magnetochemistry

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Supplementary Material

Syntheses, Structures and Magnetic Properties of M_2 (M = Fe, Co) Complexes with N_6 coordination environment: Field-Induced Slow Magnetic Relaxation in Co_2

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S1. ^{1}H-NMR spectrum

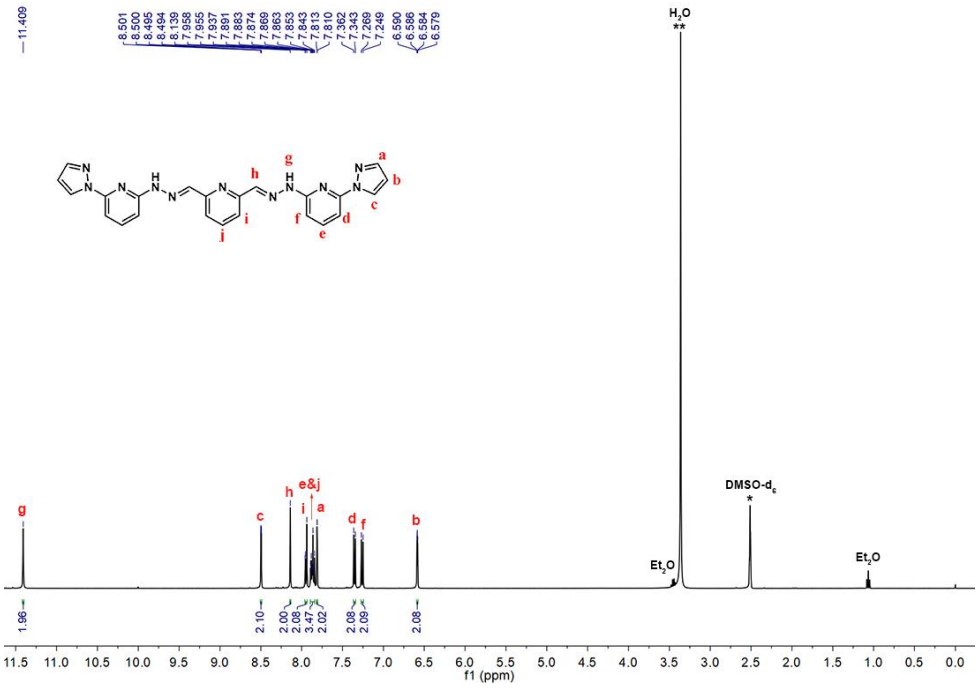


Figure S1. ^{1}H-NMR spectrum of H_2L in DMSO-d_6 at room temperature.

S2. IR spectroscopy

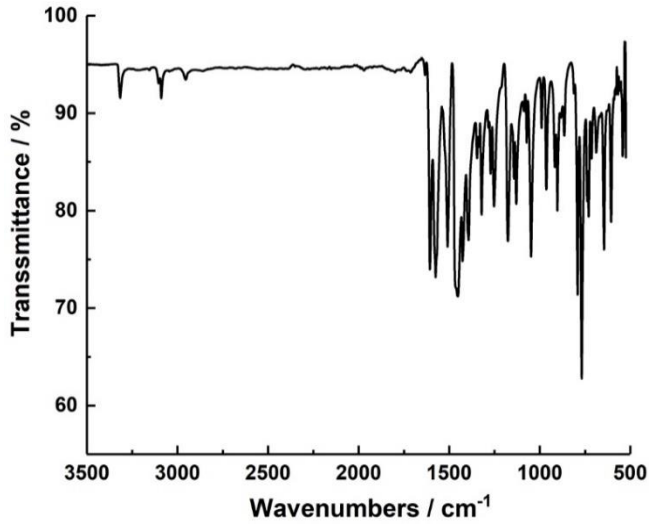


Figure S2. IR spectrum of H_2L.

