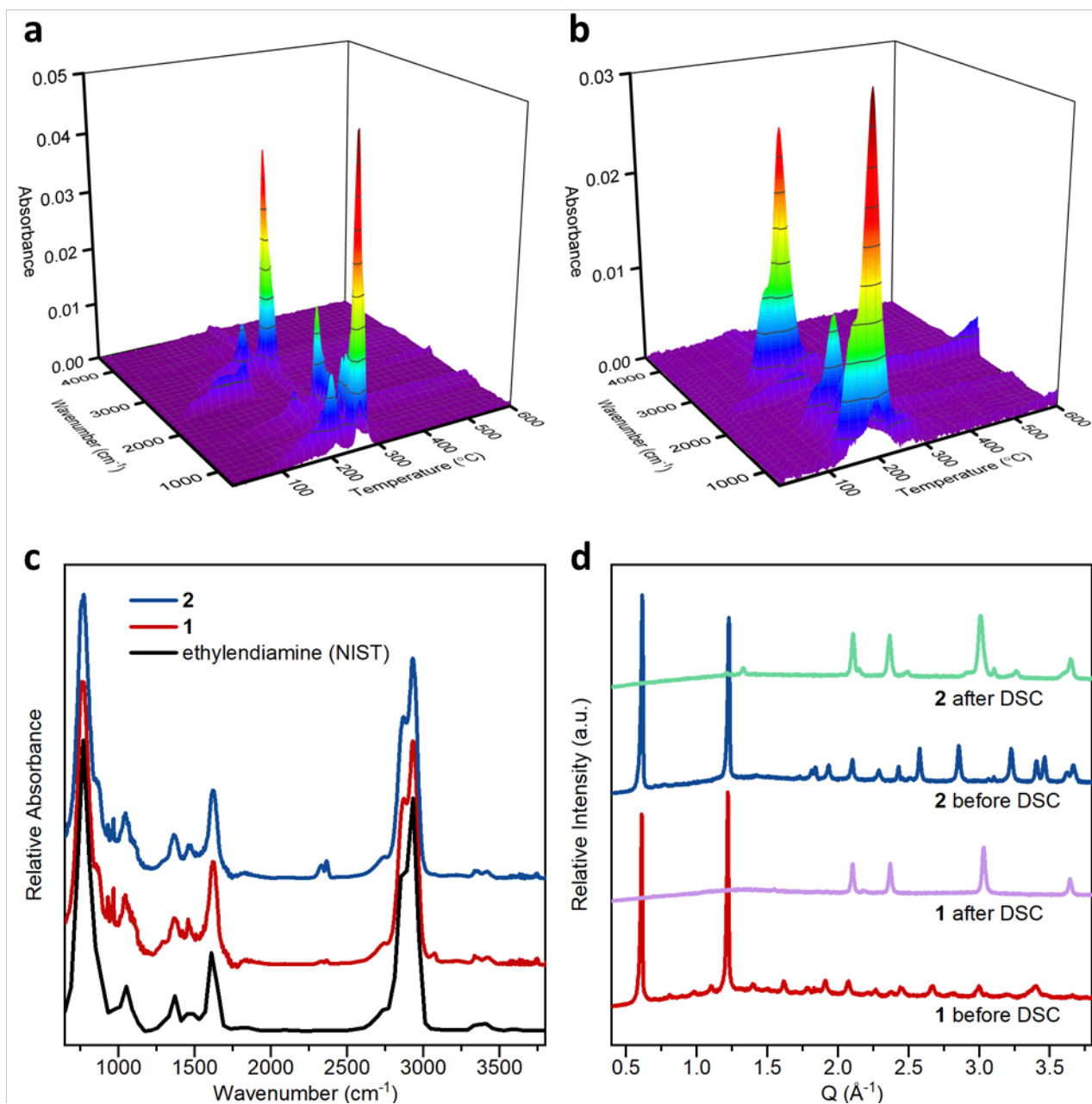


Figure S2. 3D map for FT-IR of evolved gas during TGA experiment plotting absorbance vs wavenumber and temperature for **(a) 1** and **(b) 2**. **(c)** Selected FT-IR spectra for evolved gas from **1** at 280 $^{\circ}\text{C}$ (red) and **2** at 220 $^{\circ}\text{C}$ (blue) compared to ethylenediamine spectrum from NIST. **(d)** Benchtop PXRD patterns collected before and after DSC ($\text{Cu-K}\alpha$).

