

A Capped Trigonal Prismatic Cobalt(II) Complex as a Structure Archetype for Single-Ion Magnets

Gangji Yi,^a Huihui Cui,^b Chunyang Zhang,^a Wen Zhao,^a Lei Chen,^{a,*} Yi-Quan
Zhang,^{c,*} Xue-Tai Chen,^{b,*} You Song,^b and Aihua Yuan^{a,*}

*^aState of Environmental and Chemical Engineering, Jiangsu University of Science
and Technology, Zhenjiang 212003, P. R. China;*

*^bState Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical
Engineering, Nanjing University, Nanjing 210093, P. R. China;*

*^cJiangsu Key Lab for NSLSCS, School of Physical Science and Technology, Nanjing
Normal University, Nanjing 210023, P. R. China.*

Supporting Information

Experimental Section

Materials and General Characterizations

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. All chemicals were purchased from commercial sources and used without further purification. The ligand [2,6-bis[bis(2-pyridylmethyl)amino]methyl]pyridine (BPA-TPA) was prepared as described previously.^{S1} Elemental analyses were performed on an Elementar Vario ELIII elemental analyzer. The powder XRD patterns were recorded at room temperature on a Bruker D8 Advance X-ray diffractometer.

Synthesis of [Co^{II}(BPA-TPA)(BF₄)₂] (1-Co)

To the solution of CoCl₂ (1.0 mmol, 0.130 g) in methanol (5 mL) was added the solution of AgBF₄ (2.0 mmol, 0.390 g) in methanol (10 mL). The insoluble silver chloride was immediately generated and then removed by filtration. The BPA-TPA ligand was added to the filtrate, and diethyl ether (20 mL) was allowed to slowly diffuse into the solution. After 2-4 days red crystals were obtained in 56 % yield. Anal. Calc. for C₃₁H₃₁B₂CoF₈N₇: C, 50.72; H, 4.26; N, 13.36. Found: C, 50.65; H, 4.20; N, 13.42.

Synthesis of [Fe^{II}(BPA-TPA)(ClO₄)₂] (2-Fe)

Preparation of 2-Fe was performed according to the method of Hazell *et al.*^{S2} Fe(ClO₄)₂·6H₂O was added to the solution of BPA-TPA ligand (0.5 mmol, 0.25 g) in methanol (10 mL), and the solution was stirred under dinitrogen for 10 min. The solution was allowed to stand in a closed vessel and pink crystals of formed overnight. The yield is 68 %. Anal. Calc. for C₃₁H₃₁Cl₂FeN₇O₈: C, 49.23; H, 4.13; N, 12.96. Found: C, 49.29; H, 4.06; N, 13.04.

X-ray Structure Determination

Single crystal X-ray diffraction data for both complexes were collected using a Bruker APEX DUO diffractometer with a CCD area detector (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) at 296 K.^{S3} The APEXII program was used for collecting frames of data, determining lattice parameters. Data were integrated through the SAINT. Absorption

corrections were applied using SADABS.^{S4} The structures were solved using SHELXS-97 and subsequently completed by Fourier recycling using SHELXL 97 program.^{S5}

Magnetic Measurements

Magnetic measurements of both complexes were performed with a Quantum Design SQUID VSM magnetometer. Direct current susceptibility data were collected between 1.8 and 300 K using an applied field of 2.0 kOe. Magnetization data were recorded from 0 to 7 T at 1.8, 3, and 5 K. The temperature and frequency dependent alternating-current susceptibility measurements under different applied static magnetic fields were carried out using an oscillating ac field of 2.0 Oe and ac frequencies ranging from 1 to 1000 Hz. The magnetic susceptibilities data were corrected for the sample holder as well as for diamagnetism of the constituent atoms (estimated using Pascal's constants).