Selected IR for **Co2**: (solid, ATR) $\tilde{\nu}$(cm^{-1}): 549 (w), 576 (w), 590 (m), 617 (m), 649 (w), 680 (m), 711 (m), 752 (m), 790 (m), 885 (m), 910 (m), 941 (m), 989 (s), 1014 (s), 1052 (s), 1151 (w), 1164 (m), 1178 (m), 1199 (w), 1218 (w), 1251 (m), 1274 (m), 1297 (w), 1322 (m), 1348 (m), 1405 (m), 1417 (m), 1459 (s), 1486 (m), 1508 (m), 1529 (m), 1579 (m), 1604 (m), 1623 (m), 3041 (w), 3089 (w), 3128 (w), 3236 (w).

Selected IR for **Fe2**: (solid, ATR) $\tilde{\nu}$(cm^{-1}): 549 (w), 574 (w), 592 (m), 649 (m), 680 (m), 707 (w), 730 (m), 757 (m), 788 (m), 883 (m), 916 (m), 941 (m), 987 (s), 1010 (s), 1056 (s), 1091 (s), 1178 (m), 1220 (w), 1251 (m), 1272 (m), 1295 (w), 1321 (m), 1344 (m), 1361 (m), 1396 (m),

1415 (m), 1456 (s), 1486 (m), 1519 (s), 1562 (m), 1577 (m), 1604 (m), 1627 (m), 3106 (w), 3122 (w), 3135 (w), 3255 (w).

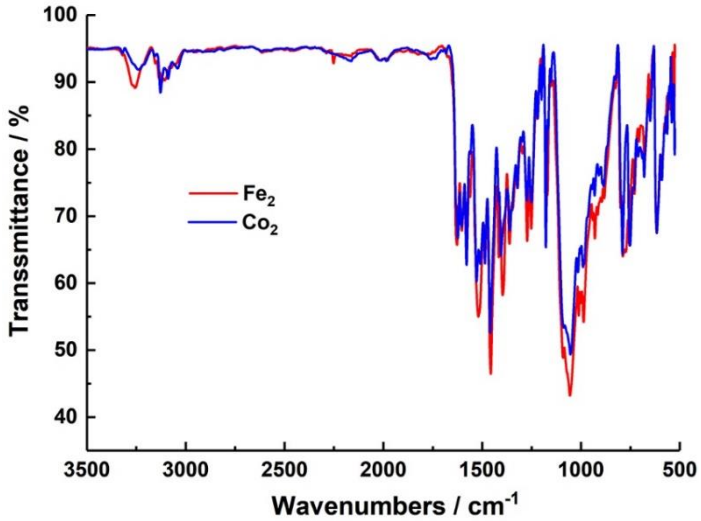


Figure S3. IR spectra of complexes **Co2** (blue curve) and **Fe2** (red curve).

S3. Crystallographic data

Table S1. Crystallographic data of **Co2** and **Fe2**.

Complexes	**Co2**	**Fe2**
Formula	$C_{50}H_{44}Cl_4Co_2N_{24}O_{16}$	$C_{50}H_{44}Cl_4Fe_2N_{24}O_{16}$
Mr [g·mol^{-1}]	1496.75	1490.59
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Color	Red	Red
T [K]	173.0	180.0
a [Å]	12.1016(8)	12.1120(5)
b [Å]	12.3889(9)	12.4270(5)
c [Å]	12.4089(8)	12.4514(5)
α [°]	82.929(2)	82.9570(1)
β [°]	94.149(3)	61.5120(1)
γ [°]	64.572(2)	64.5770(1)
V [Å]^3	61.680(2)	1479.71(1)
Z	1	1
ρ_{calcd} [g·cm^{-3}]	1.689	1.673
μ(Mo-Kα) [mm^{-1}]	0.838	0.763
F (000)	762.0	760.0
2θ range [°]	4.124 to 52.112	3.742 to 50.076
Reflns collected	33680	31461
Unique reflns	5807	5216
R_{int}	0.0619	0.0604
GOF	1.087	1.146
R_1 [I ≥ 2 σ (I)]	0.0392	0.0422
wR_2 (all data)	0.1086	0.1249

$$R_1 = \sum(|F_0| - |F_c|) / \sum|F_0|; \quad \omega R_2 = \left[\sum \omega(|F_0| - |F_c|)^2 / \sum \omega F_0^2\right]^{1/2}$$

