Supporting Information

Probing the influence of molecular symmetry on magnetic anisotropy of octahedral cobalt(II) complexes

Zhong-Yu Ding,^{‡a} Yin-Shan Meng,^{‡c,d} Yi Xiao,^a Yi-Quan Zhang, *^b Yuan-Yuan Zhu, *^{a,d} and Song

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^aSchool of Chemistry and Chemical Engineering, Hefei University of Technology and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei 230009, China.

^bJiangsu Key Laboratory for NSLSCS, School of Physical Science and Technology, Nanjing Normal University, Nanjing 210023, China.

^cBeijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

^dState Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China. yyzhu@hfut.edu.cn, zhangyiquan@njnu.edu.cn

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SI1 Synthesis details of the pybox ligands and cobalt(II) complexes

SI1.1 Materials

All solvents were purchased from Sinopharm and used without further purification unless otherwise denoted. Tetrahydrofuran (THF) was further dried over sodium and benzophenone ketyl, distilled onto LiAlH₄ under nitrogen, and distilled under high vacuum just before use. All chemicals were purchased from Aladdin, Aldrich, Alfa Aesar and Sinopharm, and were used as received.

Caution! Although not encountered in our experiments, perchlorate salts in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

SI1.2 Synthesis of ligand L¹⁻⁵

The ligands L^{1-2} were synthesized according to the procedure established by our group^{1,2}



Compound 1.³ In ice bath, to a vigorously stirred solution of bromine (73.8 mmol, 3.83 mL) in petroleum ether (25 ml) was added PBr₃ (89.4 mmol, 8.5 mL) dropwise. After stirring the mixture at room temperature for 2 h, PBr₅ was obtained in pure form by removing excess petroleum ether under reduced pressure. Then chelidamic acid (20 mmol, 3.66 g) was added and the resulting solid mixture is heated to 100 °C for 4 h. The solid mixture melted when temperature is above 85 °C. After cooling down to room temperature, chloroform (50 mL) was added. The mixture was stirred for further 30 minutes and then filtered. The dark solution was cooled to 0 °C and MeOH (90 mL) was added dropwise. The precipitated solid was filtered off and recrystallized from MeOH to afford **10** as a white solid (4.56 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 2 H), 4.03 (s, 6 H).

Compound 2.⁴ Under a N₂ atmosphere, a solution of **10** (4 mmol, 1.10 g), *p*-tolylboronic acid (4.4 mmol, 0.60 g), Pd(dppf)Cl₂ (0.2 mmol, 146 mg), K₃PO₄·3H₂O (8 mmol, 1.70 g) in new distilled DMF (40 mL) was stirred at 90 °C over 2 days. After the solution was concentrated under reduced pressure and the residue was subjected to column chromatography (SiO₂, CH₂Cl₂/AcOEt 20:1) to give **11** as a white solid (0.98 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.04 (s, 6 H), 2.43 (s, 3 H).

Compound 3. A mixture of **2** (1.43 g, 5 mmol) and 2-aminoethanol (0.67 g, 11 mmol) was stirred in methanol (10 mL) at 115 °C in sealed tube for 12 h. The solution was added to stirred water (100 mL) and white precipitation was generated immediately. After filtration and dried in vacuo, **3** was obtained as white solid product (1.63 g, 95%). ¹H NMR (600 MHz, DMSO-*d*₆): δ 9.42 (t, *J* = 6.0 Hz, 2 H), 8.40 (s, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 4.86 (t, *J* = 5.4 Hz, 2 H), 3.58 (q, *J* = 6.0 Hz, 4 H), 3.46 (q, *J* = 6.0 Hz, 4 H), 2.38 (s, 3 H). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 163.3, 150.0, 149.7, 139.8, 133.3, 130.1, 126.9, 120.7, 59.8, 41.9, 20.8.

