Electronic Supplementary Information

Water Induced Spin-Crossover Behavior and Magneto-Structural Correlation in Octacyanotungstate(IV)-Based Iron(II) Complexes

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Table S1 Crystal data for **2**–**5**.

	2	**3**	**4**	**5**
empirical formula	$C_{56}H_{56}N_{16}O_8Fe_2W$	$C_{56}H_{56}N_{16}Fe_2W$	$C_{56}H_{56}N_{16}O_8Fe_2W$	$C_{56}H_{56}N_{16}Fe_2W$
*M*r	1376.71	1248.71	1376.71	1248.71
crystal system	Tetragonal	Tetragonal	Tetragonal	Orthorhombic
space group	$I4_1/amd$	$I4_1/a$	$I4_1/amd$	$Fddd$
a /Å	20.173(2)	20.5490(18)	20.2282(6)	14.1192(9)
b /Å	20.173(2)	20.5490(18)	20.2282(6)	26.6083(17)
c /Å	14.554(3)	13.464(2)	13.8297(8)	30.5398(19)
V /Å^3	5922.3(17)	5685.5(14)	5658.8(5)	11473.4(13)
Z	4	4	4	8
$\rho_{Calc.}$/ mg m^{-3}	1.544	1.459	1.616	1.446
λ /Å	0.71073	0.71073	0.71073	0.71073
μ /mm^{-1}	2.488	2.573	2.604	2.550
crystal size /mm	0.20 x 0.20 x 0.15	0.22 x 0.20 x 0.18	0.25 x 0.20 x 0.20	0.24 x 0.20 x 0.20
F(000)	2776	2520	2776	5040
reflections collected	23390	18712	22827	19009
unique reflections	1791	3286	1734	3328
*R*int	0.1114	0.0535	0.0533	0.0221
R_1 [$I>2\sigma(I)$]	0.0967	0.0337	0.0306	0.0273
ωR_2(all data)	0.2808	0.0853	0.0747	0.0894
GOF on F^2	1.171	1.089	1.061	1.068

$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (mP)^2 + nP]$, where $P = (Fo^2 + 2Fc^2)/3$; m = 0.1584 (**2**), 0.0374 (**3**), 0.0209 (**4**) and 0.0610 (**5**); n = 12.3257 (**2**), 1.9328 (**3**), 62.2959 (**4**) and 34.9566 (**5**).