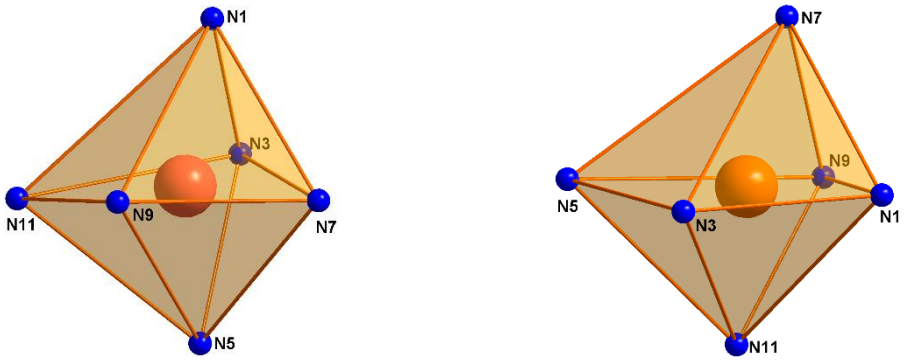
S4. Structural details of complexes

Table S2. Selected bond distances (Å) and angles (º) of **Co2 and Fe2**.

Co2		**Fe2**	
Co1-N1[1]	2.144(3)	Fe1-N1	2.181(3)
Co1-N3[1]	2.046(2)	Fe1-N3	2.105(3)
Co1-N5[1]	2.250(2)	Fe1-N5	2.267(3)
Co1-N7	2.190(2)	Fe1-N7[1]	2.226(3)
Co1-N9	2.056(2)	Fe1-N9[1]	2.110(3)
Co1-N11	2.159(3)	Fe1-N11[1]	2.196(3)
N1[1]-Co1-N5[1]	149.85(9)	N1-Fe1-N5	146.33(10)
N1[1]-Co1-N7	87.42(9)	N1-Fe1-N7[1]	87.44(10)
N1[1]-Co1-N11	103.28(1)	N1-Fe1-N11[1]	104.81(11)
N3[1]-Co1-N1[1]	75.97(9)	N3-Fe1-N1	73.85(10)
N3[1]-Co1-N5[1]	74.17(9)	N3-Fe1-N5	72.80(10)
N3[1]-Co1-N7	109.91(9)	N3-Fe1-N7[1]	111.10(10)
N3[1]-Co1-N9	172.67(1)	N3-Fe1-N9[1]	172.73(10)
N3[1]-Co1-N11	101.03(1)	N3-Fe1-N11[1]	102.65(11)
N7-Co1-N5[1]	98.80(9)	N7[1]-Fe1-N5	100.23(10)
N9-Co1-N1[1]	98.90(9)	N9[1]-Fe1-N1	101.16(10)
N9-Co1-N5[1]	111.21(9)	N9[1]-Fe1-N5	112.47(10)
N9-Co1-N7	74.72(9)	N9[1]-Fe1-N7[1]	73.48(10)
N9-Co1-N11	74.82(1)	N9[1]-Fe1-N11[1]	73.22(11)
N11-Co1-N5[1]	86.52(1)	N11[1]-Fe1-N5	86.95(11)
N11-Co1-N7	148.91(1)	N11[1]-Fe1-N7[1]	146.15(11)

[1]2-X,1-Y,1-Z

S5. Coordination geometry



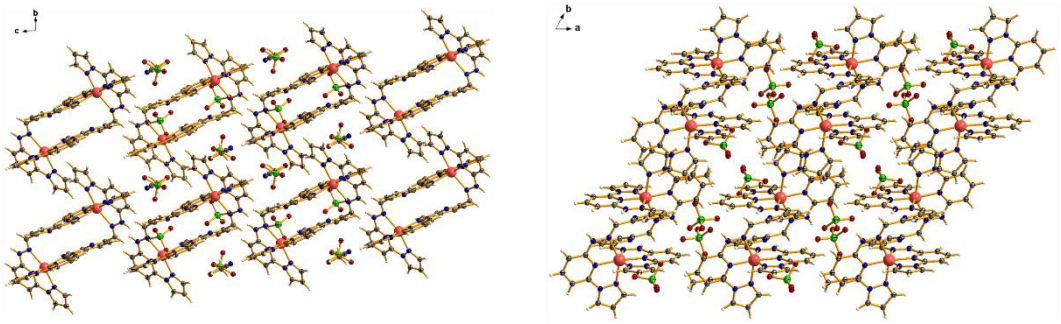
(**a**) (**b**)

