SUPPLEMENTARY MATERIAL TO THE ARTICLE:

Unprecedented Chemical Transformation: Crystallographic Evidence for 1,1,2,2-Tetrahydroxyethane Captured within an Fe_6Dy_3 Single Molecule Magnet

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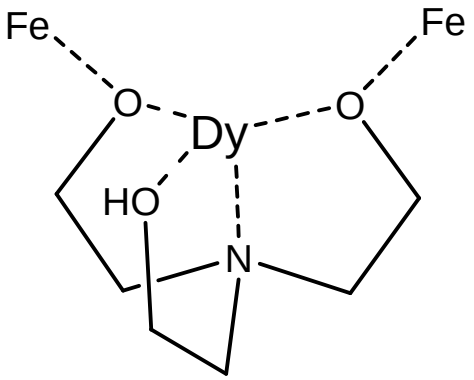
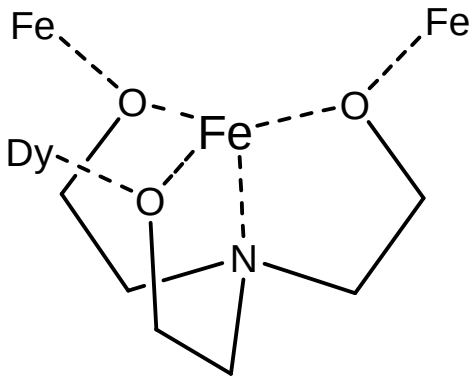
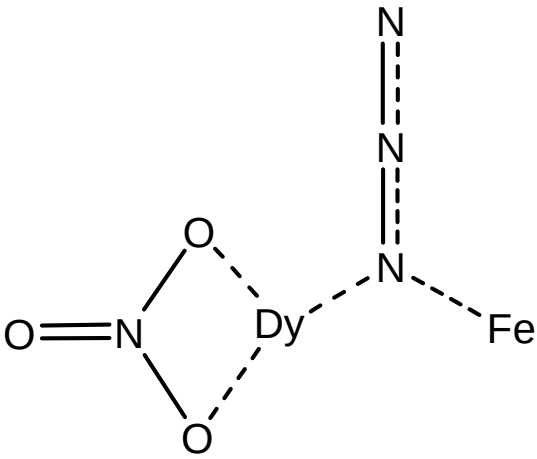


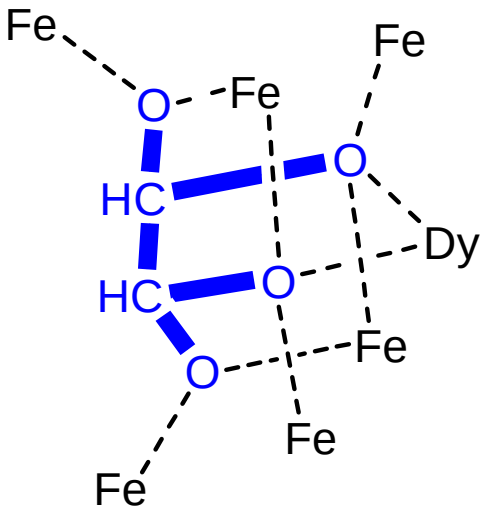
(a) μ_3-teaH^{2-}



(b) μ_4-tea^{3-}



(c) μ_2-N_3^- (end-on) and NO_3^-



(d) μ_7-$C_2H_2O_4^{4-}$

Figure S1: Different coordination modes of ligands involved in cluster **1**.

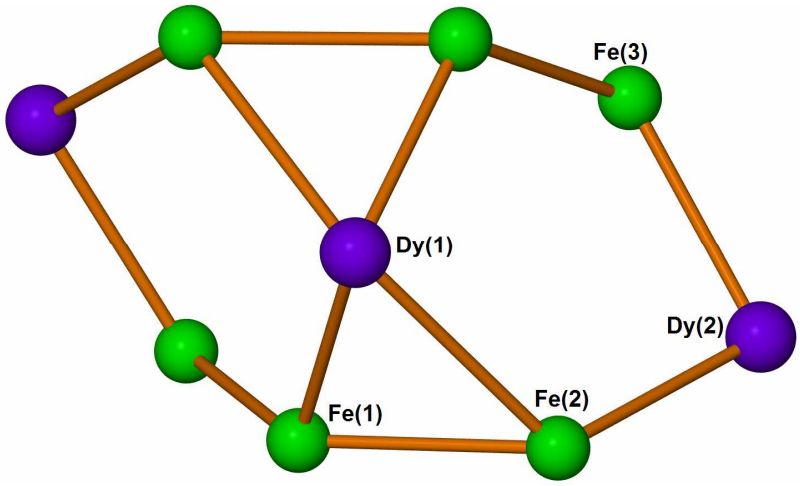


Figure S2: The **2,3,4M9-3** skeleton of compound **1.**

Table S1. Bond distances and angles for the carbon atom in the anion of 1,1,2,2-tetrahydroxyethane.

Bond Distances		Bond Angles	
C19-O11	1.363(11)	O11-C19-O10	114.1(9)
C19-O10	1.446(14)	O11-C19-C19^{i}	109.4(9)
C19-C19^{i}	1.508(17)	O10-C19-C19^{i}	102.5(6)
C19-H19A	0.9800	O11-C19-H19A	110.2

Symmetry code: (i) $-x+3/2, -y+3/2, z$.

Known formation of glyoxal: Oxidation of acetaldehyde with nitric acid was examined first by Ljubowin as early as 1875 and patented in 1933 [Patent DE573721]. Reaction takes place at ca. 40 °C and is carried out industrially as a continuous process.

