Mononuclear heptacoordinated 3d-metal helicates as a new family of single ion magnets

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Supplementary Information

Computational details

Theoretical calculations of the electronic structure for complexes 1-4 were performed using post-Hartree–Fock multi-reference wave function (WF) approach based on state-averaged complete active space self-consistent field calculations (SA-CASSCF) [1-4], followed by N-electron valence second-order perturbation theory (NEVPT2) [4-7]. Scalar relativistic effects were accounted for while using a standard second-order Douglas–Kroll–Hess (DKH) procedure [8]. For calculations, the segmented all-electron relativistically contracted version [9] of Ahlrichs polarized triple-ζbasis set, def2-TZVP [10-12], was used for all atoms. To improve the calculation time, the resolution of the identity approximation with corresponding correlation fitting of the basis set [13] was employed. Spin–orbit effects were included using the quasi-degenerate perturbation theory (QDPT) [14].

The CASSCF(n, 5) active space was constructed from 5 MOs with predominant contributions of 3d-AOs from the metal center and the number of electrons, corresponding to a metal ion electronic configuration (n = 6 for Fe(II), 7 for Co(II) and 8 for Ni(II) compounds). All possible multiplet states arising from the corresponding d^n configuration were included in the WF expansion in all cases.

Nuclei coordinates of non-hydrogen atoms were taken from diffraction experimental data, positions of hydrogen atoms were optimized employing density functional theory with the BP86 functional and Ahlrichs polarized basis set def2-TZVP [10-12] (optimized nuclei coordinates are listed in Table S4, in the current Supplementary Materials file).

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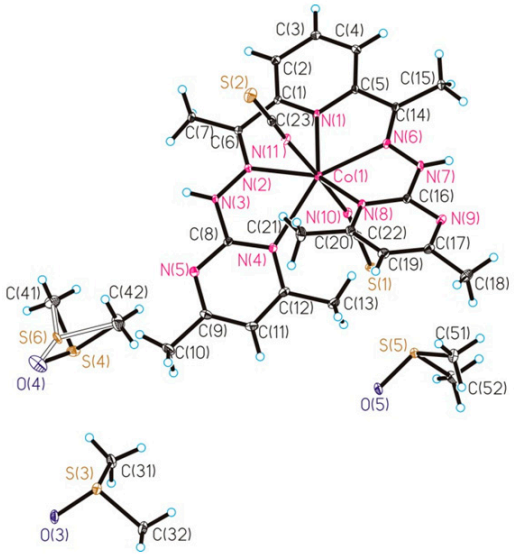
Table S1. Deviations from ideal structure, calculated with SHAPE program for several selected types of coordination polyhedral* with seven (**1**-**3**) and six (**4**) coordination number. (Zero value corresponds to ideal structure of the selected type).

Compound **1**		Compound **2**		Compound **2a** ([MLA_2] unit)		Compound **3**		Compound **4**	
PBPY-7	CTPR-7	PBPY-7	CTPR-7	PBPY-7	CTPR-7	PBPY-7	JPBPY-7	OC-6	PPY-6
2.389	4.845	3.424	1.640	2.765	2.275	2.793	4.525	4.714	17.942

* Polyhedra selected:
PBPY-7 3 D5h Pentagonal bipyramid
CTPR-7 5 C2v Capped trigonal prism
JPBPY-7 6 D5h Johnson pentagonal bipyramid (J13)
OC-6 3 Oh Octahedron
PPY-6 2 C5v Pentagonal pyramid

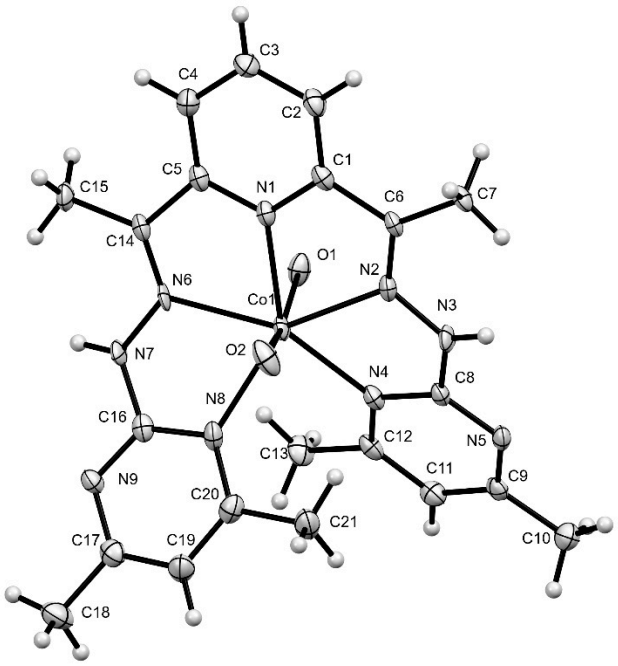
Table S2 Selected structural parameters for **1-4.** For each compound molecular structure with numbering scheme is shown for convenience.



Compound 1

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths, Å					
Co1-N1	2.178(4)	Co1- N3	2.270(4)	Co1-N4	2.096(4)
Co1- N5	2.335(4)	Co1-N6	2.087(4)	Co1-N11	2.495(4)
Co1-N12	2.216(4)	S1-C13	1.631(5)	N1-C16	1.341(6)
N1-C18	1.347(6)	N2-C20	1.378(6)	N2-N3	1.350(5)
N3-C22	1.294(6)	N4-C4	1.162(6)	N5-C21	1.349(7)
N6-C13	1.164(6)	N8-C21	1.330(6)	N9-C20	1.328(6)
N10-N12	1.354(5)	N10-C21	1.376(6)	N11-C20	1.346(6)
N12-C14	1.286(6)	N2-H2	0.8600	N10-H10	0.8600
C14-C16	1.474(6)	C16-C19	1.391(6)	C18-C22	1.470(6)
C22-C23	1.499(7)				
Bond angles, deg					
N1-Co1-N3	70.41(14)	N1-Co1-N4	91.33(14)	N1-Co1-N5	136.66(14)
N1-Co1-N6	88.31(14)	N1-Co1-N11	134.31(12)	N1-Co1-N12	70.54(14)
N3-Co1-N4	95.68(14)	N3-Co1-N5	148.15(13)	N3-Co1-N6	81.76(14)
N3-Co1-N11	66.95(13)	N3-Co1-N12	140.79(13)	N4-Co1-N5	99.23(13)
N4-Co1-N6	177.39(14)	N4-Co1-N11	77.48(14)	N4-Co1-N12	81.84(14)
N5-Co1-N6	82.79(13)	N5-Co1-N11	89.02(12)	N5-Co1-N12	69.61(13)
N6-Co1-N11	100.96(14)	N6-Co1-N12	100.46(14)	N11-Co1-N12	147.37(14)
C16-N1-C18	119.5(4)	Co1-N1-C16	119.9(3)	Co1-N1-C18	120.6(3)
N3-N2-C20	117.7(4)	Co1-N3-N2	120.0(3)	Co1-N3-C22	119.2(3)
N2-N3-C22	119.8(4)	Co1-N4-C4	170.5(4)	Co1-N5-C21	112.9(3)
Co1-N6-C13	172.5(4)	N12-N10-C21	116.9(4)	Co1-N11-C20	113.3(3)
Co1-N12-N10	117.0(3)	Co1-N12-C14	121.7(3)	N10-N12-C14	120.9(4)
N3-N2-H2	121.00	C20-N2-H2	121.00	N12-N10-H10	122.00
C21-N10-H10	122.00	S1-C13-N6	178.7(5)	N12-C14-C16	113.1(4)
N1-C16-C19	122.1(4)	N1-C16-C14	114.7(4)	C14-C16-C19	123.3(4)
N1-C18-C22	114.6(4)	N9-C20-N11	128.4(4)	N2-C20-N9	113.9(4)
N2-C20-N11	117.7(4)	N5-C21-N8	128.1(4)	N5-C21-N10	116.9(4)