Figure S4. Coordination polyhedrons of Co[II] (left) and Fe[II] (right) in complexes **Co2** and **Fe2**. Color code: Co[II], orange-red; Fe[II], orange; N, blue.

Table S3. The *CShM* values calculated by SHAPE 2.1 of Co^{II} and Fe^{II} ions in **Co2** and **Fe2**.

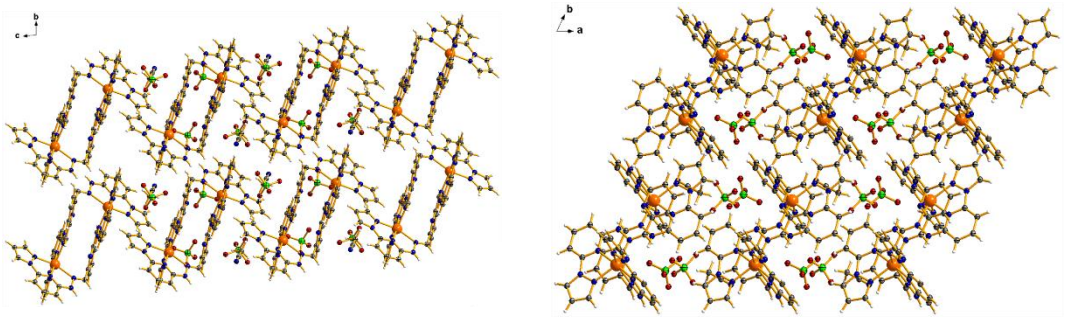
Coordination Geometry	Co	Fe
Hexagon (D_{6h})	30.305	28.793
Pentagonal pyramid (C_{5v})	18.964	18.416
Octahedron (O_h)	5.369	6.344
Trigonal prism (D_{3h})	8.404	8.371
Johnson pentagonal pyramid *J*2 (C_{5v})	22.955	22.358

S6. Packing model



(**a**) (**b**)

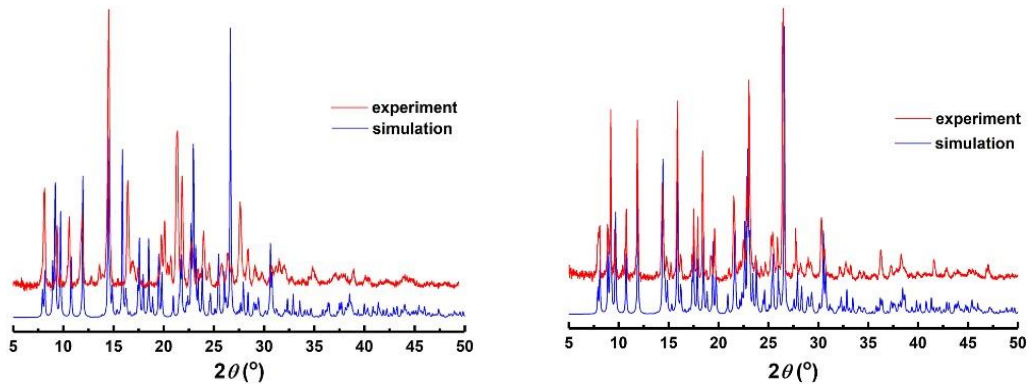
Figure S5. Packing model along the *a* and *c* axes of complex **Co2**. Color code: Co^{II}, orange-red; N, blue; C, gray; O, red; Cl, bright green; H, white.