Computational details

Complete-active-space self-consistent field (CASSCF) calculations on complexes **1-Co** and **2-Fe** on the basis of single-crystal X-ray determined geometries have been carried out with MOLCAS 8.4^{S6} program package. The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Co^{II} or Fe^{II} ion; VTZ for close N; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set. And the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. For **1-Co**, the active electrons in 10 active spaces considering the 3d-double shell effect (5+5') include all seven 3d electrons (CAS(7 in 5+5') for Co^{II}), and the mixed spin-free states are 50 (all from 10 quadruplets and all from 40 doublets for Co^{II}). And for **2-Fe**, active electrons in 5 active spaces include all d electrons (CAS (6 in 5) for Fe^{II}). We have mixed the maximum number of spin-free state which was possible with our hardware (all from 5 quintuplets, all from 45 triplets and all from 50 singlets for Fe^{II}). In the CASSCF calculation SINGLE_ANISO^{S7} program was used to obtain the spin-free-orbit energy levels,

zero-field splitting (ZFS) parameters $D(E)$ (cm^{-1}), \mathbf{g} tensors, magnetic axes, *et al.*, based on the above CASSCF/RASSI-SO calculations.

Table S1 Summary of crystal data and refinement for **1-Co** and **2-Fe**.

	1-Co	2-Fe
Molecular formula	$\text{C}_{31}\text{H}_{31}\text{B}_2\text{CoF}_8\text{N}_7$	$\text{C}_{31}\text{H}_{31}\text{Cl}_2\text{FeN}_7\text{O}_8$
CCDC no	1968362	1968363
Formula weight	734.18	756.38
Temperature / K	296(2)	296(2)
crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
$a / \text{\AA}$	11.2070(3)	11.5246(8)
$b / \text{\AA}$	12.5604(4)	12.2303(9)
$c / \text{\AA}$	13.5908(4)	14.0274(11)
β / deg	67.784(2)	97.401(4)
$V / \text{\AA}^3$	1628.81(9)	1632.4(2)
Z	2	2
$D_{\text{calc}}, \text{g/cm}^3$	1.497	1.539
μ / mm^{-1}	0.608	0.688
$F(000)$	750	780
Goodness-of-fit on F^2	1.018	1.059
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428,$ $wR_2 = 0.1012$	$R_1 = 0.0553,$ $wR_2 = 0.1601$
R indices (all data)	$R_1 = 0.0630,$ $wR_2 = 0.1144$	$R_1 = 0.0852,$ $wR_2 = 0.1985$

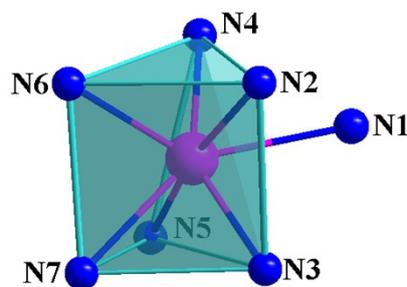
$$^a wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}, R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|.$$

Table S2 Selected bond lengths (Å) and angles (°) for **1-Co** and **2-Fe**.

1-Co		2-Fe	
Co(1)-N(1)	2.2861(19)	Fe(1)-N(1)	2.329(3)
Co(1)-N(3)	2.1123(19)	Fe(1)-N(2)	2.209(3)
Co(1)-N(4)	2.2391(19)	Fe(1)-N(4)	2.272(3)
Co(1)-N(5)	2.3327(19)	Fe(1)-N(5)	2.271(3)
Co(1)-N(6)	2.1766(19)	Fe(1)-N(6)	2.359(3)
Co(1)-N(7)	2.2910(19)	Fe(1)-N(7)	2.255(3)
Co(1)-N(2)	2.550(2)	Fe(1)-N(3)	2.554(3)
N(2)-Co(1)-N(3)	74.02(7)	N(2)-Fe(1)-N(3)	73.93(11)
N(4)-Co(1)-N(5)	80.76(7)	N(4)-Fe(1)-N(5)	85.39(11)
N(6)-Co(1)-N(7)	73.34(7)	N(6)-Fe(1)-N(7)	72.39(11)