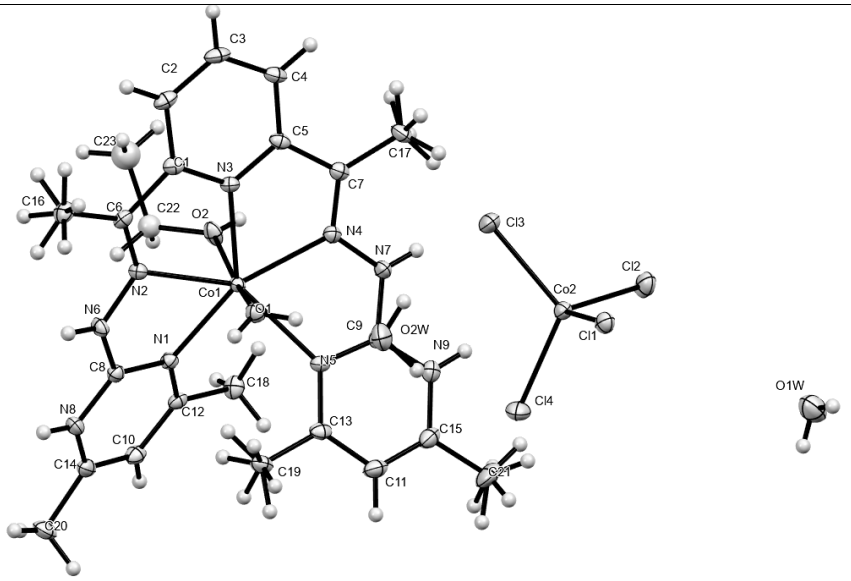
N8-C21-N10	114.9(4)	N3-C22-C18	114.2(4)	C18-C22-C23	120.9(4)
N3-C22-C23	124.9(4)				
Torsion angles, deg					
N3-Co1-N1-C16	-174.6(4)	N3-Co1-N1-C18	5.4(3)	N4-Co1-N1-C16	-79.0(3)
N4-Co1-N1-C18	101.0(3)	N5-Co1-N1-C16	26.0(4)	N5-Co1-N1-C18	-154.1(3)
N6-Co1-N1-C16	103.6(3)	N6-Co1-N1-C18	-76.5(3)	N11-Co1-N1-C16	-152.7(3)
N11-Co1-N1-C18	27.2(4)	N12-Co1-N1-C16	1.9(3)	N12-Co1-N1-C18	-178.2(4)
N1-Co1-N3-N2	-178.1(3)	N1-Co1-N3-C22	-9.3(3)	N4-Co1-N3-N2	92.5(3)
N4-Co1-N3-C22	-98.7(3)	N5-Co1-N3-N2	-25.2(5)	N5-Co1-N3-C22	143.6(3)
N6-Co1-N3-N2	-86.9(3)	N6-Co1-N3-C22	81.9(3)	N11-Co1-N3-N2	18.8(3)
N11-Co1-N3-C22	-172.4(4)	N12-Co1-N3-N2	176.6(3)	N12-Co1-N3-C22	-14.6(4)
N1-Co1-N5-C21	-45.6(4)	N3-Co1-N5-C21	173.2(3)	N4-Co1-N5-C21	56.4(3)
N6-Co1-N5-C21	-125.3(3)	N11-Co1-N5-C21	133.5(3)	N12-Co1-N5-C21	-21.3(3)
N1-Co1-N11-C20	-36.5(4)	N3-Co1-N11-C20	-14.1(3)	N4-Co1-N11-C20	-115.9(3)
N5-Co1-N11-C20	144.4(3)	N6-Co1-N11-C20	62.0(3)	N12-Co1-N11-C20	-167.9(3)
N1-Co1-N12-N10	-176.1(3)	N1-Co1-N12-C14	-3.6(3)	N3-Co1-N12-N10	-170.7(2)
N3-Co1-N12-C14	1.7(5)	N4-Co1-N12-N10	-81.7(3)	N4-Co1-N12-C14	90.7(3)
N5-Co1-N12-N10	21.3(3)	N5-Co1-N12-C14	-166.2(4)	N6-Co1-N12-N10	99.5(3)
N6-Co1-N12-C14	-88.0(3)	N11-Co1-N12-N10	-30.8(4)	N11-Co1-N12-C14	141.7(3)
Co1-N1-C16-C14	-0.4(5)	Co1-N1-C16-C19	178.8(3)	C18-N1-C16-C14	179.7(4)
C18-N1-C16-C19	-1.2(6)	Co1-N1-C18-C22	-1.8(5)	C16-N1-C18-C22	178.2(4)
C20-N2-N3-Co1	-22.1(5)	C20-N2-N3-C22	169.2(4)	N3-N2-C20-N9	-172.4(4)
N3-N2-C20-N11	7.1(6)	Co1-N3-C22-C18	11.4(5)	Co1-N3-C22-C23	-169.3(3)
N2-N3-C22-C18	-179.8(4)	N2-N3-C22-C23	-0.5(7)	Co1-N5-C21-N8	-162.5(4)
Co1-N5-C21-N10	19.6(5)	C21-N10-N12-Co1	-19.5(5)	C21-N10-N12-C14	168.0(4)
N12-N10-C21-N5	-1.3(6)	N12-N10-C21-N8	-179.4(4)	Co1-N11-C20-N2	9.0(5)
Co1-N11-C20-N9	-171.6(4)	Co1-N12-C14-C16	4.5(5)	N10-N12-C14-C16	176.7(4)
N12-C14-C16-N1	-2.6(6)	N12-C14-C16-C19	178.3(4)	N1-C18-C22-N3	-6.3(6)
N1-C18-C22-C23	174.3(4)				



Compound 2

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths, Å					
Co1-O1	2.223(3)	Co1-O2	2.214(3)	Co1-N1	2.140(4)
Co1-N2	2.141(3)	Co1-N4	2.222(3)	Co1-N6	2.155(3)
Co1-N8	2.240(4)	Cl2-O8	1.426(4)	Cl2-O9	1.374(10)
Cl2-O10	1.547(9)	N1-C5	1.352(5)	N1-C1	1.337(5)
N2-C6	1.293(5)	N2-N3	1.363(5)	N3-C8	1.383(5)
N4-C12	1.360(5)	N4-C8	1.341(5)	N5-C8	1.328(5)
N5-C9	1.344(5)	N6-N7	1.367(4)	N6-C14	1.286(6)
N7-C16	1.403(6)	N8-C20	1.363(6)	N8-C16	1.340(5)
N9-C16	1.326(5)	N9-C17	1.345(6)	C1-C6	1.485(6)
C1-C2	1.395(6)	C2-C3	1.389(6)	C3-C4	1.396(5)
C4-C5	1.387(6)	C5-C14	1.489(5)	C6-C7	1.485(5)
C9-C10	1.500(6)	C9-C11	1.381(5)	C11-C12	1.383(6)
C12-C13	1.491(5)	C14-C15	1.488(6)	C17-C19	1.387(6)
C17-C18	1.492(6)	C19-C20	1.379(7)	C20-C21	1.505(7)
Bond angles, deg					
O1-Co1-O2	166.29(13)	O1-Co1-N1	82.89(12)	O1-Co1-N2	93.10(11)
O1-Co1-N4	77.67(12)	O1-Co1-N6	82.65(12)	O1-Co1-N8	115.05(11)
O2-Co1-N1	83.72(13)	O2-Co1-N2	79.89(11)	O2-Co1-N4	110.89(14)
O2-Co1-N6	96.00(12)	O2-Co1-N8	77.17(11)	N1-Co1-N2	71.58(13)
N1-Co1-N4	137.90(12)	N1-Co1-N6	72.16(13)	N1-Co1-N8	137.43(12)
N2-Co1-N4	72.60(12)	N2-Co1-N6	143.74(14)	N2-Co1-N8	139.14(14)
N4-Co1-N6	139.80(11)	N4-Co1-N8	84.65(12)	N6-Co1-N8	72.47(13)
C1-N1-C5	121.3(4)	Co1-N1-C1	119.8(3)	Co1-N1-C5	118.8(2)
N3-N2-C6	122.1(3)	Co1-N2-C6	122.4(3)	Co1-N2-N3	115.2(2)
N2-N3-C8	116.0(3)	C8-N4-C12	115.6(3)	Co1-N4-C8	113.9(2)
Co1-N4-C12	130.2(3)	C8-N5-C9	115.7(3)	Co1-N6-C14	121.6(2)
N7-N6-C14	122.5(3)	Co1-N6-N7	115.7(3)	N6-N7-C16	115.4(3)
Co1-N8-C16	114.7(3)	Co1-N8-C20	130.8(3)	C16-N8-C20	114.4(4)
C16-N9-C17	115.5(3)	N1-C1-C6	113.6(4)	C2-C1-C6	125.4(3)
N1-C1-C2	121.0(4)	C1-C2-C3	118.4(3)	C2-C3-C4	120.2(4)
C3-C4-C5	118.5(4)	N1-C5-C14	113.8(4)	C4-C5-C14	125.5(4)
N1-C5-C4	120.6(3)	N2-C6-C7	124.8(4)	C1-C6-C7	123.4(3)
N2-C6-C1	111.8(3)	N3-C8-N5	115.5(3)	N3-C8-N4	116.6(4)
N4-C8-N5	127.9(3)	N5-C9-C10	116.3(3)	N5-C9-C11	121.1(4)
C10-C9-C11	122.6(3)	C9-C11-C12	119.4(3)	N4-C12-C13	118.8(4)
C11-C12-C13	121.2(3)	N4-C12-C11	120.1(3)	C5-C14-C15	120.9(4)
N6-C14-C15	126.5(3)	N6-C14-C5	112.6(3)	N7-C16-N9	114.7(3)
N7-C16-N8	116.5(3)	N8-C16-N9	128.8(4)	N9-C17-C19	121.1(4)
N9-C17-C18	117.7(4)	C18-C17-C19	121.2(4)	C17-C19-C20	118.7(4)
N8-C20-C21	119.1(4)	C19-C20-C21	119.8(4)	N8-C20-C19	121.1(4)
Torsion angles, deg					
O1-Co1-N1-C1	-100.4(3)	O1-Co1-N1-C5	77.0(3)	O2-Co1-N1-C1	76.7(3)
O2-Co1-N1-C5	-105.9(3)	N2-Co1-N1-C1	-4.7(3)	N2-Co1-N1-C5	172.7(3)
N4-Co1-N1-C1	-37.7(3)	N4-Co1-N1-C5	139.7(2)	N6-Co1-N1-C1	175.1(3)