Compound 4. A solution of **3** (3.43 g, 10 mmol) in dichloromethane (10 mL) was cooled in an ice bath, then SOCl₂ (10 mL) was added dropwise, and then the solution was stirred at reflux for 2 h. The solution was concentrated under reduced pressure and the resulting residue was triturated with dichloromethane (20 mL). The solution was washed with deionized H₂O (10 mL × 2), saturated aqueous NaHCO₃ (10 mL), and brine (10 mL) and dried over sodium sulfate. After the solvent was removed, the crude product was subjected to column chromatography (SiO₂, petroleum ether (PE)/AcOEt 2:1 to 1:1) to give **4** as a white solid (3.31 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ 8.59 (s, 2 H), 8.26 (t, *J* = 6.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 3.89 (q, *J* = 5.6 Hz, 4 H), 2.41 (s, 3 H). ¹³C NMR (400 MHz, CDCl₃): δ 164.0, 151.8, 149.2, 140.6, 133.5, 130.2, 127.1, 122.6, 44.0, 41.4, 21.4. MS (MALDI-TOF): *m/z* 378.1180 [M – 1]⁻.

Compound L³. To a solution of **3** (1.90 g, 5 mmol) in methanol (25 mL) was added KOH (0.7 g, 12.5 mmol), the solution was stirred under reflux for 4 hours and white precipitation was generated during the reaction. The solution was concentrated under reduced pressure. The resulting residue was triturated with dichloromethane (30 mL) and the solution washed with water (15 mL) and brine (15 mL) and dried over sodium sulfate. Compound L³ was obtained as white solid under vacuum drying (1.46 g, 95%). ¹H NMR (600 MHz, CDCl₃): δ 8.38 (s, 2 H), 7.64 (d, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 4.54 (t, *J* = 9.6 Hz, 4 H), 4.12 (t, *J* = 9.6 Hz, 4 H), 2.39 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7, 149.8, 147.2, 140.0, 133.5, 129.9, 126.9, 122.9, 68.3, 55.0, 21.2. MS (MALDI-TOF): *m/z* 308.1240 [M + 1]⁺.



Scheme S2

Compound 5 was prepared from **2** and 2-amino-2-methylpropan-1-ol as white solid in 92% yield according to the procedure similar to that for **3**. ¹H NMR (600 MHz, CDCl₃): δ 8.40 (s, 2 H), 8.32 (s, 2 H), 7.81 (d, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 7.8 Hz, 2 H), 5.07 (t, *J* = 5.4 Hz, 2 H), 3.56 (d, *J* = 5.4 Hz, 2 H), 2.38 (s, 3 H), 1.38 (s, 12 H). ¹³C NMR (600 MHz, DMSO-*d*₆): δ 162.2, 150.3, 150.1, 140.0, 130.1, 126.9, 120.4, 67.4, 54.4, 23.4, 20.9. MS (MALDI-TOF): *m/z* 400.2290 [M + 1]⁺.

Compound 6 was prepared from **5** as white solid in 95% yield according to the procedure similar to that for **4**. ¹H NMR (600 MHz, CDCl₃): δ 8.55 (s, 2 H), 7.99 (s, 2 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 7.8 Hz, 2 H), 3.91 (s, 4 H), 2.42 (s, 3 H), 1.61 (s, 12 H). ¹³C NMR (600 MHz, CDCl₃): δ 162.9, 151.7, 149.4, 140.4, 130.1, 127.0, 121.7, 54.0, 52.4, 24.8, 21.3. MS (MALDI-TOF): *m*/*z* 436.1586 [M + 1]⁺.

Compound L⁴ was prepared from **6** according to the procedure similar to that for L³. The crude product was subjected to column chromatography (SiO₂, AcOEt) to give L⁴ as white solid in 91% yield. ¹H NMR (600 MHz, CDCl₃): δ 8.41 (s, 2 H), 7.68 (d, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 4.23 (s, 4 H), 2.41 (s, 3 H), 1.42 (s, 12 H). ¹³C NMR (600 MHz, CDCl₃): δ 161.0, 149.7, 147.4, 139.9, 133.4, 129.7, 127.0, 123.0, 79.7, 68.0, 28.4, 21.2. MS (MALDI-TOF): *m/z* 364.2103 [M + 1]⁺.