Table S3 The continuous shape measure (CSM) analyses of seven-coordinate geometries for **1-Co** and **2-Fe** by SHAPE software^{S8}

CSM	1-Co	2-Fe
Heptagon	33.749	33.315
Hexagonal pyramid	16.010	16.942
Pentagonal bipyramid	4.952	4.158
Capped octahedron	3.275	4.002
Capped trigonal prism	2.715	2.994

**Figure S1** The coordination model of the central Co(II) ion for **1-Co**.

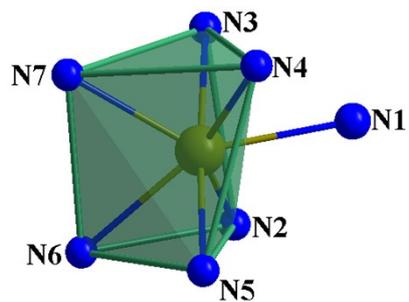


Figure S2 The coordination model of the central Fe(II) ion for **2-Fe**.

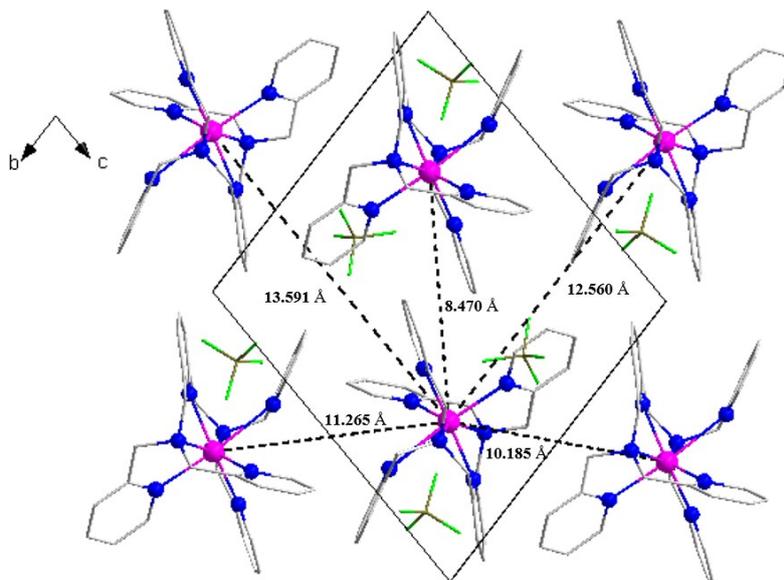


Figure S3. Crystal packing of **1-Co** along the *a* axis. The H atoms are omitted for clarity.