Table S1. Rietveld refinement results for compound **2**. The final solution was refined through the Rietveld method (Figure 5). Background, unit cell parameters, size and strain for compound **2** were first refined. Next, atomic coordinates for all sites were further refined before refining isotropic displacement parameters for intralayer Fe and S. Displacement parameters for intercalated atoms were set at $0.05 \text{ \AA}^2$ to account for site disorder. This sample had some residual Fe impurity, which is refined to 1.21(1) wt. %.

$R_{wp} = 11.22 \%$		GOF = 2.40		$\lambda = 0.45791 \text{ \AA}$		$T = 295 \text{ K}$		
Phase	Unit Cell	Atom	x/a	y/b	z/c	Uiso	Site	Occ.
Compound 2	$A2_122$	Fe1	0.75	0.0	0.75017(4)	0.00594(8)	4b	.94
[Fe _{9.4} S ₁₀]Fe _{0.6} en _{2.7} 98.79(4) Wt. %	$a = 3.68981(4)$	S	0.75	0.0	0.31079(5)	0.0173(2)	4b	1.0
	$b = 3.69953(5)$	Fe2	0.048(6)	0.07(3)	0.485(1)	0.05	8c	0.03
	$c = 20.5053(1)$	N	0.365(3)	0.435(4)	0.4592(3)	0.05	8c	0.30
	$V = 279.908(4)$	C	0.660(4)	0.200(3)	0.505(1)	0.05	8c	0.30
α-Fe	$Im\bar{3}m$	Fe	0.0	0.0	0.0	0.01	2a	1
1.21(1) Wt. %	$a = 2.86653(3)$							
	$V = 23.5543(7)$							

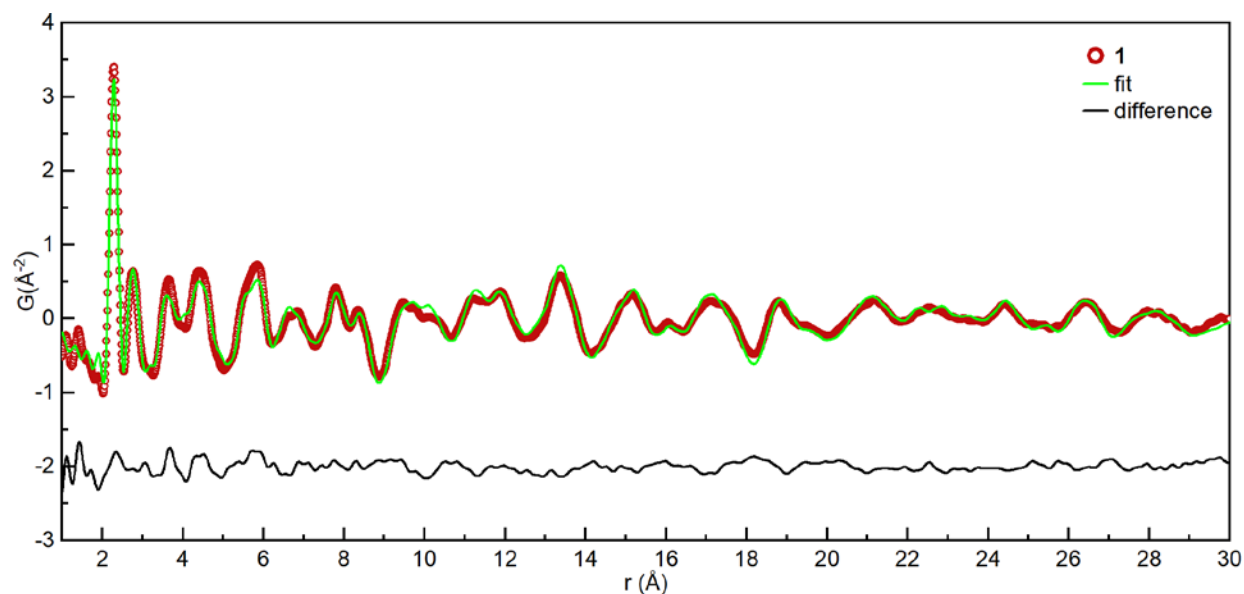


Figure S3. PDF of compound **1** (red circles) fitted against its structure as determined from SCXRD at 90 K (green line) with difference (black line).¹ In general fitting for compound **1** followed the same procedure for compound **2** (main text). However, the compound **1** unit cell has 144 unique atomic sites with Fe_8S_{10} layer when reduced to $P1$. So, no attempts were made to refine atomic positions. Furthermore, thermal displacements were constrained to be identical for all Fe and Se in the layers. In total only 6 displacement parameters were refined. Final fit from 1-30 Å converged to $R_w = 21.0\%$.