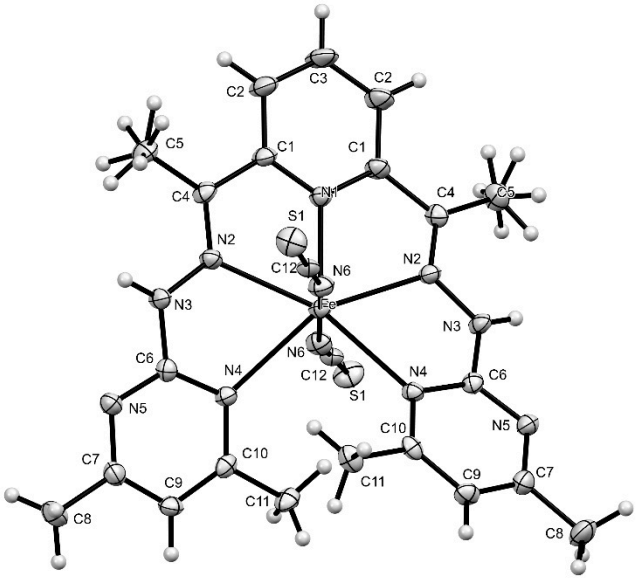
N6-Co1-N1-C5	-7.5(2)	N8-Co1-N1-C1	140.0(3)	N8-Co1-N1-C5	-42.6(3)
O1-Co1-N2-N3	-97.3(2)	O1-Co1-N2-C6	89.8(3)	O2-Co1-N2-N3	94.6(3)
O2-Co1-N2-C6	-78.4(3)	N1-Co1-N2-N3	-178.8(3)	N1-Co1-N2-C6	8.3(3)
N4-Co1-N2-N3	-21.3(2)	N4-Co1-N2-C6	165.8(3)	N6-Co1-N2-N3	-179.1(2)
N6-Co1-N2-C6	8.0(4)	N8-Co1-N2-N3	38.0(3)	N8-Co1-N2-C6	-135.0(3)
O1-Co1-N4-C8	115.0(3)	O1-Co1-N4-C12	-71.5(3)	O2-Co1-N4-C8	-53.9(3)
O2-Co1-N4-C12	119.7(3)	N1-Co1-N4-C8	50.5(4)	N1-Co1-N4-C12	-136.0(3)
N2-Co1-N4-C8	17.7(3)	N2-Co1-N4-C12	-168.8(4)	N6-Co1-N4-C8	177.5(3)
N6-Co1-N4-C12	-9.0(5)	N8-Co1-N4-C8	-127.9(3)	N8-Co1-N4-C12	45.6(4)
O1-Co1-N6-N7	99.0(2)	O1-Co1-N6-C14	-75.1(3)	O2-Co1-N6-N7	-94.7(2)
O2-Co1-N6-C14	91.2(3)	N1-Co1-N6-N7	-176.2(3)	N1-Co1-N6-C14	9.8(3)
N2-Co1-N6-N7	-175.8(2)	N2-Co1-N6-C14	10.1(4)	N4-Co1-N6-N7	38.1(3)
N4-Co1-N6-C14	-136.0(3)	N8-Co1-N6-N7	-20.3(2)	N8-Co1-N6-C14	165.7(3)
O1-Co1-N8-C16	-58.6(3)	O1-Co1-N8-C20	120.9(3)	O2-Co1-N8-C16	114.8(3)
O2-Co1-N8-C20	-65.7(3)	N1-Co1-N8-C16	49.2(3)	N1-Co1-N8-C20	-131.3(3)
N2-Co1-N8-C16	172.2(2)	N2-Co1-N8-C20	-8.3(4)	N4-Co1-N8-C16	-132.4(3)
N4-Co1-N8-C20	47.2(3)	N6-Co1-N8-C16	14.2(2)	N6-Co1-N8-C20	-166.3(3)
Co1-N1-C1-C2	178.9(3)	Co1-N1-C1-C6	1.5(4)	C5-N1-C1-C2	1.6(5)
C5-N1-C1-C6	-175.9(3)	Co1-N1-C5-C4	-176.8(3)	Co1-N1-C5-C14	5.2(4)
C1-N1-C5-C4	0.6(5)	C1-N1-C5-C14	-177.4(3)	Co1-N2-N3-C8	22.9(4)
C6-N2-N3-C8	-164.2(3)	Co1-N2-C6-C1	-9.9(4)	Co1-N2-C6-C7	170.9(3)
N3-N2-C6-C1	177.6(3)	N3-N2-C6-C7	-1.6(5)	N2-N3-C8-N4	-6.6(5)
N2-N3-C8-N5	172.8(3)	Co1-N4-C8-N3	-12.1(4)	Co1-N4-C8-N5	168.7(3)
C12-N4-C8-N3	173.4(3)	C12-N4-C8-N5	-5.8(6)	Co1-N4-C12-C11	-169.7(3)
Co1-N4-C12-C13	10.2(5)	C8-N4-C12-C11	3.7(5)	C8-N4-C12-C13	-176.4(3)
C9-N5-C8-N3	-175.8(3)	C9-N5-C8-N4	3.4(6)	C8-N5-C9-C10	178.2(3)
C8-N5-C9-C11	1.0(5)	Co1-N6-N7-C16	24.3(3)	C14-N6-N7-C16	-161.7(3)
Co1-N6-C14-C5	-9.9(4)	Co1-N6-C14-C15	170.8(3)	N7-N6-C14-C5	176.4(3)
N7-N6-C14-C15	-2.9(5)	N6-N7-C16-N8	-11.2(4)	N6-N7-C16-N9	169.6(3)
Co1-N8-C16-N7	-6.5(4)	Co1-N8-C16-N9	172.6(3)	C20-N8-C16-N7	173.9(3)
C20-N8-C16-N9	-7.0(5)	Co1-N8-C20-C19	-176.6(2)	Co1-N8-C20-C21	4.5(5)
C16-N8-C20-C19	2.9(5)	C16-N8-C20-C21	-176.0(3)	C17-N9-C16-N7	-175.5(3)
C17-N9-C16-N8	5.5(5)	C16-N9-C17-C18	179.1(3)	C16-N9-C17-C19	0.3(5)
N1-C1-C2-C3	-2.5(5)	C6-C1-C2-C3	174.6(3)	N1-C1-C6-N2	5.2(4)
N1-C1-C6-C7	-175.7(3)	C2-C1-C6-N2	-172.1(3)	C2-C1-C6-C7	7.1(6)
C1-C2-C3-C4	1.4(5)	C2-C3-C4-C5	0.6(5)	C3-C4-C5-N1	-1.6(5)
C3-C4-C5-C14	176.1(3)	N1-C5-C14-N6	2.9(4)	N1-C5-C14-C15	-177.8(3)
C4-C5-C14-N6	-175.0(3)	C4-C5-C14-C15	4.3(5)	N5-C9-C11-C12	-2.6(6)
C10-C9-C11-C12	-179.6(4)	C9-C11-C12-N4	0.1(6)	C9-C11-C12-C13	-179.8(4)
N9-C17-C19-C20	-3.6(5)	C18-C17-C19-C20	177.7(3)	C17-C19-C20-N8	1.8(5)
C17-C19-C20-C21	-179.2(3)				