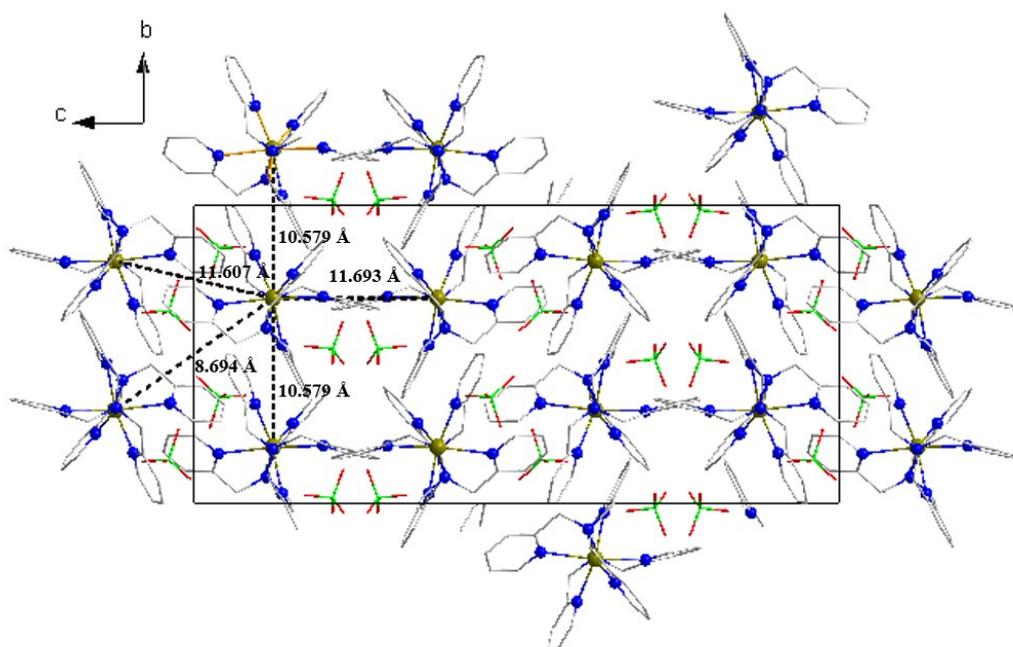


Figure S4. Crystal packing of **2-Fe** along the *a* axis. The H atoms are omitted for clarity.

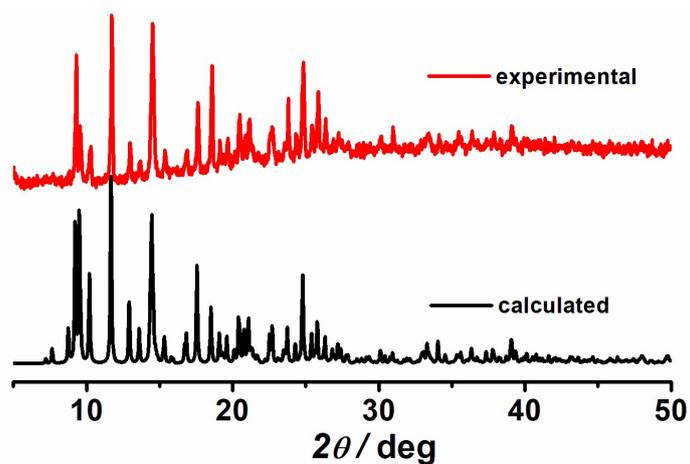


Figure S5 The power X-ray diffraction patterns of **1-Co** at room temperature.

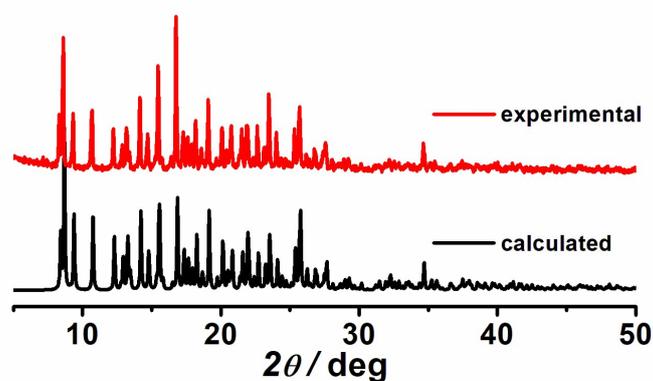


Figure S6 The power X-ray diffraction patterns of **2-Fe** at room temperature.

Table S4 The continuous shape measure (CSM) analyses of six-coordinate geometries for **1-Co** and **2-Fe** by SHAPE software^{S8}

CSM	1-Co	2-Fe
Hexagon	27.163	28.542
Pentagonal pyramid	13.385	13.207
Octahedron	11.716	10.197
Trigonal prism	3.914	4.240