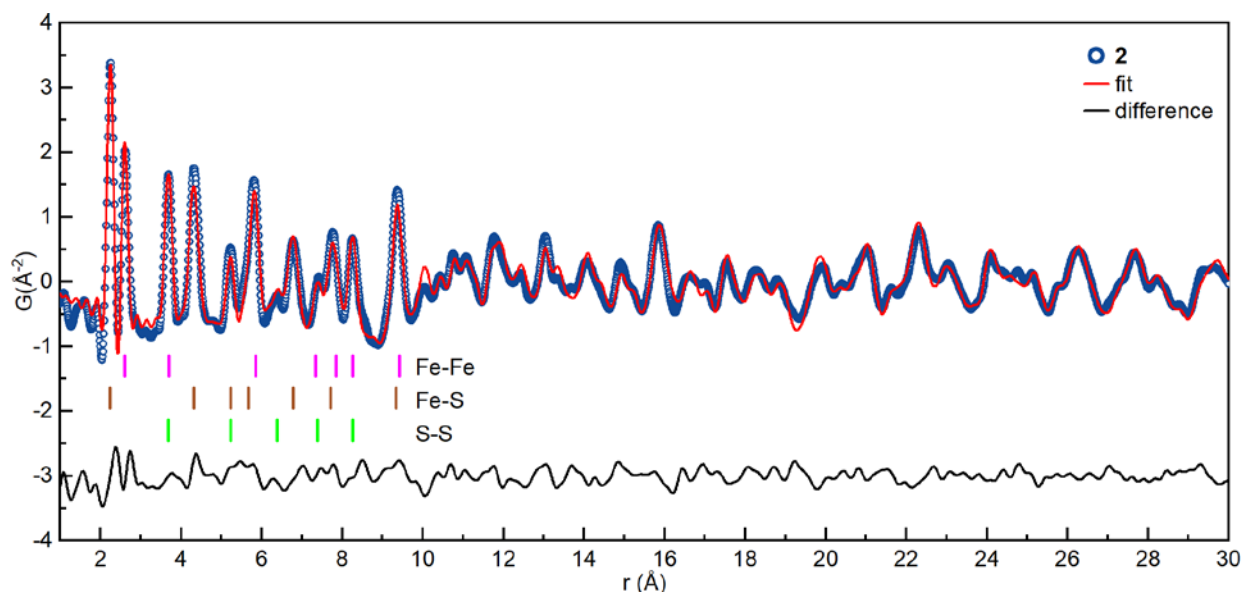


Figure S4. PDF of compound **2** (blue circles) fit against the model A2122 subgroup (red line) with difference curve (black line). The PDF fit only used intralayer Fe and S atomic sites as the intercalates' relative weak scattering has no appreciable effect. The fitting proceeded by first fitting sample scale and linear correlation, then unit cell dimensions. Finally, atomic sites and displacement parameters were fitted while constrained to a A2122 cell. The final fit, from $r = 1\text{-}30$ Å, converged to $R_w = 21.6\%$. For comparison, compound **1**, fit against its known structure, converged to $R_w = 21.0\%$.

Table S2. PDF fit results for compound **2**.

$Q_{\text{max}} = 23.5 \text{ \AA}^{-1}$ $Q_{\text{damp}} = 0.04 \text{ \AA}^{-1}$ $Q_{\text{broad}} = 0.01 \text{ \AA}^{-1}$ $T = 295 \text{ K}$									
Phase	Triclinic Cell	Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	Occ.
Compound 2	$a = 3.710(1) \text{ \AA}$	Fe1	0.75	0	0.7497(7)	0.004(3)	0.010(4)	0.10(2)	0.94
A2 ₁ 22	$b = 3.685(7) \text{ \AA}$	Fe2	0.25	0	0.2533(6)	0.004(3)	0.010(4)	0.10(2)	0.94
[Fe _{9.4} S ₁₀]Fe _{0.6} en _{2.7}	$c = 20.52(6) \text{ \AA}$	Fe3	0.75	0.5	0.2466(6)	0.004(3)	0.010(4)	0.10(2)	0.94
	$\alpha = 90.0^\circ$	Fe4	0.25	0.5	0.7533(6)	0.004(3)	0.010(4)	0.10(2)	0.94
	$\beta = 90.0^\circ$	S1	0.75	0	0.3133(6)	0.02(1)	0.01(1)	0.02(1)	1.0
Scale 0.35(2)	$\gamma = 90.0^\circ$	S2	0.25	0	0.6866(6)	0.02(1)	0.01(1)	0.02(1)	1.0
Linear correlation factor = 2.21(4)		S3	0.75	0.5	0.8134(6)	0.02(1)	0.01(1)	0.02(1)	1.0
		S4	0.25	0.5	0.1866(6)	0.02(1)	0.01(1)	0.02(1)	1.0
$R_w = 21.59\%$									