Scheme S2

Compound 7. A mixture of **1** (2.74 g, 10 mmol) and 2-amino-2-methylpropan-1-ol (1.87 g, 21 mmol) was stirred in methanol (10 mL) at 115 °C in sealed tube for 12 h. After cooled to room temperature, the solution was poured into cold water (100 mL). The white precipitate was filtered and washed with a small amount of water and then dried under vacuum. The white crystalline product was subjected to next step without further purification (3.69 g, 95%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.29 (s, 2 H), 8.27 (br, 2 H), 5.01 (t, *J* = 5.6 Hz, 2 H), 3.54 (d, *J* = 5.6 Hz, 4 H), 1.35 (s, 12 H). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 161.1, 150.6, 135.3, 126.7, 67.1, 54.6, 23.3. MS (MALDI-TOF): *m/z* 386.0676 [M – 1]⁻. Anal. Calcd for C₁₅H₂₂BrN₃O₄: C, 46.40; H, 5.71; N, 10.82. Found: C, 46.45; H, 5.74; N, 10.99.

Compound 8. Under a N₂ atmosphere, a solution of 7 (4 mmol, 1.55 g), 4-pyridineboronic acid (4.4 mmol, 0.54 g), Pd(dppf)Cl₂ (0.2 mmol, 146 mg), K₃PO₄·3H₂O (8 mmol, 1.70 g) in new distilled DMF (40 mL) was stirred at 90 °C over 2 days. After cooled to room temperature, the solution was poured into water and the precipitate was collected by filtration under reduce pressure. The crude product was subjected to column chromatography (SiO₂, AcOEt) to give 7 as a white solid (1.30 g, 84%). ¹H NMR (600 MHz, CDCl₃): δ 8.78 (d, *J* = 4.8 Hz, 2 H), 8.58 (s, 2 H), 8.10 (s, 2 H), 7.65 (d, *J* = 4.8 Hz, 2 H), 3.74 (s, 4 H), 1.50 (s, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 162.8, 151.0, 149.2, 144.1, 122.2, 121.4, 70.5, 55.6, 24.1. MS (MALDI-TOF): *m/z* 385.1939 [M – 1]⁻.

Compound 9 was prepared from **8** as white solid in 88% yield according to the procedure similar to that for 4.¹H NMR (600 MHz, CDCl₃): δ 8.80 (d, J = 4.8 Hz, 2 H), 8.59 (s, 2 H), 7.96 (s, 2 H), 7.70 (d, J = 4.8 Hz, 2 H), 3.91 (s, 4 H), 1.62 (s, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 162.2, 150.2, 150.2, 148.8, 145.0, 122.1, 121.7, 54.2, 52.4, 24.8. MS (MALDI-TOF): m/z 423.1334 [M + 1].

Synthesis of L⁵ was prepared from **9** as white solid in 87% yield according to the procedure similar to that for L³. ¹H NMR (600 MHz, CDCl₃): δ 8.74 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 2 H), 8.44 (s, 2 H), 7.66 (dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz, 2 H), 4.24 (s, 4 H), 1.42 (s, 12 H). ¹³C NMR (125 MHz, CDCl₃): δ

160.8, 150.8, 148.1, 147.2, 144.1, 123.4, 121.6, 80.0, 68.2, 28.5. MS (MALDI-TOF): *m/z* 351.1825 [M + 1].