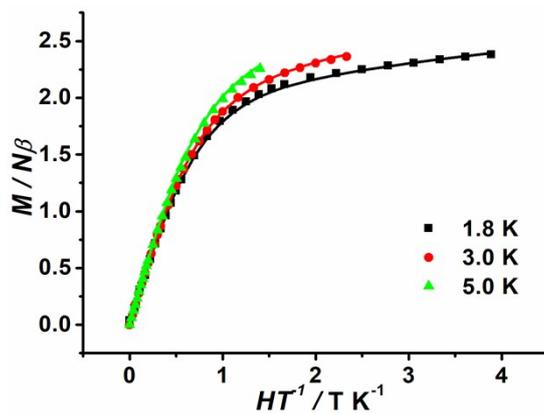


Figure S7 The M versus H/T curves at different temperatures for 1-Co.

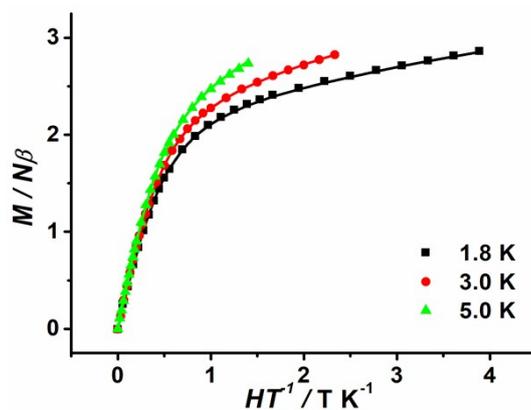


Figure S8 The M versus H/T curves at different temperatures for 2-Fe.

Table S5 Zero field splitting parameters obtained fitting the experimental data using the PHI program for 1-Co and 2-Fe.

	1-Co	2-Fe
Fitting of the $\chi_M T$ versus T		
D , cm^{-1}	21.4	-15.7
$ E $, cm^{-1}	1.00	3.27
g	2.21	2.16
Fitting of the M versus H at 1.8, 3 and 5 K		
D , cm^{-1}	13.7	-10.6
$ E $, cm^{-1}	0.01	2.30
g	2.25	2.21
ab initio calculations		
D , cm^{-1}	17.1	-10.0
$ E $, cm^{-1}	-2.7	3.1
g_x, g_y, g_z	2.349, 2.282, 2.148	2.002, 2.106, 2.247

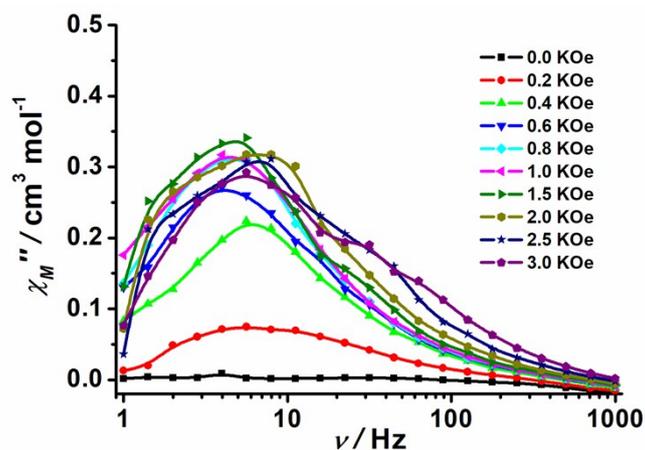


Figure S9 Frequency dependence of the out-of-phase (χ_M'') ac susceptibility at 1.8 K under the applied dc fields from 0 to 3.0 KOe for **1-Co**. The solid lines are foreye guide.