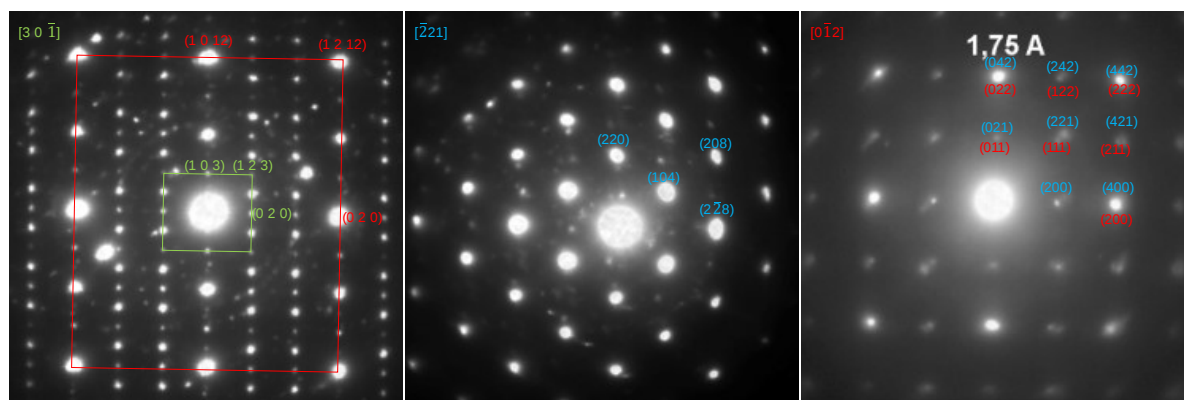


Figure S5. Selected ED images of compound **2** indexed in the $3.70 \times 3.69 \times 20.51 \text{ \AA}^3$ subcell (red), $2a \times 2b \times c$ (blue), and $4a \times 3b \times c$ (green) supercells.

^{57}Fe Mössbauer Spectroscopy

Compound 1

The spectrum for compound **1** measured at RT represents an overlap of several signals, majority of which are magnetically split into sextets. After multiple attempts to fit, the following model can be proposed: spectrum can be fitted with five sub-spectra. Two sub-spectra have large isomer shifts, $> 1 \text{ mm/s}$, which are characteristic for octahedral Fe signals, and three sub-spectra with lower isomer shifts, $< 0.6 \text{ mm/s}$, which are characteristic for tetrahedral Fe signals. All sub-spectra except of the octahedral signals are magnetically split into sextets indicating magnetic ordering above RT. A detailed analysis shows that the second tetrahedral signal with the isomer shift of 0.525 mm/s and the intensity of 38% has a random magnetic hyperfine field direction, the other two tetrahedral signals have their magnetic hyperfine fields oriented perpendicular to the plane of the sample. The magnetic hyperfine field for the octahedral signal is also randomly distributed. The 100 K and 6 K spectra for this compound are also fitted with five components with slightly increased δ values due to the second order Doppler shift and increased B_{hf} value due to collective magnetic excitation.²⁻³

Compound 2

The room-temperature spectrum for compound **2** is completely different. Besides the signal from elemental Fe, no hyperfine splitting is observed, thus the spectrum can be fitted as a combination of two doublets, corresponding to octahedral Fe^{2+} in the coordination complex and tetrahedral Fe^{2+} in the Fe-S layer. With lowering temperature, the octahedral Fe^{2+} signal remains doublet, while tetrahedral Fe show partial magnetic ordering with small fraction of hyperfine component.

Table S3. Summary of refined ^{57}Fe Mössbauer parameters: centroid shift, δ , quadrupole splitting/quadrupole shift, $\Delta E_Q/\epsilon$, magnetic hyperfine field, B_{hf} , fullwidth at half maxima (Γ), and intensity, I . Intensity fraction of each component of compound 2 is computed after subtracting signal of elemental Fe impurity (not shown).

