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ELECTRONIC SUPPORTING INFORMATION

Rare "Janus"-Faced $\{Fe^{II}_7\}$ Single-Molecule Magnet Exhibiting Intramolecular Ferromagnetic Interactions

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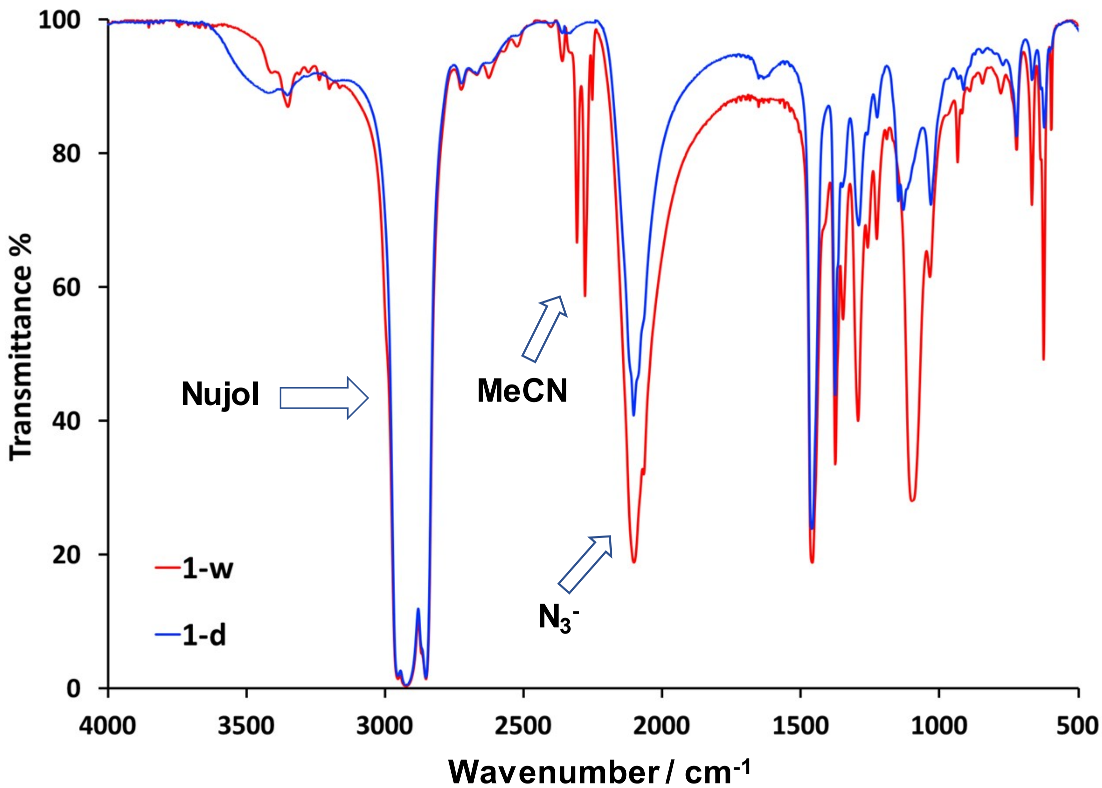

Fig. S1 IR spectra of **1-w** and **1-d**.

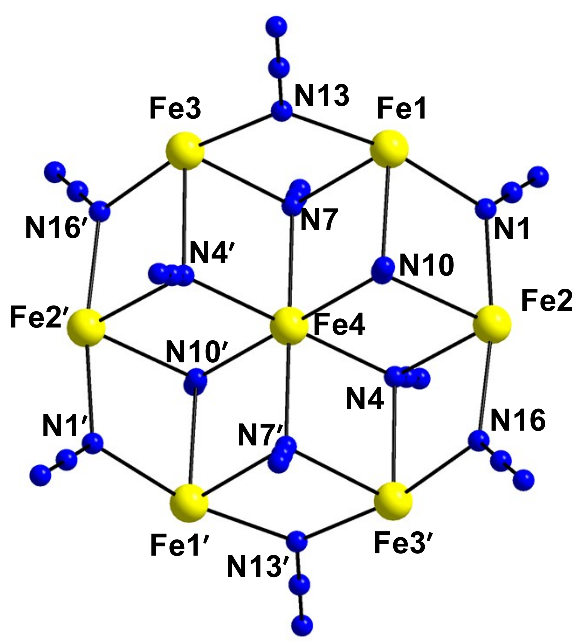

Fig. S2 The $[Fe_7(\mu_3\text{-}N_3)_6(\mu\text{-}N_3)_6]^{2+}$ inorganic core of **1**. Color scheme: Fe^{II} yellow, N blue. Symmetry operation for the primed atoms: 1-*x*, -*y*, 1-*z*.