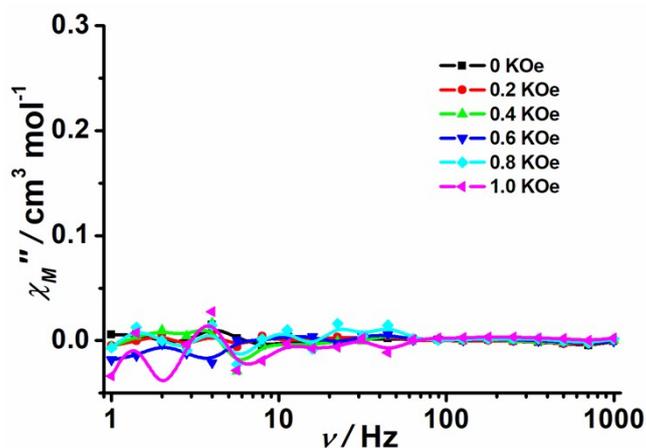


Figure S10 Frequency dependence of the out-of-phase (χ_M'') ac susceptibility at 1.8 K under the applied dc fields from 0 to 1.0 KOe for **2-Fe**. The solid lines are for eye guide.

Table S6 The parameters obtained by fitting Cole-Cole plot for **1-Co**.

T / K	χ_S	χ_T	τ	a
1.8	0.132	0.866	0.03804	0.19
1.9	0.127	0.817	0.03304	0.18
2.0	0.123	0.769	0.02843	0.17
2.2	0.117	0.698	0.02135	0.15
2.4	0.111	0.635	0.01298	0.11
2.6	0.107	0.583	0.00607	0.06
2.8	0.104	0.545	0.00242	0.03
3.0	0.108	0.508	0.00094	0.01
3.4	0.147	0.455	0.00017	0.01

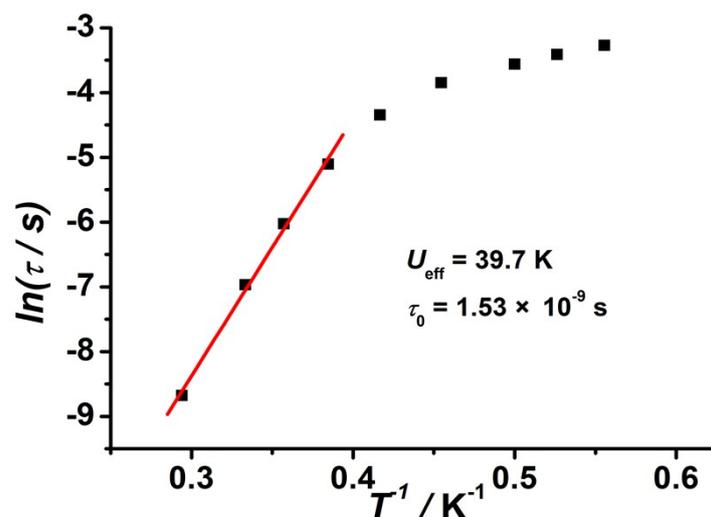


Figure S11 Relaxation time of the magnetization $\ln(\tau)$ vs T^{-1} plot under the 1.0 KOe applied field for **1-Co**.

Table S7 The reported seven-coordinate Co(II)-SIMs

Complex	D (E) / cm^{-1}	U_{eff} / K	Ref.
[Co(BPA-TPA)(BF ₄) ₂] ^a	13.7 (0.01) ^d	39.7	this work
[Co(H ₂ dapb)(H ₂ O)(NO ₃)](NO ₃) ^b (H ₂ dapb = 2,6-diacetylpyridine bis(benzoyl hydrazine))	32.4 (0) ^d	81.2	S9a
[CoL _{N5} (H ₂ O) ₂](Cl ₂ ·4H ₂ O) ^b (L _{N5} = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane-2,12-diene)	24.6 (0.014) ^d	29.8	S9a
[Co(dapb)(im) ₂](H ₂ O) ^b (im=imidazole)	24.8 (0.0016) ^d	62.3	S9a
[Co(DAPBH)(NO ₃)(H ₂ O)](NO ₃) ^b DAPBH=2,6-diacetylpyridinebis(2'-pyridylhydrazone)	30 ^e	50	S9b
[Co(4-tert-butylpyridine) ₃ (NO ₃) ₂] ^b	35.8 (0.07) ^e	25.5	S9c
[Co(isoquinoline) ₃ (NO ₃) ₂] ^b	35.7 (1.81) ^e	15.8	S9c
[CoL](ClO ₄) ₂ ^b (L=3,12-Bis(2-methylpyridine)-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1,14,16-triene)	34 ^d	24.3	S9d
[Co(tdmmb)(H ₂ O) ₂][BF ₄] ₂ ^b	35.1 (-2.7) ^f	42.2	S9e
[Co(tdmmb)(CN) ₂](H ₂ O) ₂ ^b	37.7 (-3.4) ^f	48.9	S9e
[Co(tdmmb)(NCS) ₂] ^b	34.5 (-3.6) ^f	49.2	S9e
[Co(tdmmb)(SPh) ₂] ^b (tdmmb=1,3,10,12-tetramethyl-1,2,11,12-tetraaza[[3](2,6)-pyridino[3](2,9)-1,10-phenanthroline]-2,10-diene)	39.7 (-6.8) ^f	54.7	S9e