Compound 1					Compound 2				
	Components	6 K	100 K	293 K		Components	6 K	100 K	293 K
$\text{O}_\text{h}\text{-Fe}^{2+}$	δ_1 (mm/s)	1.134(5)	1.043(5)	1.028(5)	$\text{O}_\text{h}\text{-Fe}^{2+}$	δ_1 (mm/s)	1.123(5)	1.076(5)	0.986(5)
	ΔE_{Q1} (mm/s)	1.598(5)	1.201(5)	0.710(5)		ΔE_{Q2} (mm/s)	1.536(5)	1.466(5)	0.775(5)
	Γ_1 (mm/s)	0.32(5)	0.24(5)	0.24(5)		Γ_1 (mm/s)	0.31(5)	0.34(5)	0.23(5)
	I_1 (%)	6(2)	6(2)	7(2)		I_2 (%)	15(2)	13(2)	6(2)
$\text{O}_\text{h}\text{-Fe}^{2+}$	δ_2 (mm/s)	1.272(5)	1.282(5)	1.286(5)	$\text{T}_\text{d}\text{-Fe}^{2+}$	δ_2 (mm/s)	0.592(5)	0.575(5)	0.472(5)
	$B_{\text{hf}2}$ (T)	10.1(2)	10.9(2)	10.5(2)		ΔE_{Q1}	0.211(5)	0.206(5)	0.209(5)
	ϵ_2 (mm/s)	1.357(5)	1.244(5)	1.217(5)		Γ_1 (mm/s)	0.36(5)	0.38(5)	0.36(5)
	Γ_2 (mm/s)	0.21(5)	0.21(5)	0.21(5)		I_1 (%)	67(2)	73(2)	94(2)
	I_2 (%)	5(2)	5(2)	4(2)					
$\text{T}_\text{d}\text{-Fe}^{2+}$	δ_3 (mm/s)	0.503(5)	0.484(5)	0.394(5)	$\text{T}_\text{d}\text{-Fe}^{2+}$	δ_3 (mm/s)	0.536(5)	0.534(5)	
	$B_{\text{hf}3}$ (T)	29.6(2)	29.3(2)	27.7(2)		$B_{\text{hf}3}$ (T)	27.4(2)	27.4(2)	
	ϵ_3 (mm/s)	0.200(5)	0.196(5)	0.169(5)		ϵ_3 (mm/s)	-0.030(5)	0.053(5)	
	Γ_3 (mm/s)	0.26(5)	0.24(5)	0.24(5)		Γ_1 (mm/s)	0.69(5)	0.71(5)	
	I_3 (%)	26(2)	26(2)	26(2)		I_3 (%)	14(2)	14(2)	
$\text{T}_\text{d}\text{-Fe}^{2+}$	δ_4 (mm/s)	0.620(5)	0.601(5)	0.525(5)	$\text{T}_\text{d}\text{-Fe}^{2+}$	δ_4 (mm/s)	0.620(5)		
	$B_{\text{hf}4}$ (T)	26.8(2)	26.6(2)	25.0(2)		$B_{\text{hf}4}$ (T)	28.6(2)		
	ϵ_4 (mm/s)	0.035(5)	0.038(5)	0.042(5)		ϵ_4 (mm/s)	0.281(5)		
	Γ_4 (mm/s)	0.26(5)	0.24(5)	0.24(5)		Γ_1 (mm/s)	0.24(5)		
	I_4 (%)	39(2)	38(2)	38(2)		I_4 (%)	4(2)		
$\text{T}_\text{d}\text{-Fe}^{3+}$	δ_5 (mm/s)	0.245(5)	0.251(5)	0.188(5)	$\text{T}_\text{d}\text{-Fe}^{3+}$	δ_5 (mm/s)			
	$B_{\text{hf}5}$ (T)	16.2(2)	16.0(2)	15.0(2)		$B_{\text{hf}5}$ (T)			
	ϵ_5 (mm/s)	0.098(5)	0.076(5)	0.067(5)		ϵ_5 (mm/s)			
	Γ_5 (mm/s)	0.28(5)	0.24(5)	0.26(5)		Γ_5 (mm/s)			
	I_5 (%)	24(2)	25(2)	25(2)		I_5 (%)			