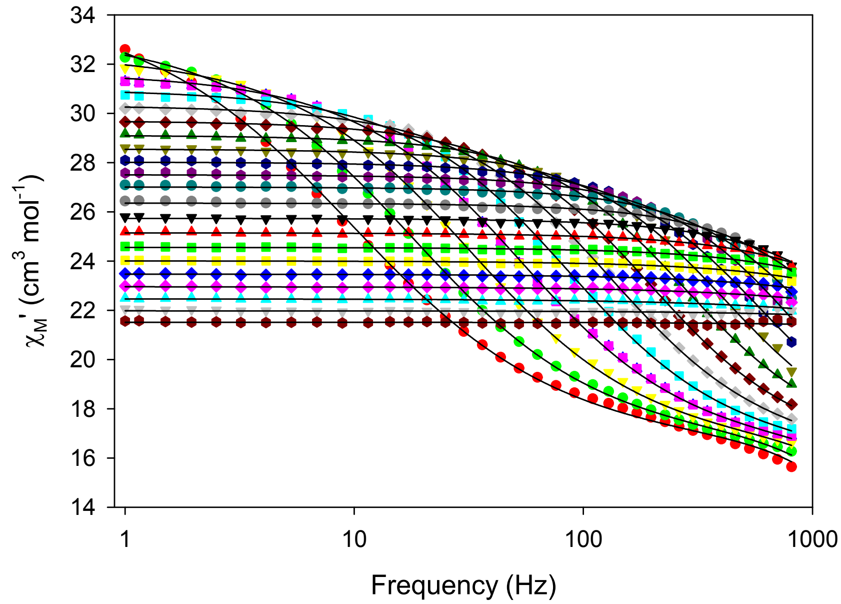

Fig. S3 Frequency dependence of the in-phase (χ_M') component of the *ac* magnetic susceptibility at different temperatures (2.5 – 5.0 K) for **1-d** at zero *dc* field; the solid lines are the best fits to the generalized Debye model.

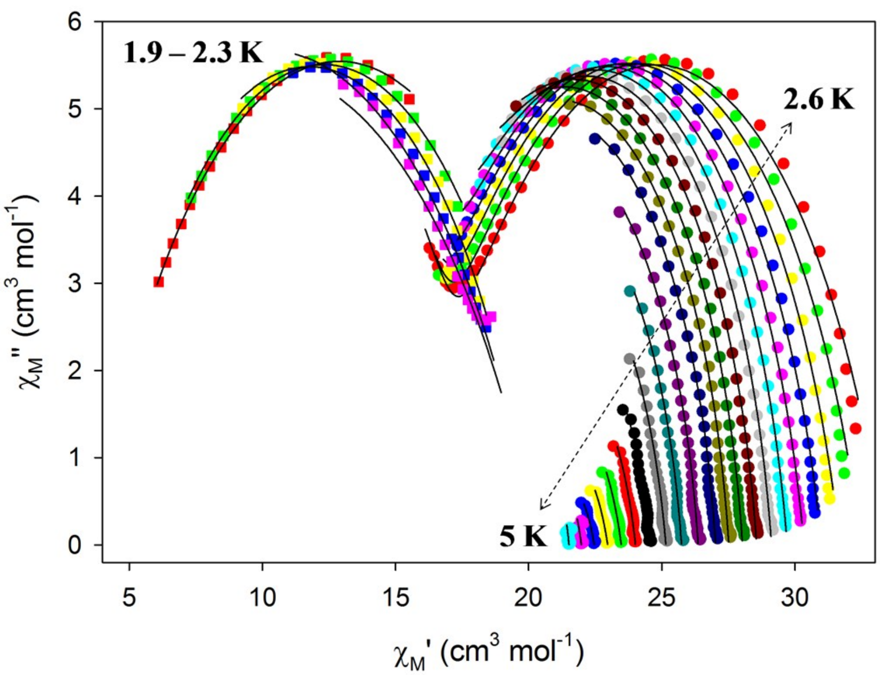

Fig. S4 Cole-Cole plots for **1-d** at zero applied *dc* field and different temperatures; the solid lines are the best fits to the generalized Debye model.