SI1.3 Synthesis of cobalt(II) complexes

Preparation of[Co(L¹) ₂](ClO₄)₂ (1). The single crystals were obtained by evaporation at room temperature. To a solution of L¹ (43 mg, 0.2 mmol) in methanol (5 mL) was added a solution of Co(ClO₄)₂·6H₂O (36 mg, 0.1 mmol) in methanol (5 mL) under stirring. The color of solution turned to orange immediately and no precipitate formed. The solution was filtrated and left to stand at roomtemperature with slow evaporation. Orange lump like single crystals suitable for X-ray crystallographic analysis were obtained after several days. Yield: 85%. Anal. Calcd for. Anal. Calcd for C₂₂H₂₂Cl₂CoN₆O₁₂: C, 38.17; H, 3.20; N, 12.14. Found: C, 38.28, H, 3.25, N, 12.03. IR (single crystal) v= 3090 (w), 2999 (w), 2017 (w), 1649 (m), 1633 (w), 1581 (m), 1489 (w), 1396 (m), 1288 (m), 1269 (m), 1201 (m), 1159 (w), 1093 (s), 1072 (m), 1018 (w), 984 (w), 958 (w), 918 (m), 837 (w), 827 (w), 754 (w), 748 (w), 669 (w), 660 (m), 625 (m).

Preparation of[Co(L²)₂](ClO₄)₂ (2). The single crystals were obtained from L² and Co(ClO₄)₂·6H₂O according to the procedure identical to that for 1. Yield: 75%. Anal. Calcd forC₃₀H₃₈Cl₂CoN₆O₁₂: C, 44.79; H, 4.76; N, 10.45. Found: C, 44.77; H, 4.74; N, 10.45. IR (single crystal):v = 3601 (br), 3064 (w), 2976 (w), 2935 (w), 2908 (w), 2874 (w), 1645 (w), 1620 (w), 1583 (s), 1477 (w), 1462 (w), 1414 (w), 1390 (w), 1371 (m), 1346 (w), 1319 (m), 1279 (w), 1254 (w), 1211 (w), 1173 (w), 1097 (s), 1024 (w), 991 (w), 937 (w), 901 (w), 825 (w), 764 (w), 700 (w), 636 (w), 623 (w).

Preparation of[Co(L²)₂](ClO₄)₂·MeCN (3). The single crystals were obtained by vapor diffusion. To a solution of L² (54 mg, 0.2 mmol) in 5 mL of methanol was added a solution of Co(ClO₄)₂·6H₂O (36 mg, 0.1 mmol) in methanol (5 mL) under stirring. The orange transparent solution was stirred for for about 10 minutes and concentrated under reduced pressure. The resulting residue was dissolved in acetonitrile (5 mL) and then ether (about 10 mL) was allowed to vapor diffuse into the solution during a period of three days. Orange cubic crystals were obtained. Yield: 82%. Anal. Calcd forC₃₂H₄₁Cl₂CoN₇O₁₂: C, 45.45; H, 4.89; N, 11.60. Found, C, 44.64; H, 4.75; N, 10.58. IR (single crystal): v = 3080 (w), 2978 (w), 2935 (w), 2874 (w), 2017 (br), 1637 (w), 1620 (w), 1570 (m), 1485 (w), 1462 (w), 1402 (m), 1381 (m), 1369 (w), 1333 (w), 1298 (m), 1252 (w), 687 (w), 675 (w), 623 (w).

Preparation of[Co(L³)₂](ClO₄)₂ (4). The single crystals were obtained from L³ and Co(ClO₄)₂·6H₂O according to the procedure identical to that for **3**. Yield: 77%. Anal. Calcd forC₃₆H₃₄Cl₂CoN₆O₁₂: C, 49.56, H, 3.93, N, 9.63. Found: 49.45, H, 3.88, N, 9.71. IR (single crystal): v = 3086 (w), 3064 (w), 2985 (w), 2947 (w), 2879 (w), 1653 (w), 1630 (w), 1610 (w), 1587 (s), 1520 (w), 1483 (w), 1464 (w), 1419 (w), 1377 (m), 1333 (w), 1306 (w), 1273 (m), 1257 (w), 1213 (w), 1205 (w), 1192 (w), 1101

(s), 1086 (s), 1022 (w), 1009 (w), 991 (w), 978 (w), 964 (w), 914 (w), 825 (w), 764 (w), 687 (w), 623 (m).