Compound 2a

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths, Å					
Co1-O1	2.1572(18)	N8-C8	1.332(3)	Co1-O2	2.1844(19)
N9-C15	1.337(3)	Co1-N1	2.230(2)	N9-C9	1.329(3)
Co1-N2	2.172(2)	C1-C2	1.397(3)	Co1-N3	2.155(2)
C1-C6	1.483(3)	Co1-N4	2.171(2)	C2-C3	1.385(4)
Co1-N5	2.325(2)	C3-C4	1.387(4)	Co2-Cl1	2.2968(7)
C4-C5	1.398(3)	Co2-Cl2	2.2669(7)	C5-C7	1.486(3)
Co2-Cl3	2.2864(8)	Co2-Cl4	2.2741(7)	C6-C16	1.489(4)
O2-C22	1.439(4)	C7-C17	1.497(4)	N1-C8	1.345(3)
N1-C12	1.357(3)	C10-C14	1.391(4)	N2 -C6	1.290(3)
C10-C12	1.386(3)	C11-C13	1.380(4)	N2-N6	1.355(3)
C11-C15	1.379(4)	N3-C1	1.337(3)	C12-C18	1.500(3)
N3-C5	1.338(3)	C13-C19	1.493(4)	N4 -C7	1.288(3)
C14-C20	1.496(4)	N4-N7	1.357(3)	C15-C21	1.493(4)
N5-C13	1.359(3)	C22-C23	1.504(4)	N5-C9	1.335(3)
N6-C8	1.373(3)	N7-C9	1.387(3)	N8-C14	1.338(3)
Bond angles, deg					
O1-Co1-O2	167.03(7)	O1-Co1-N1	107.69(7)	O1-Co1-N2	79.41(7)
O1-Co1-N3	84.65(7)	O1-Co1-N4	95.64(7)	Co1-N1-C8	112.82(15)
O1-Co-N5	79.84(7)	O2-Co1-N1	80.96(7)	Co1-N2-C6	121.48(16)
O2-Co1-N2	94.70(8)	N6-N2-C6	122.8(2)	O2-Co1-N3	82.52(8)
Co1-N2-N6	114.19(14)	O2-Co1-N4	82.04(8)	O2-Co1-N5	111.07(7)
N1-Co1-N2	71.66(7)	Co1-N3-C1	119.06(16)	N1-Co1-N3	138.01(8)
C1-N3-C5	121.3(2)	N1-Co1-N4	142.69(8)	Co1-N3-C5	119.54(16)
N1-Co1-N5	84.96(7)	N7-N4-C7	119.8(2)	N2-Co1-N3	71.58(8)
Co1-N4-C7	121.69(17)	N2-Co1-N4	142.87(8)	Co1-N4-N7	118.15(15)
N2-Co1-N5	142.01(7)	Co1-N5-C9	113.59(15)	N3-Co1-N4	71.33(8)
N3-Co1-N5	137.04(7)	N4-Co1-N5	70.69(7)	N2-N6-C8	115.9(2)
N4-N7-C9	115.83(19)	N3-C1-C6	114.6(2)	N3-C5-C7	113.9(2)
N2-C6-C1	111.9(2)	N4-C7-C5	112.6(2)	N5-C9-N7	117.7(2)
N1-C8-N6	117.0(2)				

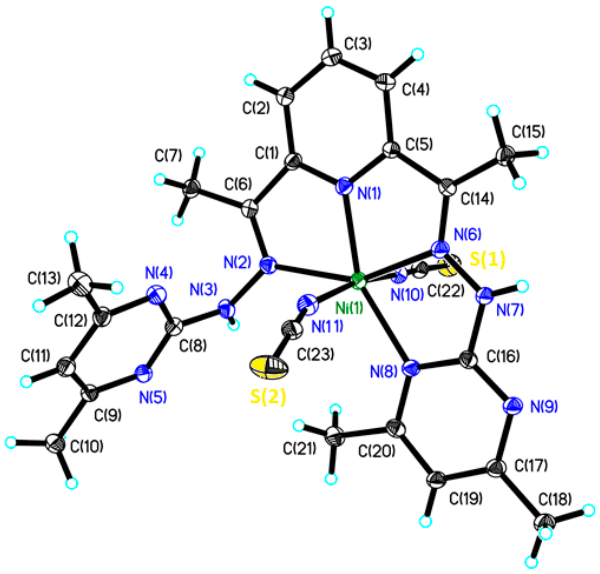
Torsion angles, deg					



Compound 3

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths, Å					
Fe-N1	2.240(2)	Fe-N2	2.318(3)	Fe-N4	2.481(2)
Fe-N6	2.095(2)	Fe-N2a	2.318(3)	Fe-N4a	2.481(3)
Fe-N6a	2.095(2)	S1-C12	1.630(3)	N1-C1a	1.346(5)
N1-C1	1.346(4)	N2-N3	1.365(3)	N2-C4	1.293(4)
N3-C6	1.377(4)	N4-C6	1.343(4)	N4-C10	1.350(4)
N5-C7	1.345(4)	N5-C6	1.329(4)	N6-C12	1.162(4)
C1-C2	1.394(4)	C1-C4	1.467(4)	C2-C3	1.377(5)
C4-C5	1.502(5)	C7-C9	1.379(5)	C7-C8	1.497(4)
C9-C10	1.377(4)	C10-C11	1.500(5)		
Bond angles, deg					
N1-Fe-N2	68.70(7)	N1-Fe-N4	133.22(7)	N1-Fe-N6	93.17(7)
N1-Fe-N2a	68.71(8)	N1-Fe-N4a	133.22(7)	N1-Fe-N6a	93.15(8)
N2-Fe-N4	66.93(8)	N2-Fe-N6	79.50(9)	N2-Fe-N2a	137.41(9)
N2-Fe-N4a	152.79(8)	N2-Fe-N6a	102.85(9)	N4-Fe-N6	92.76(8)
N2a-Fe-N4	152.78(9)	N4-Fe-N4a	93.56(8)	N4-Fe-N6a	82.90(8)
N2a-Fe-N6	102.86(9)	N4a-Fe-N6	82.89(9)	N6-Fe-N6a	173.68(10)
N2a-Fe-N4a	66.92(9)	N2a-Fe-N6a	79.49(9)	N4a-Fe-N6a	92.77(9)
Fe-N1-C1	120.26(18)	C1-N1-C1a	119.5(3)	Fe-N1-C1a	120.26(18)
N3-N2-C4	119.6(3)	Fe-N2-C4	119.52(19)	Fe-N2-N3	117.82(19)
N2-N3-C6	117.6(3)	C6-N4-C10	114.6(2)	Fe-N4-C6	113.73(16)
Fe-N4-C10	131.4(2)	C6-N5-C7	115.5(3)	Fe-N6-C12	166.0(3)
C2-C1-C4	123.2(3)	N1-C1-C2	121.5(3)	N1-C1-C4	115.3(3)
C1-C2-C3	118.8(3)	C2-C3-C2a	119.9(3)	N2-C4-C5	125.5(3)
C1-C4-C5	120.6(2)	N2-C4-C1	113.8(3)	N4-C6-N5	128.3(3)
N3-C6-N4	118.3(2)	N3-C6-N5	113.4(3)	N5-C7-C8	116.8(3)
C8-C7-C9	122.1(3)	N5-C7-C9	121.1(3)	C7-C9-C10	118.7(3)
N4-C10-C9	121.5(3)	C9-C10-C11	119.8(3)	N4-C10-C11	118.7(2)

S1-C12-N6	178.9(2)				
Torsion angles, deg					
N2-Fe-N1-C1	7.68(13)	N2-Fe-N1-C1a	-172.31(13)	N4-Fe-N1-C1	27.03(14)
N4-Fe-N1-C1a	-152.95(13)	N6-Fe-N1-C1	-69.76(14)	N6-Fe-N1-C1a	110.26(14)
N2a-Fe-N1-C1	-172.33(13)	N4a-Fe-N1-C1	-152.97(13)	N6a-Fe-N1-C1	110.24(14)
N1-Fe-N2-N3	-174.30(18)	N1-Fe-N2-C4	-14.05(17)	N4-Fe-N2-N3	20.92(16)
N4-Fe-N2-C4	-178.8(2)	N6-Fe-N2-N3	-76.68(18)	N6-Fe-N2-C4	83.57(19)
N2a-Fe-N2-N3	-174.30(15)	N2a-Fe-N2-C4	-14.1(2)	N4a-Fe-N2-N3	-26.2(3)
N4a-Fe-N2-C4	134.08(19)	N6a-Fe-N2-N3	97.33(18)	N6a-Fe-N2-C4	-102.42(19)
N1-Fe-N4-C6	-36.17(18)	N1-Fe-N4-C10	150.33(18)	N2-Fe-N4-C6	-16.56(15)
N2-Fe-N4-C10	169.9(2)	N6-Fe-N4-C6	60.79(17)	N6-Fe-N4-C10	-112.7(2)
N2a-Fe-N4-C6	-173.71(17)	N2a-Fe-N4-C10	12.8(3)	N4a-Fe-N4-C6	143.83(16)
N4a-Fe-N4-C10	-29.7(2)	N6a-Fe-N4-C6	-123.82(18)	N6a-Fe-N4-C10	62.7(2)
Fe-N1-C1-C4	-1.9(2)	C1a-N1-C1-C2	-0.2(3)	C1a-N1-C1-C4	178.07(18)
Fe-N1-C1-C2	179.8(2)	N3-N2-C4-C1	177.6(2)	N3-N2-C4-C5	1.2(4)
Fe-N2-N3-C6	-24.2(3)	C4-N2-N3-C6	175.6(2)	Fe-N2-C4-C1	17.7(3)
Fe-N2-C4-C5	-158.7(2)	N2-N3-C6-N5	-172.8(2)	N2-N3-C6-N4	7.4(3)
Fe-N4-C6-N3	11.2(3)	Fe-N4-C10-C11	-12.5(3)	C6-N4-C10-C9	-4.7(3)
C6-N4-C10-C11	174.0(2)	Fe-N4-C6-N5	-168.5(2)	C10-N4-C6-N3	-174.1(2)
C10-N4-C6-N5	6.1(4)	Fe-N4-C10-C9	168.72(17)	C6-N5-C7-C9	-3.5(3)
C7-N5-C6-N3	178.2(2)	C7-N5-C6-N4	-2.1(4)	C6-N5-C7-C8	176.4(2)
C4-C1-C2-C3	-177.7(2)	N1-C1-C4-N2	-10.3(3)	N1-C1-C4-C5	166.2(2)
N1-C1-C2-C3	0.4(4)	C2-C1-C4-N2	168.0(3)	C2-C1-C4-C5	-15.5(4)
C1-C2-C3-C2a	-0.2(4)	C8-C7-C9-C10	-175.4(2)	N5-C7-C9-C10	4.5(4)
C7-C9-C10-N4	-0.1(4)	C7-C9-C10-C11	-178.8(2)		