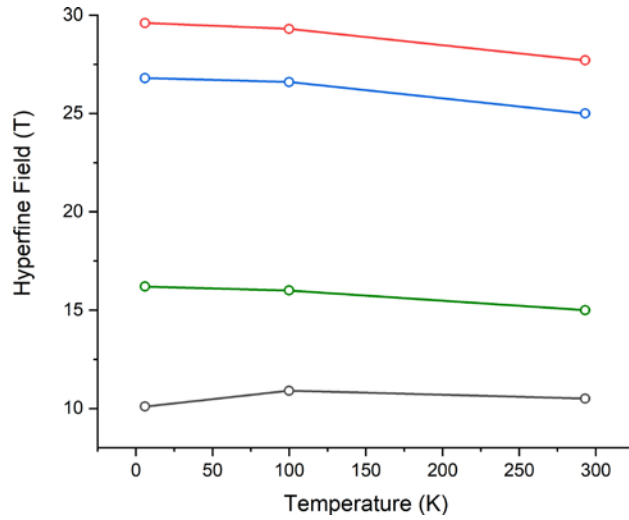


Figure S6. Temperature dependences of the hyperfine magnetic field for four magnetic components of the compound 1. Numerical data are provided in the Table 1 in the main text.

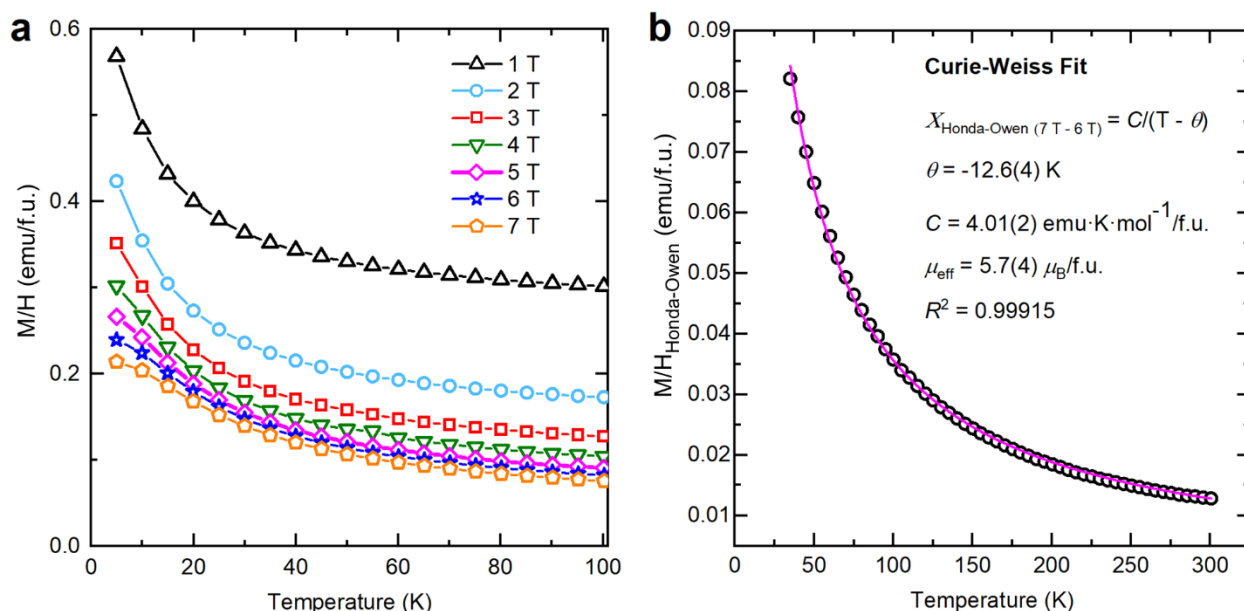


Figure S7. Compound 2, $[\text{Fe}_{9.4}\text{S}_{10}][\text{Fe}(\text{en})_3]_{0.6} \cdot \text{en}_{0.9}$: **(a)** Temperature-dependence of magnetic susceptibility from 5-100 K at 1-7 T applied fields. **(b)** Honda-Owen's extrapolation of temperature-dependence of magnetic susceptibility (black circles) with Curie-Weiss fitting (magenta line and text), 34-300 K fitting range. Calculated from 7 T and 6 T susceptibility data $\chi_{\text{H-O}} = [M_{7\text{T}} - M_{6\text{T}}]/[7\text{T} - 6\text{T}]$ with $[\text{Fe}_{9.4}\text{S}_{10}][\text{Fe}(\text{en})_3]_{0.6} \cdot \text{en}_{0.9}$ formula unit. The sample was purified with magnet prior to the measurements.