(**a**) (**b**)

Figure S6. Packing model along the *a* and *c* axes of complex **Fe2**. Color code: Fe^{II}, orange; N, blue; C, gray; O, red; Cl, bright green; H, white.

S7. Powder-XRD analyses



(**a**) (**b**)

Figure S7. Powder-XRD analyses of complexes **Co2** and **Fe2**. The blue lines are simulated by single crystal data.

S8. Magnetic susceptibility measurement

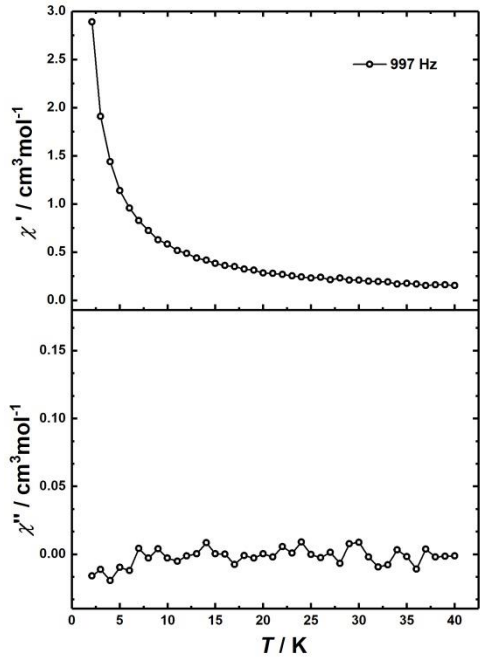


Figure S8. Temperature-dependent ac susceptibility of **Co2** under 0 Oe dc field.

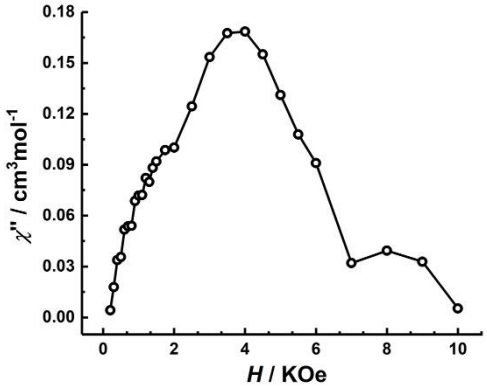


Figure S9. Field-dependent ac susceptibility of **Co2** at 1.9 K with ac frequency of 997 Hz.

Table S4. Parameters for the best fit of frequency-dependent ac susceptibility of **Co2** under 3500 Oe dc field.

T / K	$\chi_{S,tot}$	$\Delta\chi_1$	τ_1 / s	α_1	$\Delta\chi_2$	τ_2 / s	α_2	*Residual*
1.9	3.9142E-23	1.52999	0.22852	1.18103E-15	0.91746	0.00113	0.322	0.01503
2.2	7.58546E-23	1.19439	0.16888	1.43037E-15	1.00823	9.60745E-4	0.26601	0.0284
2.5	9.73326E-23	0.86095	0.14367	1.97141E-15	1.15141	9.95134E-4	0.21743	0.01406
3.0	1.14254E-22	0.45612	0.12313	3.18189E-15	1.28076	8.94003E-4	0.20257	0.00691
3.5	2.86916E-22	0.23226	0.11278	2.12437E-15	1.29226	7.01787E-4	0.15632	0.00772
4.0	6.20395E-22	0.1171	0.11026	2.39422E-15	1.24048	5.2808E-4	0.12195	0.00533
4.5	1.28678E-21	0.06296	0.13693	2.59157E-15	1.16561	3.74276E-4	0.11159	0.00132
5.0	8.24386E-22	0.03445	0.14876	6.10415E-15	1.08299	2.54585E-4	0.0922	0.00104
6.0	2.18471E-21	0.01334	0.13016	6.06514E-15	0.92773	1.05117E-4	0.06157	0.00185
7.0	5.83233E-23	0.02416	0.23616	3.30722E-28	0.80705	4.44762E-5	0.04719	8.65002E-4
8.0	1.41642E-22	0.00572	0.08477	1.50287E-31	0.70619	1.83869E-5	0.04856	0.00143