[Co(H ₂ daps)(MeOH) ₂] ^b	43.1 (3.3) ^d	33.5	S9f
[Co(H ₄ daps)(NCS)(MeOH)]·(ClO ₄)·(MeOH) ^b	41.5 (1.5) ^d	28.4	S9f
[Co(H ₄ daps)(NCS) ₂]·(MeOH) ₂ ^b	38.8 (2.1) ^d	23.6	S9f
(Ph ₄ P) ₂ [Co(NO ₃) ₄]	10.9 (1.56) ^e	12	S9g
(MePh ₃ P) ₂ [Co(NO ₃) ₄]	12.74 (2.20) ^e	20	S9g
[Co(2,2'-bipyridine)(NO ₃) ₂ (CH ₃ CN)] ^b	32.9 (0.2) ^e	56.7	S9h
[Co(1,10-phenanthroline)(NO ₃) ₂ (CH ₃ CN)] ^b	31.4 (0.1) ^e	46.0	S9h
[Co(8-carboxymethoxy-2-carboxylicquinoline)(H ₂ O) ₃]·H ₂ O] ^b	70.4 (8.89) ^d	5.3	S9i
[Co(pypzbeyz)(NO ₃) ₂] ^b pypzbeyz=N-((6-(1H-pyrazol-1-yl)pyridin-2-yl)methylene)benzohydrazide	29.9 (0.31) ^d	49.8	S9j
[CoL]·H ₂ O ^b H ₂ L=3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1,14,16-triene-3,12-diacetic acid)	29.1 (0) ^d		S9k
[Co(L)Cl ₂]·2CH ₃ OH ^b	38 ^d		S9l
[Co(L)Br ₂] ^b	41 ^d	4.2	S9l
[Co(L)I ₂] ^b L=3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene	35 ^d	4.5	S9l
[Co(H ₄ L)(DMF)(H ₂ O)](NO ₃) ₂ ·(DMF)	35.92 (1.42) ^d	25	S9m
[Co(H ₄ L)(MeOH)(H ₂ O)](NO ₃) ₂ ·(MeOH)	37.23 (0.93) ^d	15	S9m
[Co(H ₄ L)(DEF)(H ₂ O)](NO ₃) ₂ H ₄ L = 2,2'-(pyridine-2,6-diylbis(ethan-1-yl-1-ylidene))bis(N-phenylhydrazinecarboxamide)	43.76 (0.84) ^d	4	S9m
[Co(L-N ₃ O ₂)(MeCN) ₂][BPh ₄] ₂	36.9 (0.2) ^d	32	S9n
[CoL ⁵ -ONHtBu]Cl ₂ ^c	9.2 (0.02) ^d	13.2	S9o

^acapped trigonal prism; ^bpentagonal bipyramid; ^ccapped octahedron; ^dValues obtained from the fit of dc magnetic data; ^eValues obtained from the electron paramagnetic resonance; ^fValues obtained from calculations.