Table S2 Selected bond lengths (Å) and angles (°) for **1**–**5.**

	1			**2** (123 K)	**3** (296 K)	**4** (296 K)	**5** (296 K)
	296 K	200 K	123 K				
Fe1–N2	2.086(6)	2.026(7)	1.954(7)	2.096(19)	2.113(3)	2.077(4)	2.090(3)
Fe1–N3	2.236(7)	2.136(9)	2.046(8)	2.23(5)	2.231(4)	2.241(4)	2.256(3)
Fe1–N4	2.233(7)	2.134(8)	2.040(7)	2.15(3)	2.246(4)	2.261(5)	2.230(3)
W1–C1	2.177(8)	2.171(10)	2.171(9)	2.15(2)	2.159(5)	2.174(4)	2.178(4)
W1–C2	2.135(7)	2.139(8)	2.144(8)	2.143(17)	2.145(4)	2.120(4)	2.128(3)
C1–N1	1.148(9)	1.148(11)	1.144(11)	1.17(2)	1.142(6)	1.156(6)	1.134(5)
C2–N2	1.138(9)	1.130(11)	1.145(10)	1.12(2)	1.152(5)	1.152(6)	1.149(4)
N2–Fe1–N2A	177.2(4)	177.2(5)	178.0(4)	180.0	180.00(6)	180.0	180.00(17)
N2–Fe1–N4A	89.9(3)	90.3(3)	90.1(3)	90.000(1)	90.81(15)	90.0	90.33(13)
N2A–Fe1–N4A	92.1(3)	91.8(3)	91.4(3)	90.000(2)	89.19(15)	90.0	89.67(13)
N2–Fe1–N4	92.1(3)	91.8(3)	91.4(3)	90.000(2)	89.19(15)	90.0	89.67(13)
N2A–Fe1–N4	89.9(3)	90.3(3)	90.1(3)	90.000(1)	90.81(15)	90.0	90.33(13)
N4–Fe1–N4A	86.3(4)	86.7(5)	87.5(4)	180.0	180.0	180.0	180.0
N2–Fe1–N3A	88.2(2)	87.9(3)	88.7(3)	91(2)	90.59(13)	89.95(15)	89.95(13)
N2A–Fe1–N3A	89.9(3)	90.2(3)	89.8(3)	89(2)	89.41(13)	90.05(15)	90.05(13)
N4A–Fe1–N3A	176.4(3)	176.7(3)	177.9(3)	90.000(6)	90.06(15)	90.0	91.36(13)
N4–Fe1–N3A	90.6(3)	90.6(3)	90.7(3)	90.000(2)	89.94(15)	90.0	88.64(13)
N2–Fe1–N3	89.9(3)	90.2(3)	89.8(3)	89(2)	89.41(13)	90.05(15)	90.05(13)
N2A–Fe1–N3	88.2(2)	87.9(3)	88.7(3)	91(2)	90.59(13)	89.95(15)	89.95(13)
N3–Fe1–N4A	90.6(3)	90.6(3)	90.7(3)	90.000(2)	89.94(15)	90.0	88.64(13)
N4–Fe1–N3	176.4(3)	176.7(3)	177.9(3)	90.000(6)	90.06(15)	90.0	91.36(13)
N3A–Fe1–N3	92.5(4)	92.1(4)	91.0(4)	180.0	180.0	180.0	180.00(17)

Symmetry code: A = −*x*+1/4, *y*-3/4, *z*+3/4 for **1** (296, 200 and 123 K); –*x*+1, –*y*, –*z*+1 for **2**; −*x*+1, −*y*+1, −*z*+1 for **3**; −*x*+1, *y*, −*z*+1 for **4;** −*x*+1, −*y*+1, −*z*+1 for **5**.

Table S3. Results of Continuous Shape Measure Analysis for $[W^{V}(CN)_8]^{4-}$ units[a]

Geometry	SAPR-8	BTPR-8	DD-8	configuration
1 (296 K)	2.874	2.637	0.110	DD-8
1 (200 K)	2.848	2.638	0.062	DD-8
1 (123 K)	2.845	2.686	0.044	DD-8
2	2.879	2.553	0.102	DD-8
3	2.999	2.625	0.275	DD-8
4	2.981	2.587	0.263	DD-8
5	0.753	1.756	0.944	intermediate SAPR-8/DD-8

[a] The value are Continuous Shape Measure (CShM) parameters and CShM=0 for the ideal geometry and increases with the increase of the degree of distortion;

SAPR-8 corresponds to the square antiprism geometry;

BTPR-8 corresponds to the biaugmented trigonal prism geometry;

DD-8 corresponds to the dodecahedron geometry.

Table S4. Intermolecular hydrogen bonds of **1**.

D–H···A	D–H (Å)	D···A (Å)	D–H···A (°)
O5–H5A···O2#1	0.820(2)	2.91(4)	145(8)
O1–H1AC···N1#2	0.86(2)	2.88(3)	125(4)

Symmetry code: #1 *x*, *y*, *z*+1; #2 –*x*+3/4, *y*+7/4, *z*+1/4.