Compound 4

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths, Å					
Ni1-N3	2.049(3)	Ni1-N4	2.011(3)	Ni1-N5	2.179(3)
Ni1-N6	2.032(4)	Ni1-N7	2.155(3)	Ni1-N8	2.030(4)
S1-C22	1.634(6)	S2-C23	1.629(5)	N1-C2	1.347(6)
N1-C6	1.329(5)	N2-N3	1.355(5)	N2-C6	1.383(5)

N3-C7	1.291(6)	N4-C9	1.345(5)	N4-C13	1.334(5)
N5-N9	1.401(5)	N5-C14	1.290(5)	N6-C23	1.159(6)
N7-C4	1.338(5)	N7-C6	1.347(5)	N8-C22	1.132(7)
N9-C16	1.368(5)	N10-C16	1.341(5)	N10-C17	1.341(6)
N11-C16	1.350(5)	N11-C20	1.340(5)	C1-C2	1.490(6)
C2-C3	1.396(5)	C3-C4	1.385(6)	C4-C5	1.507(5)
C7-C9	1.489(5)	C7-C8	1.488(5)	N2-H2	0.8600
N9-H9	0.8600	C9-C10	1.396(6)	C10-C11	1.384(6)
C11-C12	1.382(7)	C12-C13	1.389(6)	C13-C14	1.486(5)
C14-C15	1.490(6)	C17-C19	1.392(6)	C17-C18	1.507(7)
C19-C20	1.386(6)	C20-C21	1.501(6)		
Bond angles, deg					
N3-Ni1-N4	76.89(14)	N3-Ni1-N5	152.20(13)	N3-Ni1-N6	93.86(14)
N3-Ni1-N7	76.54(13)	N3-Ni1-N8	94.01(15)	N4-Ni1-N5	75.36(13)
N4-Ni1-N6	93.54(14)	N4-Ni1-N7	153.38(13)	N4-Ni1-N8	95.79(16)
N5-Ni1-N6	89.49(14)	N5-Ni1-N7	131.12(13)	N5-Ni1-N8	87.16(15)
N6-Ni1-N7	89.86(14)	N6-Ni1-N8	168.95(15)	N7-Ni1-N8	84.45(15)
C2-N1-C6	116.3(3)	N3-N2-C6	116.4(3)	Ni1-N3-N2	116.8(2)
Ni1-N3-C7	119.7(3)	N2-N3-C7	123.5(3)	Ni1-N4-C9	117.2(3)
Ni1-N4-C13	120.3(3)	C9-N4-C13	122.4(3)	Ni1-N5-N9	128.2(3)
Ni1-N5-C14	115.7(3)	N9-N5-C14	115.6(3)	Ni1-N6-C23	178.1(3)
Ni1-N7-C4	130.9(3)	Ni1-N7-C6	112.9(2)	C4-N7-C6	116.1(3)
Ni1-N8-C22	161.9(4)	N5-N9-C16	121.8(3)	C16-N10-C17	115.8(4)
C16-N11-C20	116.5(3)	N1-C2-C1	117.5(3)	N1-C2-C3	120.7(4)
C1-C2-C3	121.8(4)	N3-N2-H2	122.00	C6-N2-H2	122.00
C2-C3-C4	118.4(4)	N7-C4-C5	116.2(4)	N7-C4-C3	121.2(4)
C3-C4-C5	122.6(4)	N2-C6-N7	117.4(3)	N1-C6-N2	115.3(3)
N1-C6-N7	127.3(3)	N3-C7-C9	111.8(3)	N3-C7-C8	125.1(4)
C8-C7-C9	123.0(4)	N4-C9-C10	119.7(3)	N4-C9-C7	114.4(3)
N5-N9-H9	119.00	C16-N9-H9	119.00	C7-C9-C10	125.9(3)
C9-C10-C11	118.2(4)	C10-C11-C12	121.1(5)	C11-C12-C13	118.2(4)
N4-C13-C14	113.7(4)	C12-C13-C14	125.9(4)	N4-C13-C12	120.4(4)
C13-C14-C15	120.1(4)	N5-C14-C13	114.7(4)	N5-C14-C15	125.2(4)
N9-C16-N11	114.4(3)	N10-C16-N11	126.7(4)	N9-C16-N10	118.9(3)
N10-C17-C18	117.2(4)	N10-C17-C19	121.8(4)	C18-C17-C19	121.1(5)
C17-C19-C20	118.1(4)	N11-C20-C19	121.1(4)	C19-C20-C21	121.3(4)
N11-C20-C21	117.7(4)	S1-C22-N8	178.7(5)	S2-C23-N6	177.5(4)
Torsion angles, deg					
N4-Ni1-N3-N2	177.4(3)	N4-Ni1-N3-C7	-0.1(4)	N5-Ni1-N3-N2	173.9(3)
N5-Ni1-N3-C7	-3.6(5)	N6-Ni1-N3-N2	-89.9(3)	N6-Ni1-N3-C7	92.7(4)
N7-Ni1-N3-N2	-0.9(3)	N7-Ni1-N3-C7	-178.4(4)	N8-Ni1-N3-N2	82.4(3)
N8-Ni1-N3-C7	-95.1(4)	N3-Ni1-N4-C9	2.4(3)	N3-Ni1-N4-C13	178.9(3)
N5-Ni1-N4-C9	-179.3(3)	N5-Ni1-N4-C13	-2.8(3)	N6-Ni1-N4-C9	-90.8(3)
N6-Ni1-N4-C13	85.8(3)	N7-Ni1-N4-C9	6.0(5)	N7-Ni1-N4-C13	-177.5(3)
N8-Ni1-N4-C9	95.2(3)	N8-Ni1-N4-C13	-88.3(3)	N3-Ni1-N5-N9	-168.0(3)
N3-Ni1-N5-C14	3.6(5)	N4-Ni1-N5-N9	-171.5(4)	N4-Ni1-N5-C14	0.1(3)