Table S8 Calculated spin-free energies (cm^{-1}) of the lowest ten terms of complexes **1-Co** ($S = 3/2$) and **2-Fe** ($S = 2$) using CASSCF/RASSI-SO with MOLCAS 8.4.

	1-Co	2-Fe
	E/cm^{-1}	E/cm^{-1}
1	0.0	0.0
2	3918.1	591.6
3	4867.9	4625.7
4	5209.4	5233.3
5	7106.6	6492.7
6	8387.7	19202.6
7	10053.2	20522.6
8	21125.0	21174.1
9	21875.8	22046.4
10	25197.0	22560.7

Table S9 Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of **1-Co** and **2-Fe** using CASSCF/RASSI-SO with MOLCAS 8.4.

	Spin-orbit states	Energy (cm^{-1})	Spin-free states, Spin, Weights				
1-Co	1	0.0	1,1.5,0.97 64	2,1.5,0.01 40	3,1.5,0.00 64	4,1.5,0.00 14	17,0.5,0.0 005
	2	35.4	1,1.5,0.98 37	4,1.5,0.00 56	3,1.5,0.00 51	2,1.5,0.00 44	19,0.5,0.0 003
2-Fe	1	0.0	1,2.0,0.94 02	2,2.0,0.05 48	4,2.0,0.00 14	5,2.0,0.00 14	3,2.0,0.00 12
		2.7	1,2.0,0.93 64	2,2.0,0.05 95	5,2.0,0.00 15	3,2.0,0.00 11	4,2.0,0.00 07
	2	22.9	1,2.0,0.97 58	2,2.0,0.01 84	4,2.0,0.00 33	3,2.0,0.00 08	5,2.0,0.00 08
	3	41.7	1,2.0,0.97 37	2,2.0,0.02 32	4,2.0,0.00 11	5,2.0,0.00 10	3,2.0,0.00 03
		45.9	1,2.0,0.98 81	2,2.0,0.00 81	4,2.0,0.00 20	5,2.0,0.00 08	3,2.0,0.00 03

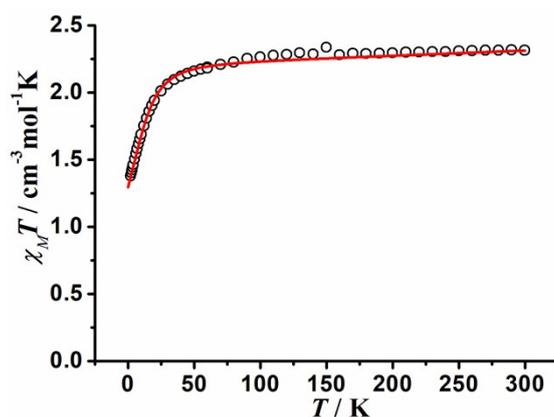


Figure S12 Calculated (red solid line) data of magnetic susceptibilities of **1-Co**.

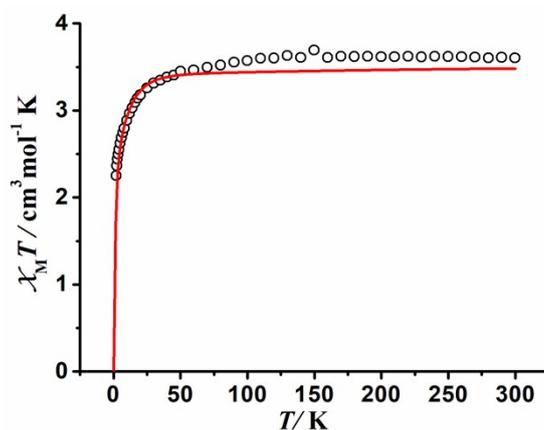


Figure S13 Calculated (red solid line) data of magnetic susceptibilities of **2-Fe**.

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