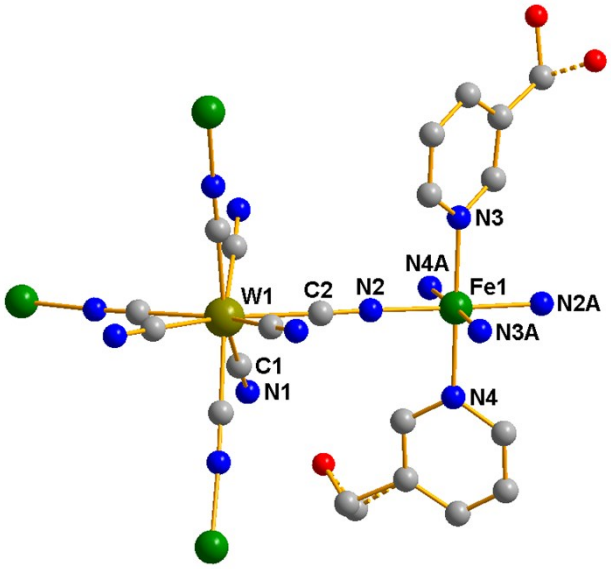

Fig. S1 The overall molecular structure of complex **1** at 200 K and 123 K. Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue; O, red. Hydrogen atoms, lattice water molecules and crystallographically equivalent 3-pyCH_2OH molecules have been omitted for clarity. Symmetry code: A, –*x*+7/4, –*y*+3/4, –*z*+3/4.

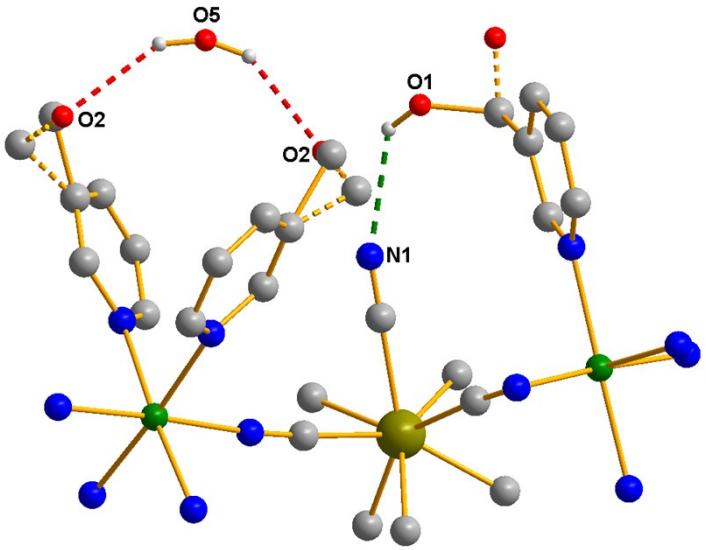

Fig. S2 Hydrogen bonds in $Fe^{II}_2[W^{IV}(CN)_8](3\text{-py}CH_2OH)_8 \cdot 4.67H_2O$ (**1**). Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue; O, red.

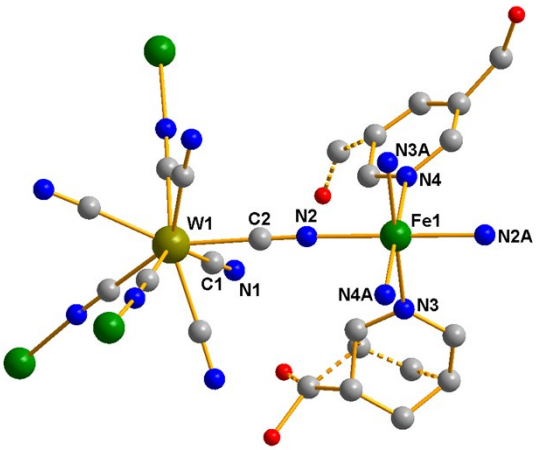

Fig. S3 Crystal structure of complex **2**. Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue; O, red. Hydrogen atoms and crystallographically equivalent 3-pyCH_2OH molecules have been omitted for clarity. Symmetry code: A, *x*, –*y*, 1-*z*.

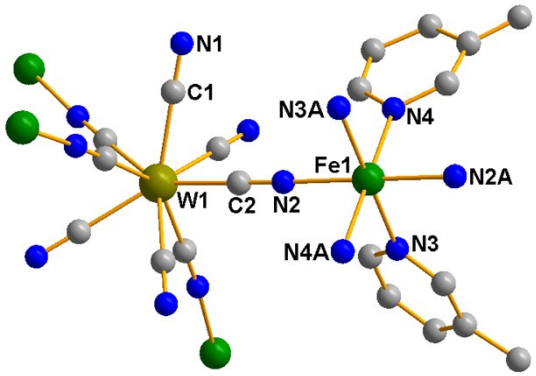

Fig. S4 Crystal structure of complex **3**. Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue. Hydrogen atoms and crystallographically equivalent 3-CH_3py molecules have been omitted for clarity. Symmetry code: A –*x*+1, –*y*+1, –*z*+1.