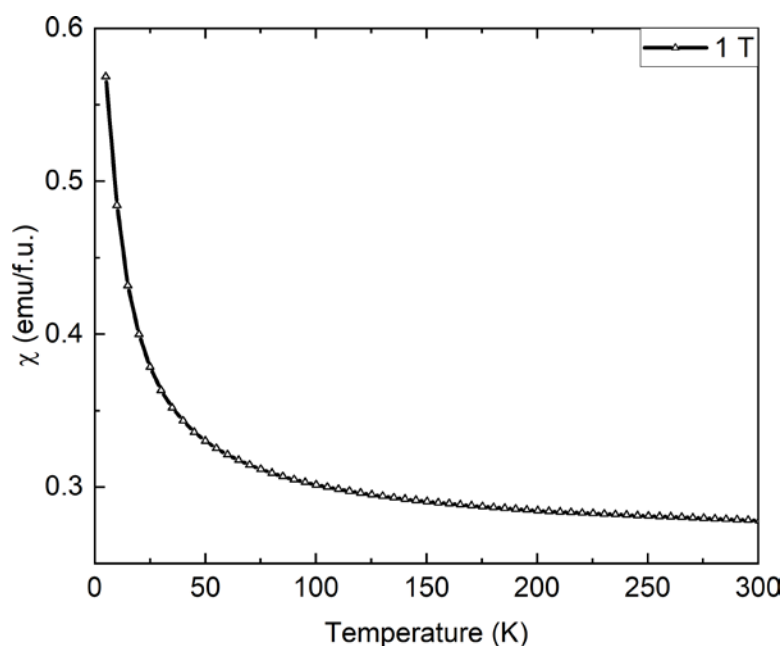


Figure S8. Compound 2, $[\text{Fe}_{9.4}\text{S}_{10}][\text{Fe}(\text{en})_3]_{0.6} \cdot \text{en}_{0.9}$: Temperature-dependence of magnetic susceptibility from 5-300 K at 1 T applied field. Calculated per $[\text{Fe}_{9.4}\text{S}_{10}][\text{Fe}(\text{en})_3]_{0.6} \cdot \text{en}_{0.9}$ formula unit. The sample was purified with magnet with magnet prior to the measurements.

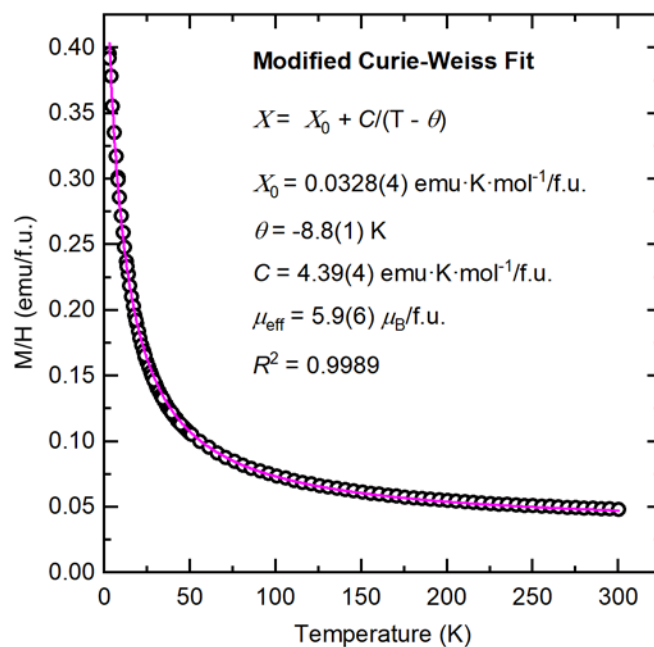


Figure S9. Compound **1** $[\text{Fe}_8\text{S}_{10}]\text{Fe}(\text{en})_3 \cdot \text{en}_{0.5}$: Temperature-dependence of magnetic susceptibility at 0.1 T applied field (black circles) from 3-300 K with modified Curie-Weiss fitting (magenta line and text). Calculated per $[\text{Fe}_8\text{S}_{10}]\text{Fe}(\text{en})_3 \cdot \text{en}_{0.5}$ formula unit.