N6-Ni1-N5-N9	94.7(3)	N6-Ni1-N5-C14	-93.7(3)	N7-Ni1-N5-N9	5.4(4)
N7-Ni1-N5-C14	177.0(3)	N8-Ni1-N5-N9	-74.7(3)	N8-Ni1-N5-C14	96.9(3)
N3-Ni1-N7-C4	176.0(4)	N3-Ni1-N7-C6	0.9(3)	N4-Ni1-N7-C4	172.3(3)
N4-Ni1-N7-C6	-2.8(5)	N5-Ni1-N7-C4	-0.9(4)	N5-Ni1-N7-C6	-175.9(2)
N6-Ni1-N7-C4	-90.0(4)	N6-Ni1-N7-C6	94.9(3)	N8-Ni1-N7-C4	80.5(4)
N8-Ni1-N7-C6	-94.6(3)	C6-N1-C2-C1	-177.9(4)	C6-N1-C2-C3	0.6(7)
C2-N1-C6-N2	177.0(4)	C2-N1-C6-N7	-2.0(6)	C6-N2-N3-Ni1	0.9(4)
C6-N2-N3-C7	178.2(4)	N3-N2-C6-N1	-179.1(3)	N3-N2-C6-N7	0.0(5)
Ni1-N3-C7-C8	175.8(4)	Ni1-N3-C7-C9	-1.9(5)	N2-N3-C7-C8	-1.5(8)
N2-N3-C7-C9	-179.2(4)	Ni1-N4-C9-C7	-4.1(5)	Ni1-N4-C9-C10	177.1(3)
C13-N4-C9-C7	179.5(4)	C13-N4-C9-C10	0.7(6)	Ni1-N4-C13-C12	-176.4(3)
Ni1-N4-C13-C14	4.7(5)	C9-N4-C13-C12	-0.1(6)	C9-N4-C13-C14	-179.0(3)
Ni1-N5-N9-C16	97.3(4)	C14-N5-N9-C16	-74.3(5)	Ni1-N5-C14-C13	2.2(4)
Ni1-N5-C14-C15	-177.9(3)	N9-N5-C14-C13	174.8(3)	N9-N5-C14-C15	-5.3(6)
Ni1-N7-C4-C3	-176.3(3)	Ni1-N7-C4-C5	4.2(5)	C6-N7-C4-C3	-1.3(6)
C6-N7-C4-C5	179.1(4)	Ni1-N7-C6-N1	178.2(3)	Ni1-N7-C6-N2	-0.8(4)
C4-N7-C6-N1	2.4(6)	C4-N7-C6-N2	-176.6(3)	N5-N9-C16-N10	8.3(6)
N5-N9-C16-N11	-172.8(3)	C17-N10-C16-N9	-177.8(4)	C17-N10-C16-N11	3.4(6)
C16-N10-C17-C18	175.1(4)	C16-N10-C17-C19	-4.0(6)	C20-N11-C16-N9	-179.2(3)
C20-N11-C16-N10	-0.3(6)	C16-N11-C20-C19	-2.1(6)	C16-N11-C20-C21	178.8(4)
N1-C2-C3-C4	0.2(7)	C1-C2-C3-C4	178.6(4)	C2-C3-C4-N7	0.2(7)
C2-C3-C4-C5	179.7(4)	N3-C7-C9-N4	3.8(6)	N3-C7-C9-C10	-177.5(4)
C8-C7-C9-N4	-173.9(4)	C8-C7-C9-C10	4.8(7)	N4-C9-C10-C11	-1.9(7)
C7-C9-C10-C11	179.4(5)	C9-C10-C11-C12	2.6(8)	C10-C11-C12-C13	-2.0(8)
C11-C12-C13-N4	0.7(7)	C11-C12-C13-C14	179.5(4)	N4-C13-C14-N5	-4.4(5)
N4-C13-C14-C15	175.7(4)	C12-C13-C14-N5	176.8(4)	C12-C13-C14-C15	-3.1(6)
N10-C17-C19-C20	1.9(6)	C18-C17-C19-C20	-177.2(4)	C17-C19-C20-N11	1.4(6)
C17-C19-C20-C21	-179.5(4)				

Table S3. Crystallographic data for **1-4**

Parameters	**1**	**2**	**2a**	**3**	**4**
Chemical formula	$C_{29}H_{43}CoN_{11}O_3S_5$	$C_{21}H_{29}Cl_2CoN_9O_{10.75}$	C23 H33 Co N9 O2, Cl4 Co, 2(H2 O)	$C_{25}H_{30}FeN_{11}OS_3$	$C_{25}H_{28}N_{12}NiS_2$
Molecular weight, g/mole	812.97	709.36	763.28	652.63	619.42
Temperature, K	100.0(1)	100.0(1)	100.0(1)	101(2)	100(2)
CCDC	2043149	2141475	2194696	2141312	2141313
Crystal symmetry	Triclinic	Monoclinic	Monoclinic	Hexagonal	Orthorhombic
Space group	P -1	C 1 2/c 1	P21/n	P 31 2 1	P 21 21 21
Unit cell dimensions					
a , Å	9.4207(4)	20.827(4)	10.6168(3)	14.9564(5)	8.4760(17)
b , Å	12.6341(5)	17.085(3)	18.3834(6)	14.9564(5)	18.025(4)
c , Å	17.0803(7)	19.299(4)	16.3496(5)	11.5048(4)	18.913(4)
α , °	109.380(4)	90	90	90	90
β , °	93.196(4)	122.33(3)	91.253(3)	90	90
γ , °	99.822(3)	90	90	120.0	90.0
Volume (*V*), Å^3	1875.79(13)	5803(2)	3190.24(17)	2228.76(13)	2889.5(1)
Z	2	8	4	3	4

Density calc.(ρ), g/cm^3	1.439	1.624	1.589	1.445	1.424
μ(MoKα) , mm^{-1}	0.783	0.848	1.420	0.759	1.151
Crystal size, mm	0.40×0.38×0.36	0.35×0.34×0.32	0.15 x 0.25 x 0.40	0.38x0.35x0.30	0.50 x 0.10 x 0.01
Theta range for data collection	≤ 30.08	≤ 26.0	2.9, 29.6	≤ 29.07	≤ 30.971
Measured reflections	21524	11999	16820	7535	16786
Independent reflections >2Θ(I)	12033/9861	5670/4521	8859/6879	3833/3331	6476/5851
Index ranges	-13<h<11 -18<k<18 -24<l<22	-24<h<25 -21<k<13 -22<l<23	-14<h<13 -22<k<25 -20<l<22	-5<h<20 -17<k<17 -15<l<5	-10<=h<=10, -23<=k<=14, -24<=l<=24
Number of parameters refined	452	407	413	192	368
Goodness-of-fit	1.133	1.072	0.988	1.049	1.060
Final R indices	R_1 = 0.0694	R_1 = 0.0648	0.0394	0.0409	R1 = 0.0425

Table S4. Optimized nuclei coordinates for **1**-**4** used for molecular modelling of the magnetic properties. Non-hydrogen atoms are fixed from the X-ray diffraction experiment, position of hydrogen atoms are optimized at BP86/def2-TZVP level of theory

Compound (1)			
27	0.000000000	0.000000000	0.000000000
16	0.901795000	-0.786350000	4.730219000
16	-1.338036000	1.045799000	-4.567067000
7	1.861004000	1.105226000	-0.246025000
7	-1.603483000	2.637918000	0.716531000
1	-1.851884000	3.624880000	0.787029000
7	-0.362168000	2.202595000	0.415089000
7	-0.861123000	-2.053807000	-0.702337000
7	1.342324000	-2.734111000	-0.429801000
1	2.028501000	-3.475892000	-0.296890000
7	-2.130317000	0.425473000	1.226189000
7	1.645580000	-1.415097000	-0.445996000
6	0.657869000	-0.642262000	3.114785000
6	-0.857881000	0.765258000	-3.033540000
7	0.502500000	-0.502758000	1.971783000
7	-0.238192000	-4.374676000	-0.542509000
7	-3.643424000	2.253819000	1.632467000
7	-0.530517000	0.585051000	-1.931382000
6	2.862805000	-1.018705000	-0.568013000
6	3.003620000	0.446013000	-0.485950000
6	1.875832000	2.449370000	-0.158275000
6	4.220713000	1.104974000	-0.625295000
1	5.144369000	0.556587000	-0.797970000
6	-2.502517000	1.718605000	1.213105000
6	0.013732000	-3.069250000	-0.551641000
6	0.572823000	3.057203000	0.148632000
6	0.399221000	4.545775000	0.153221000
1	0.261963000	4.938505000	1.175083000
1	1.257470000	5.057975000	-0.288528000
1	-0.484870000	4.841445000	-0.436371000
6	3.056295000	3.180756000	-0.301170000
1	3.068079000	4.265007000	-0.211397000
6	-1.505854000	-4.723035000	-0.776257000

6	4.044093000	-1.902441000	-0.788251000
1	3.775063000	-2.780623000	-1.395566000
1	4.842799000	-1.376329000	-1.321462000
1	4.467943000	-2.270255000	0.161552000
6	4.228987000	2.487378000	-0.537903000
1	5.169194000	3.031602000	-0.644738000
6	-4.497325000	1.411899000	2.226096000
6	-4.175753000	0.071459000	2.404139000
1	-4.845213000	-0.601253000	2.939728000
6	-2.986557000	-0.393022000	1.884273000
6	-3.101042000	-1.370281000	-1.406675000
1	-2.888872000	-0.437346000	-0.878528000
1	-3.022368000	-1.146344000	-2.483215000
1	-4.130643000	-1.695750000	-1.207135000
6	-2.115044000	-2.439413000	-1.050744000
6	-2.462606000	-3.771649000	-1.107742000
1	-3.477603000	-4.066593000	-1.372964000
6	-2.587253000	-1.826538000	2.063749000
1	-2.837627000	-2.155140000	3.082762000
1	-3.139045000	-2.480278000	1.371176000
1	-1.514908000	-1.958635000	1.900511000
6	-1.839321000	-6.179889000	-0.670953000
1	-1.170750000	-6.776371000	-1.308719000
1	-1.682647000	-6.526732000	0.362496000
1	-2.879536000	-6.382284000	-0.954956000
6	-5.789270000	1.986881000	2.712570000
1	-6.297686000	2.524392000	1.898938000
1	-6.459224000	1.212007000	3.103874000
1	-5.601660000	2.723658000	3.508243000
Compound (2)			
27	-8.293963000	4.886328000	-10.612583000
8	-8.156455000	4.624618000	-12.816167000
1	-7.391054000	5.016950000	-13.273342000
1	-8.326350000	3.771022000	-13.254054000
7	-6.213180000	4.475774000	-10.317308000
7	-11.285415000	4.826082000	-10.954537000
1	-12.246187000	4.502574000	-11.084998000
7	-12.196266000	6.788023000	-10.178161000
7	-5.415317000	5.575962000	-10.208514000
1	-4.421792000	5.527392000	-9.975705000
7	-7.164782000	6.695950000	-11.235669000
7	-5.064626000	7.764496000	-10.791132000
7	-9.846172000	6.347574000	-9.926306000
7	-8.016987000	2.764313000	-10.610717000
7	-10.222356000	3.968628000	-10.902263000
6	-9.732205000	7.489468000	-9.190277000
6	-6.810783000	2.251238000	-10.348602000
6	-11.097098000	6.057968000	-10.309470000
6	-5.908263000	6.739395000	-10.769532000
6	-6.754441000	8.905743000	-12.004359000
1	-7.084775000	9.789328000	-12.550068000
6	-5.765127000	3.279916000	-10.114335000