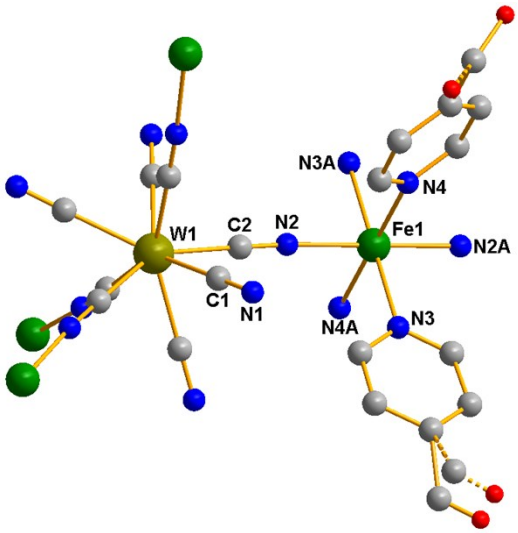

Fig. S5 Crystal structure of complex **4**. Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue; O, red. Hydrogen atoms and crystallographically equivalent 4-pyCH_2OH molecules have been omitted for clarity. Symmetry code: A, 1-*x*, –*y*, 1-*z*.

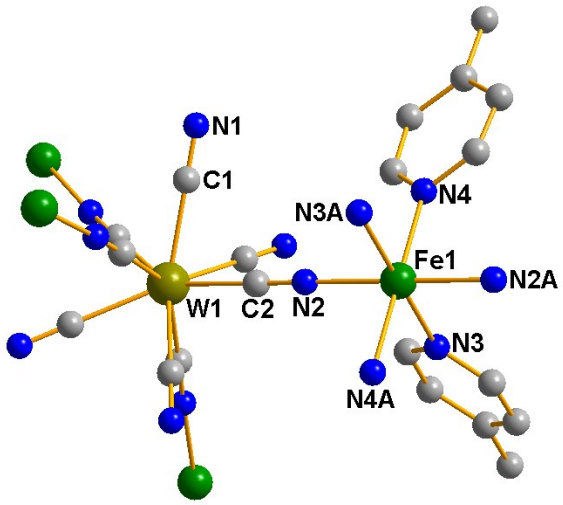

Fig. S6 Crystal structure of complex **5**. Color code: W^{IV}, dark yellow; Fe^{II}, green; C, gray; N, blue. Hydrogen atoms and crystallographically equivalent 4-CH_3py molecules have been omitted for clarity. Symmetry code: A, 1-*x*, 1-*y*, 1-*z*.