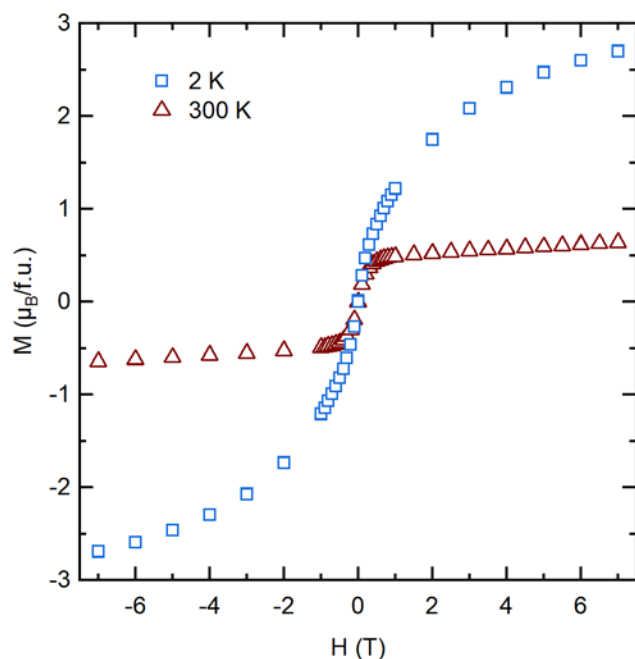


Figure S10. Compound 2, $[\text{Fe}_{9.4}\text{S}_{10}][\text{Fe}(\text{en})_3]_{0.6} \cdot \text{en}_{0.9}$: Field-dependence of magnetization per formula units at 2 K (blue squares) and 300 K (brown triangles). Although the sample was purified with magnet prior to the measurements, there is still a clear ferromagnetic contamination visible in the 300 K $M(H)$ data.

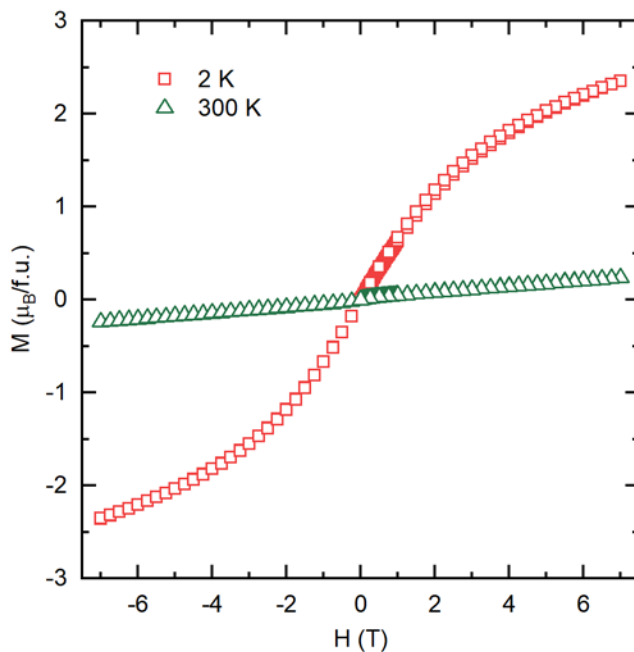


Figure S11. Compound 1 $[\text{Fe}_8\text{S}_{10}]\text{Fe}(\text{en})_3 \cdot \text{en}_{0.5}$: Field-dependence of magnetization per formula unit at 2 K (red squares) and 300 K (green triangles). An absence of elemental Fe admixture is obvious from 300 K data when compared with figure above.

Table S4. Bond valence sum (BVS) for intralayer Fe atoms in compound **1**, $[\text{Fe}_8\text{S}_{10}]\text{Fe}(\text{en})_3\cdot\text{en}_{0.5}$. Average bond distances are calculated from the SCXRD solution, collected at 90 K.¹ $\text{BVS} = \text{CN} \cdot \exp[(R_0 - d_{\text{Fe-S(ave)}})/b]$, where $\text{CN} = 4$, $R_0 = 2.08$, and $b = 0.37$.⁴ Average Fe oxidation state is +2.25, thus, for 16 unique Fe sites, we expect 4 Fe^{3+} sites and 12 Fe^{2+} sites. However, the top four greatest BVS values are not statistically unique. This could result from delocalization across the Fe-S layer, or as a result from the layer's puckered nature, where significant tetrahedral distortions may prohibit resolution of assigned sites by BVS method.

Fe site	Average Fe-S bond (Å)	BVS	Tentative oxidation state	Distribution
Fe1	2.28255	2.31	3+	2.27(3) across all sites 2.307(5) across 3+ assignments 2.26(3) across 2+ assignments
Fe2	2.2886	2.28	2+	
Fe3	2.28528	2.30	2+	
Fe4	2.28693	2.29	2+	
Fe5	2.29348	2.25	2+	
Fe6	2.28303	2.31	3+	
Fe7	2.28445	2.30	3+	
Fe8	2.29595	2.23	2+	
Fe9	2.293	2.25	2+	
Fe10	2.28888	2.27	2+	
Fe11	2.29713	2.22	2+	
Fe12	2.2879	2.23	2+	
Fe13	2.2843	2.30	3+	
Fe14	2.29663	2.23	2+	
Fe15	2.2927	2.25	2+	
Fe16	2.2956	2.23	2+	

References

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