Physical measurements: The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on a polycrystalline sample of 9.6 mg. ac susceptibility measurements have been measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder.

The Mössbauer spectra were required using a conventional spectrometer in the constant – acceleration mode equipped with ^{57}Co source (3.7 GBq) in rhodium matrix. Isomer shifts are given relative to α-Fe at room temperature. The sample was inserted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat which has a split- pair superconducting magnet system for applied fields up to 5 T, with the field of the sample oriented perpendicular to the gamma-ray direction, while the sample temperature can be varied between 3.0 and 300 K.

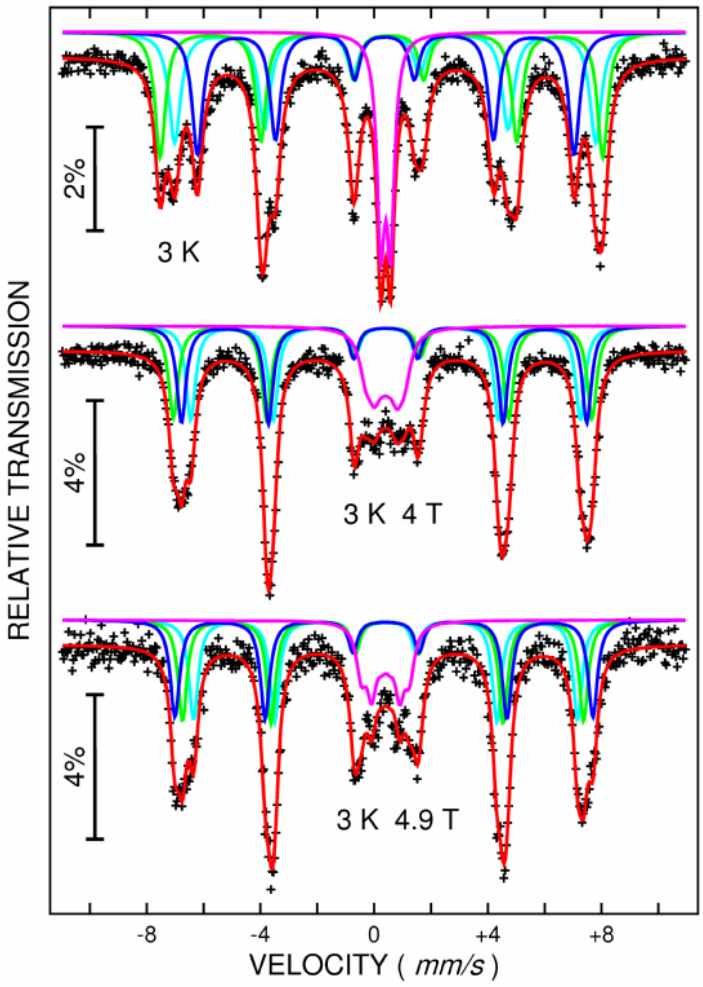


Figure S3. ^{57}Fe Mössbauer spectra for {Fe_6Dy_3} at 3K in zero- and applied external magnetic fields. The central onset (pink) corresponds to a diamagnetic impurity of {Fe_8} cluster with the spin ground state S = 0. This impurity appears when we leave the reaction for longer crystallization time to get enough material for the Mössbauer measurements.

Table S2. Mössbauer hyperfine parameters for $\{Fe_6Dy_3\}$ at 3K in zero- and applied external magnetic fields.

T, H_{appl}	Fe sites	δ[a], mm/s	ε[c], mm/s	Γ, mm/s	θ, ^{o}	$^*H_{eff}$, T
3K, 0T	Fe(1)	0.51(1)	-0.03(1)	0.50(1)	58.9[d]	45.9(2)
	Fe(2)	0.49(1)	-0.26(1)	0.44(1)	58.9[d]	48.2(2)
	Fe(3)	0.49(1)	0.04(1)	0.45(1)	58.9[d]	41.1(1)
3K, 4T	Fe(1)	0.51[b]	-0.01(1)	0.40(1)	68.4[d]	42.4(1)
	Fe(2)	0.49[b]	-0.17(1)	0.41(1)	68.4[d]	45.6(3)
	Fe(3)	0.49[b]	-0.06(1)	0.39(1)	68.4[d]	44.2(4)
3K, 4.9T	Fe(1)	0.51[b]	0	0.38(1)	69.0[d]	41.8(4)
	Fe(2)	0.49[b]	-0.14(1)	0.38(1)	69.0[d]	43.7(3)
	Fe(3)	0.49[b]	-0.08(1)	0.39(1)	69.0[d]	45.5(3)

[a]Relative to α-Fe at room temperature; [b]Fixed values; [c]For magnetically-split spectra the quadrupole shifts, $\varepsilon = ½\Delta E_Q(3\cos^2\varphi - 1)$. φ - angle between the internal hyperfine field, H_{hf}, and the main electrical field gradient (EFG) principal axis (V_{zz}). The quadrupole shifts are easy to observe from the magnetic spectra as a difference in the splitting of 1 and 2 and 5 and 6 iron(III) lines. [d]Constrained to the same value for all sites. δ is the isomer shift, θ - angle between H_{eff} and direction of γ-rays, H_{eff} – the effective hyperfine field. The statistical errors are given in parentheses. The relative areas for the sextets have been constrained to the 1:1:1 ratio. $^*H_{eff} = H_{hf} + H_{appl}$.