6	-5.506422000	8.870461000	-11.413117000
6	-8.937445000	7.798212000	-12.526237000
1	-9.341164000	6.787125000	-12.631987000
1	-9.637713000	8.404016000	-11.930486000
1	-8.897616000	8.268351000	-13.519169000
6	-9.063753000	1.969813000	-10.929108000
6	-8.909330000	0.593278000	-11.004208000
1	-9.741484000	-0.058704000	-11.265002000
6	-11.582547000	1.994455000	-11.531680000
1	-12.171457000	2.579079000	-12.255327000
1	-11.360252000	1.031807000	-12.002542000
1	-12.233388000	1.791770000	-10.663495000
6	-6.598921000	0.872860000	-10.363630000
1	-5.622906000	0.447538000	-10.136830000
6	-7.659366000	0.046066000	-10.710014000
1	-7.517938000	-1.034213000	-10.748971000
6	-10.828061000	8.286831000	-8.936871000
1	-10.726091000	9.186628000	-8.331442000
6	-12.053601000	7.927517000	-9.478947000
6	-10.340687000	2.708505000	-11.128827000
6	-4.547035000	10.021217000	-11.481070000
1	-4.118028000	10.218364000	-10.489052000
1	-3.705404000	9.755496000	-12.139627000
1	-5.020232000	10.930663000	-11.867660000
6	-7.581856000	7.802530000	-11.906652000
6	-13.264806000	8.776223000	-9.283006000
1	-13.817545000	8.881169000	-10.226923000
1	-13.952775000	8.285702000	-8.574539000
1	-13.013233000	9.767299000	-8.888872000
6	-4.373022000	2.953773000	-9.714475000
1	-4.100609000	3.458284000	-8.772317000
1	-4.226621000	1.880788000	-9.559589000
1	-3.647383000	3.276306000	-10.480037000
6	-8.388233000	7.867026000	-8.628435000
1	-7.749966000	6.992392000	-8.471155000
1	-7.867993000	8.566432000	-9.300100000
1	-8.517944000	8.389683000	-7.671909000
8	-8.253216000	4.649405000	-8.411711000
1	-7.845069000	3.859472000	-8.012602000
1	-9.092666000	4.785064000	-7.935854000
Compound (**3**)			
26	0.000000000	0.000000000	0.000000000
16	4.836228000	-0.397656000	0.021791000
7	-0.001403000	0.005854000	2.239862000
7	0.556115000	-2.084919000	0.847921000
7	0.937927000	-3.051016000	-0.036832000
1	1.474862000	-3.876627000	0.224300000
7	-0.138247000	-1.806899000	-1.694192000
7	0.792545000	-3.988124000	-2.090686000
7	2.089813000	0.086307000	-0.114680000
6	0.444897000	-1.065572000	2.921217000
6	0.459536000	-1.087469000	4.314477000

1	0.801586000	-1.966026000	4.857962000
6	-0.003132000	0.013070000	5.000804000
1	-0.004274000	0.015700000	6.091873000
6	0.869952000	-2.201533000	2.096613000
6	1.666381000	-3.325301000	2.694568000
1	1.161267000	-4.297911000	2.570983000
1	1.862483000	-3.172824000	3.757343000
1	2.647520000	-3.397722000	2.194343000
6	0.502337000	-2.931891000	-1.337879000
6	0.352652000	-3.932790000	-3.360535000
6	0.735106000	-5.068758000	-4.257706000
1	0.470246000	-6.029357000	-3.793733000
1	1.825686000	-5.076942000	-4.403468000
1	0.250044000	-4.994760000	-5.238571000
6	-0.411105000	-2.873330000	-3.804250000
1	-0.814231000	-2.855856000	-4.816652000
6	-0.640897000	-1.819881000	-2.947151000
6	-1.490448000	-0.667399000	-3.394154000
1	-2.534368000	-1.007028000	-3.484055000
1	-1.182199000	-0.306111000	-4.384517000
1	-1.476510000	0.145096000	-2.665297000
6	3.231663000	-0.124869000	-0.066300000
7	-0.557855000	2.088975000	0.836315000
7	-0.938555000	3.050432000	-0.053953000
1	-1.475891000	3.877285000	0.202227000
7	0.139691000	1.797673000	-1.703440000
7	-0.790597000	3.976794000	-2.112494000
6	-0.449236000	1.080479000	2.915048000
6	-0.465620000	1.109659000	4.308156000
1	-0.810946000	1.988720000	4.848321000
6	-0.873254000	2.212113000	2.083987000
6	-1.670428000	3.338988000	2.675060000
1	-1.188736000	4.316981000	2.505489000
1	-1.827131000	3.218237000	3.748133000
1	-2.668188000	3.378894000	2.205153000
6	-0.501335000	2.924510000	-1.353814000
6	-0.349116000	3.914824000	-3.381485000
6	-0.730440000	5.046085000	-4.285059000
1	-0.500304000	6.010379000	-3.810802000
1	-1.816379000	5.030451000	-4.463761000
1	-0.217570000	4.987122000	-5.252893000
6	0.415194000	2.853062000	-3.818699000
1	0.820208000	2.831655000	-4.830298000
6	0.643910000	1.804106000	-2.955818000
6	1.494015000	0.649307000	-3.395727000
1	2.537072000	0.990750000	-3.488345000
1	1.186075000	0.278222000	-4.381795000
1	1.486571000	-0.157306000	-2.659891000
16	-4.836936000	0.397402000	0.013656000
7	-2.090353000	-0.087259000	-0.116843000
6	-3.232261000	0.124164000	-0.070998000

Compound (**4**)

28	0.000000000	0.000000000	0.000000000
16	-4.481714000	-1.374860000	0.676537000
7	-0.629535000	0.973095000	1.816530000
7	-0.234019000	0.574693000	-2.088495000
7	-2.816790000	2.692731000	-3.421524000
7	0.555057000	-1.319879000	1.464928000
7	0.787751000	-1.530792000	-1.039804000
7	0.261145000	-0.974130000	2.741370000
1	0.454486000	-1.559443000	3.553359000
7	-0.662239000	0.554264000	4.177277000
7	-2.737472000	0.297119000	-3.217126000
7	1.754063000	1.022861000	0.065935000
7	-1.916107000	-0.667092000	-0.073729000
7	-0.944629000	1.662075000	-2.613033000
16	4.177033000	2.398922000	0.153274000
1	-0.774546000	2.525758000	-2.102497000
6	0.211556000	-0.271321000	-2.954839000
6	-2.218352000	1.527226000	-3.094409000
6	1.467656000	-2.499201000	-3.085630000
1	1.530933000	-2.468173000	-4.172000000
6	1.296582000	-2.555925000	-0.332946000
6	1.109914000	-2.438722000	1.139365000
6	-0.367134000	0.244450000	2.918931000
6	2.009313000	-3.555931000	-2.377917000
1	2.501842000	-4.366920000	-2.916864000
6	0.121630000	-0.113598000	-4.433370000
1	0.025509000	0.947350000	-4.694390000
1	1.010305000	-0.526828000	-4.927883000
1	-0.768586000	-0.634694000	-4.818716000
6	-1.671061000	2.520527000	3.282936000
1	-2.218908000	3.450477000	3.429375000
6	0.856595000	-1.476620000	-2.371292000
6	-1.330866000	1.708229000	4.366450000
6	-4.060086000	2.607593000	-3.914013000
6	-4.004609000	0.240335000	-3.651429000
6	-1.300457000	2.113953000	2.011749000
6	-1.613561000	2.920014000	0.777536000
1	-2.237358000	2.318866000	0.100548000
1	-2.141853000	3.848204000	1.024714000
1	-0.673867000	3.168395000	0.261970000
6	1.478731000	-3.520674000	2.091848000
1	0.592697000	-3.867912000	2.648150000
1	1.906451000	-4.389436000	1.582374000
1	2.221325000	-3.171241000	2.828514000
6	2.768379000	1.583592000	0.076041000
6	-1.717941000	2.057543000	5.761669000
1	-0.844510000	2.004854000	6.427642000
1	-2.157776000	3.060106000	5.823350000
1	-2.450646000	1.328299000	6.140446000
6	1.910662000	-3.618284000	-0.999117000
1	2.326891000	-4.463711000	-0.453932000
6	-4.657429000	-1.117377000	-3.692534000