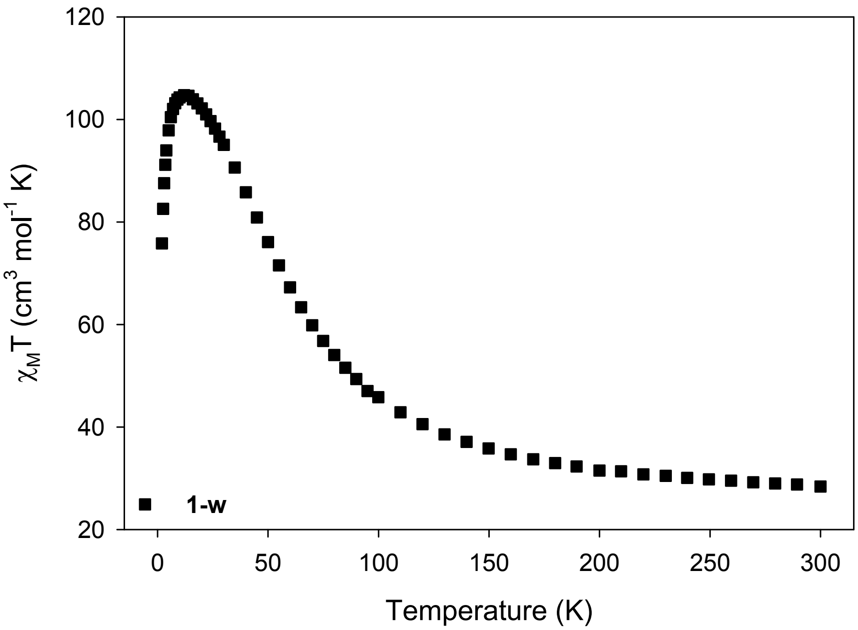

Fig. S5 Temperature dependence of the $\chi_M T$ product for **1-w** at an applied *dc* field of 0.1 T in the temperature range 2-300 K.

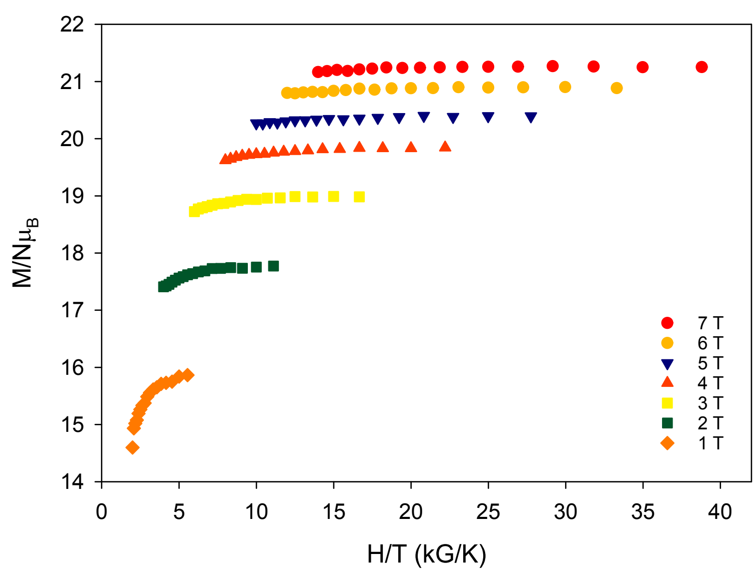

Fig. S6 Magnetization (*M*) *vs* field (*H*) and temperature (*T*) data, plotted as reduced magnetization ($M/N\mu_B$) *vs* *H/T*, for **1-w** at applied fields of 1-7 T and in the 1.8-5 K temperature range.