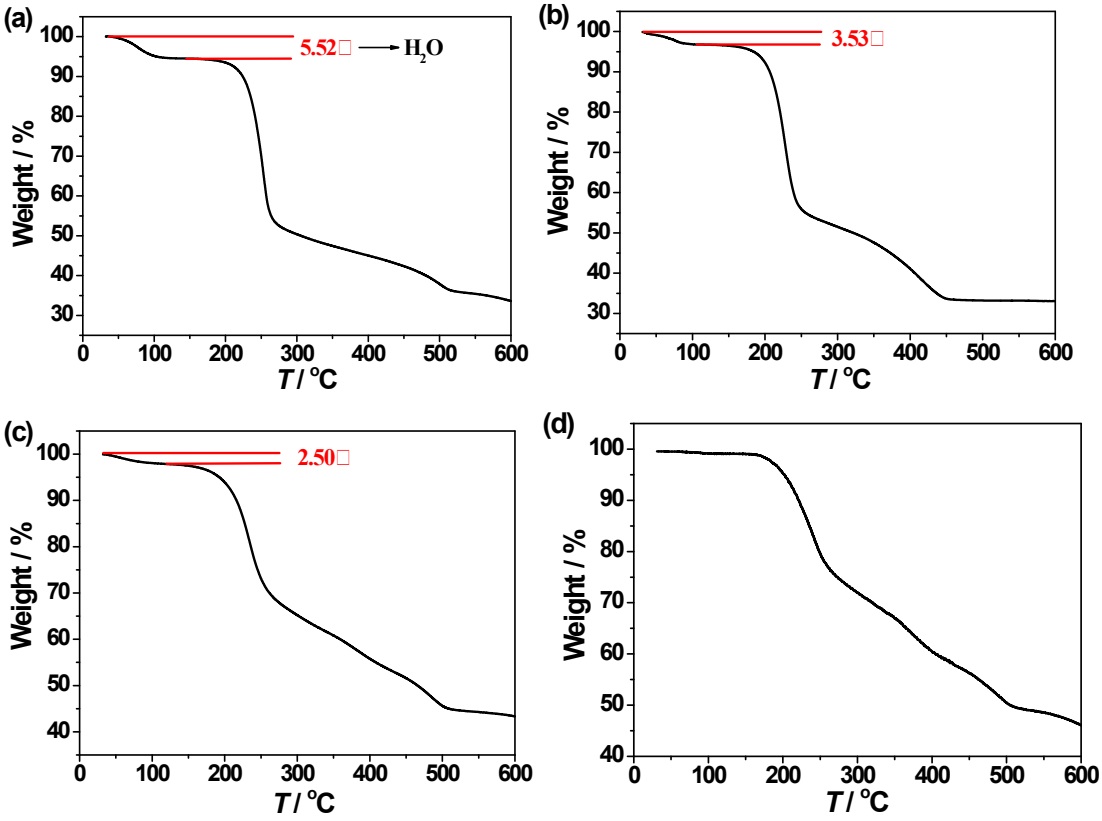

Fig. S7 TGA curves of complex **1** (a), $\mathbf{1}^{A}$ (b), $\mathbf{1}^{B}$ (c) and $\mathbf{1}^{C}$ (d).

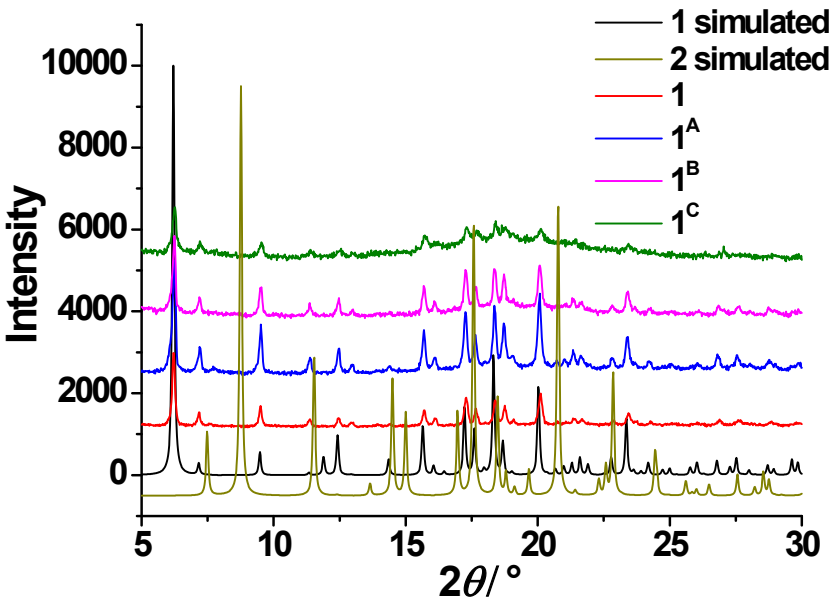

Fig. S8 Powder XRD data for complexes **1** (red), **1**^{A} (blue), **1**^{B} (pink), **1**^{C} (green) and **2** (dark yellow) at room temperature