1	-4.823984000	-1.465349000	-2.660088000
1	-5.619819000	-1.086183000	-4.217006000
1	-3.996076000	-1.849275000	-4.176779000
6	-4.700612000	1.383908000	-4.031694000
1	-5.722472000	1.316089000	-4.403163000
6	-4.740578000	3.884736000	-4.313619000
1	-4.108800000	4.451702000	-5.012952000
1	-5.712834000	3.690471000	-4.781351000
1	-4.894882000	4.525207000	-3.432183000
6	-2.971377000	-0.943236000	0.227660000

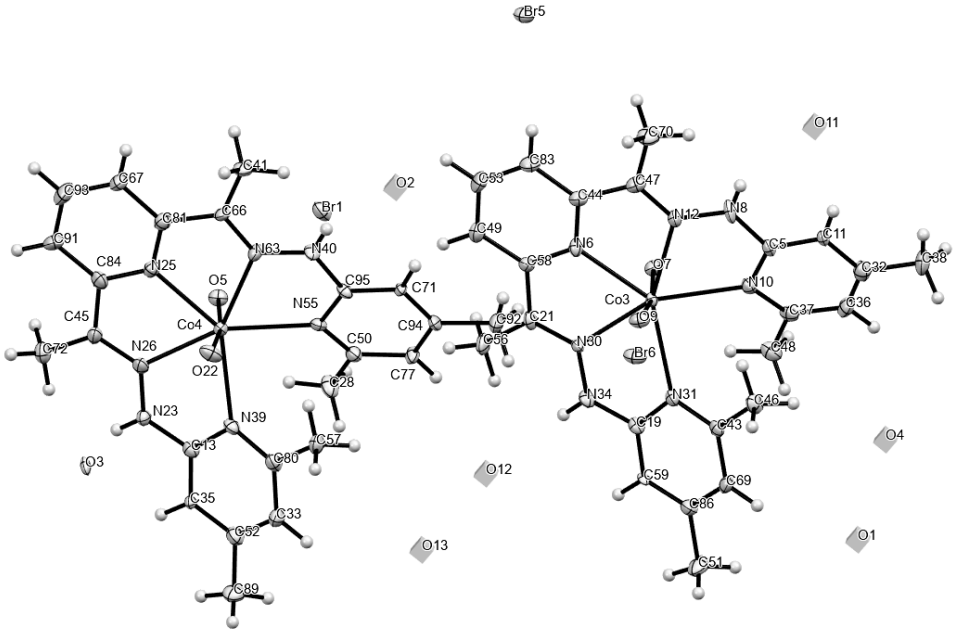


Figure S1. Molecular structure of the reaction product of **L** with Co(II) bromide in methanol. Composition of the coordinated unit is $[CoL(H_2O)_2]^{2+}$, bromide anions are out-of-coordination sphere. The structure was not solved completely and is not published.

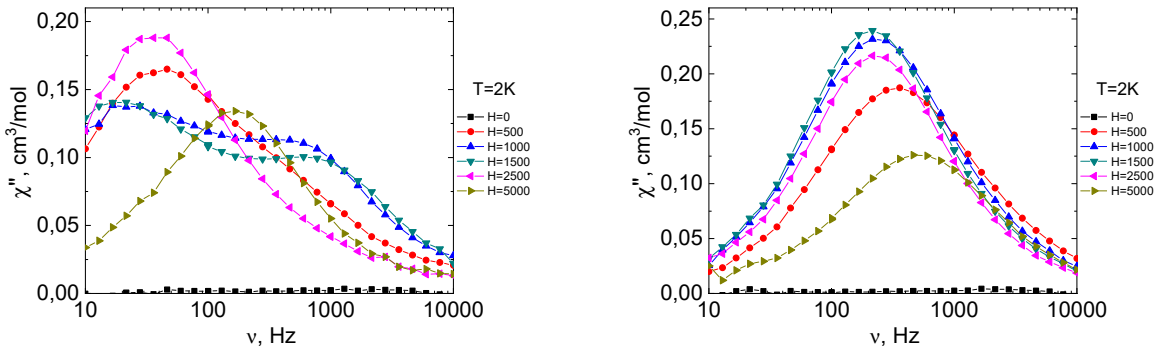


Figure S2. Frequency dependences of the out-of-phase χ'' AC susceptibility χ_M for **1**(left) and **2**(right) at different applied magnetic fields H_{DC} and T = 2 K.

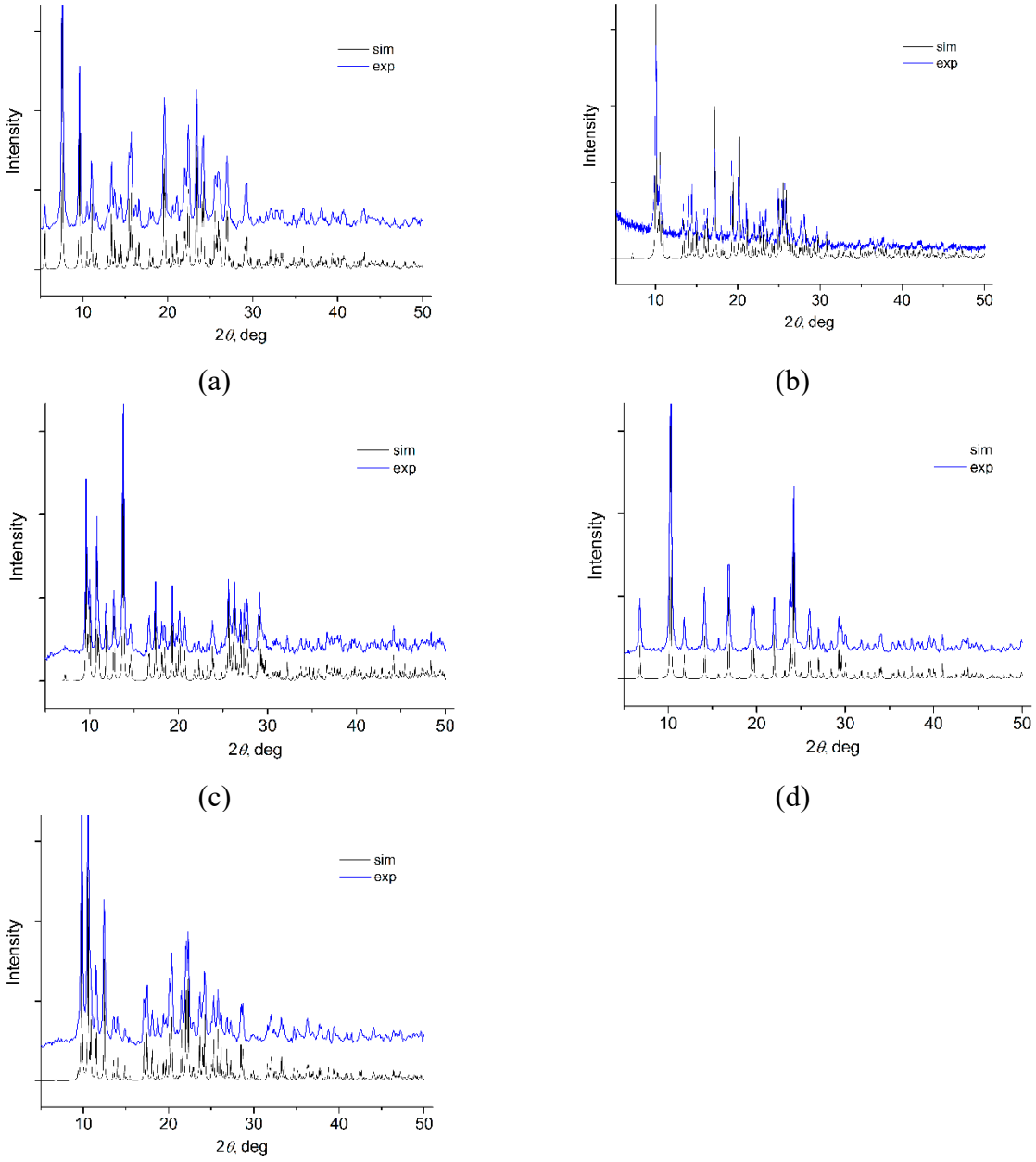


Figure S3. Powder X-ray diffraction pattern of polycrystalline samples of **1** (a), **2** (b) **2a** (c), **3** (d) and **4** (e): experimental (blue), and calculated from single crystal data (black).