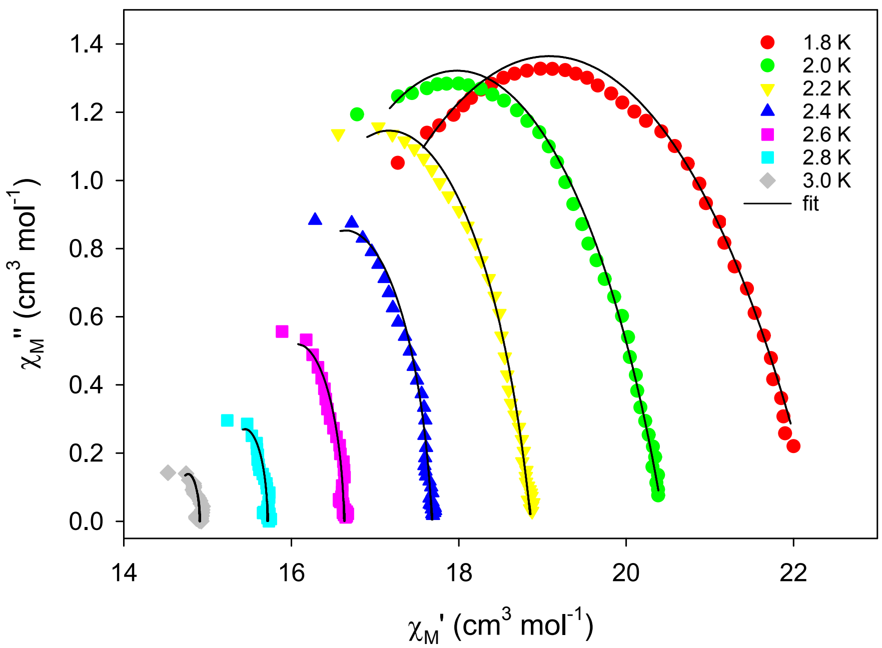

Fig. S7 Cole-Cole plots for **1-w** at zero applied *dc* field and different temperatures; the solid lines are the best fits to the generalized Debye model.

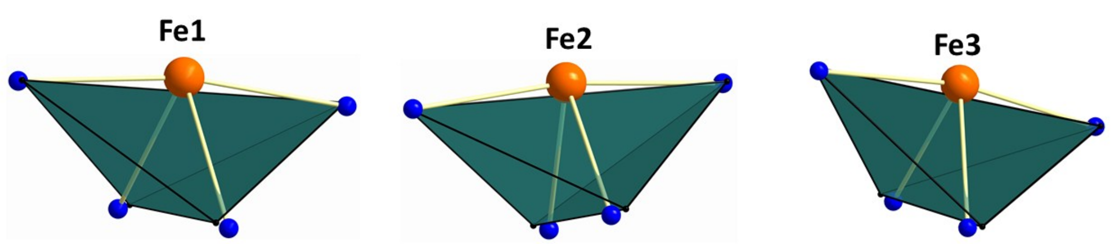

Fig. S8 Seesaw geometry of the potentially 4-coordinate Fe1, Fe2 and Fe3 atoms in **1-d**. Points connected by the black lines define the vertices of the ideal polyhedron. The so-called Continuous Shape Measures (CShM) approach essentially allows one to numerically evaluate by how much a particular polyhedron deviates from an ideal shape. The obtained CShM values are listed in Table S4. Values of CShM between 0.1 and 3 usually correspond to a not negligible but still small distortion from ideal geometry, while values larger than 3 refer to very distorted coordination environments.[S1,S2,S3]

Table S1. Crystallographic data for complex **1**·4MeCN.

Formula	$C_{32}H_{48}Fe_7N_{52}O_8Cl_2$
M, g mol^{-1}	1751.07
Crystal system	Triclinic
Space group	P-1
a / Å	11.4046(7)
b / Å	12.5476(8)
c / Å	13.4127(9)
α / °	93.108(2)
β / °	94.573(2)
γ / °	98.460(2)
V / Å^3	1888.2(2)
Z	1
T / K	100(1)
λ / Å	0.71073
Radiation type	Mo Ka
ρ_{calc} / g cm^{-3}	1.540
μ / mm^{-1}	1.454
Measd / independent (R_{int}) reflns	15101 / 6891
Obsd reflns [$I > 2\sigma(I)$]	5294
$R_1{}^a$	0.0404
$wR_2{}^b$	0.0833
GOF on F^2	1.084
$(\Delta\rho)_{max,min}$ / e Å^{-3}	0.428, -0.508

^{a} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S2. Selected interatomic distances (Å) and angles (°) for complex **1**[a]

Bond lengths			
Fe(1)-N(1)	2.108(3)	Fe(3)-N(4′)	2.250(3)
Fe(1)-N(7)	2.244(2)	Fe(3)-N(7)	2.246(2)
Fe(1)-N(10)	2.264(3)	Fe(3)-N(13)	2.103(3)
Fe(1)-N(13)	2.124(3)	Fe(3)-N(16′)	2.119(3)
Fe(1)-N(19)	2.123(3)	Fe(3)-N(23)	2.126(3)
Fe(1)-N(20)	2.134(3)	Fe(3)-N(24)	2.148(3)
Fe(2)-N(1)	2.112(3)	Fe(4)-N(4)	2.187(2)
Fe(2)-N(4)	2.234(2)	Fe(4)-N(4′)	2.187(2)
Fe(2)-N(10)	2.241(2)	Fe(4)-N(7)	2.200(2)
Fe(2)-N(16)	2.114(3)	Fe(4)-N(7′)	2.220(2)
Fe(2)-N(21)	2.136(3)	Fe(4)-N(10)	2.175(2)
Fe(2)-N(22)	2.158(3)	Fe(4)-N(10′)	2.175(2)
Bond angles			
Fe(1)-N(1)-Fe(2)	104.5(1)	Fe(2)-N(4)-Fe(3′)	96.5(1)
Fe(1)-N(10)-Fe(2)	95.6(9)	Fe(2)-N(16)-Fe(3′)	104.4(1)
Fe(1)-N(7)-Fe(3)	96.6(9)	Fe(2)-N(4)-Fe(4)	98.0(9)
Fe(1)-N(13)-Fe(3)	104.9(1)	Fe(2)-N(10)-Fe(4)	98.1(9)
Fe(1)-N(7)-Fe(4)	98.0(1)	Fe(3)-N(4′)-Fe(4)	97.8(9)
Fe(1)-N(10)-Fe(4)	98.1(1)	Fe(3)-N(7)-Fe(4)	97.5(9)

[a] Symmetry transformation used to generate equivalent atoms: ′ = 1-*x*, -*y*, 1-*z*.

Table S3. Bond valence sum (BVS)[a] calculations for the Fe atoms in centrosymmetric **1**.[S4]

Atom	Fe^{II}	Fe^{III}
Fe1	**2.07**	2.35
Fe2	**2.07**	2.35
Fe3	**2.08**	2.36
Fe4	**1.94**	2.20

[a] The values in boldface are the ones closest to the charge for which they were calculated. The oxidation state is the nearest whole number to the boldfaced value.

Table S4. Different spin configurations employed and their corresponding energy values for extracting the *J*-values of complex **1**.

	Fe1	**Fe2**	**Fe3**	**Fe4**	**Fe5**	**Fe6**	**Fe7**	**Energy**
HS	↑	↑	↑	↑	↑	↑	↑	-12409.7277191
BS1	↓	↑	↑	↑	↑	↑	↑	-12409.7244548
BS2	↑	↓	↑	↓	↑	↓	↑	-12409.7224925

Table S5. Shape measures of the potentially four-coordinate Fe1, Fe2, and Fe3 coordination polyhedra in **1-d**. The values in boldface indicate the closest polyhedron according to the continuous shape measures.

Polyhedron[a]	Fe1	Fe2	Fe3
SP-4	22.14	22.36	21.94
T-4	11.81	11.47	11.70
SS-4	**0.85**	**0.82**	**0.84**

[a]Abbreviations: SP-4, square planar; T-4, tetrahedron; SS-4, seesaw.

References

[S1] M. Llunell, D. Casanova, J. Girera, P. Alemany and S. Alvarez, *SHAPE*, version 2.0, Barcelona, Spain, 2010.

[S2] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693-1708.

[S3] H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1993, **115**, 8278-8289.

[S4] W. Liu and H. H. Thorp, *Inorg. Chem.*, 1993, **32**, 4102-4105.