Preparation of $[Co(L^4)_2](ClO_4)_2$ (5). The single crystals were obtained from L⁴ and $Co(ClO_4)_2 \cdot 6H_2O$ according to the procedure identical to that for 1. Yield: 83%. Anal. Calcd for $C_{46}H_{53}Cl_2CoN_7O_{12}$: C, 53.86; H, 5.21; N, 9.56. Found: C, 54.01; H, 5.11; N, 9.43. IR (single crystal): v = 3072 (w), 2974 (w), 2933 (w), 2872 (w), 1645 (w), 1622 (w), 1581 (s), 1520 (w), 1479 (w), 1462 (m), 1416 (w), 1389 (w), 1371 (m), 1346 (w), 1319 (m), 1292 (w), 1277 (w), 1254 (w), 1211 (w), 1194 (w), 1174 (w), 1093 (s), 1018 (w), 991 (w), 937 (m), 901 (w), 818 (w), 762 (w), 698 (w), 623 (m), 607 (w).

Preparation of[Co(L⁴)₂](ClO₄)₂ (6).The single crystals were obtained from L⁵ and Co(ClO₄)₂·6H₂O according to the procedure identical to that for **3**. Yield: 75%. Anal. Calcd forC₄₀H₄₈Cl₂CoN₈O₁₄: C, 48.30; H, 4.86; N, 11.27. Found: C, 48.53; H, 4.74; N, 11.43.IR (single crystal):v = 3606 (br), 3068 (br), 2976 (w), 2933 (w), 2908 (w), 2874 (w), 1645 (w), 1620 (w), 1583 (s), 1547 (w), 1479 (w), 1462 (w), 1414 (w), 1390 (w), 1371 (m), 1346 (w), 1319 (m), 1279 (w), 1254 (w), 1211 (w), 1173 (w), 1097 (s), 1024 (w), 991 (w), 937 (w), 903 (w), 825 (w), 764 (w), 700 (w), 636 (w), 623 (w).

SI1.4 Physical measurements

X-ray Data Collection and Structure Determinations. Crystal suitable for X-ray diffraction were covered in a thin layer of hydrocarbon oil, mounted on a glass fiber attached to a copper pin, and cold temperature was obtained through placed the crystals under an N₂ cold stream. Data for **1** and **5** were collected on a Bruker CCD area detecter using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 296 K. Intensity data were collected in the variable ω -scan made. Data for **2** was collected on a Rigaku SuperNova Atlas Dual system with a (Mo) microfocus source and focusing multilayer mirror optics ($\lambda = 0.71073$ Å). Intensities were collectedusing CrysAlisPro (Rigaku, Version 1.171.36.32) and absorption corrections were applied using 'multi-scan' method. Data for **3** and **4** were carried on a Rigaku Saturn724+ CCD diffractometer with Confocal-monochromator Mo-K α radiation ($\lambda = 0.71073$ Å). Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption corrections were applied using the 'multi-scan' method.

Crystal structures were all solved by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97 and Olex 2 (version 1.2.6).^{16,17} All non-hydrogen atoms were refined with anisotropic thermal parameters, while all hydrogen atoms were placedat calculated positions and refined using a riding model. Full crystallographic tables for five structures are presented in Table 1.

Magnetic properties measurements. Magnetic susceptibility data were collected using a Quantum Design MPMS XL-5 or PPMS-9T (EC-II)SQUID magnetometer. Measurements for all the samples were performed on microcrystalline powder restrained by a parafilm and loaded in a capsule. The magnetic susceptibility data were corrected for the diamagnetism of the samples using Pascal constants¹⁵ and the sample holder and parafilm by corrected measurement.

Other characterization. The chemical shifts (δ) in ¹H NMR were reported in ppm relative to tetrametylsilane (Me₄Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvent: CDCl₃ (7.26 ppm) or DMSO-*d*₆ (2.50 ppm). Coupling constants (*J*) were expressed in hertz. ¹³C NMR spectra were recorded at 100 MHz or 125 MHz, and the chemical shifts (δ) were reported in ppm relative to CDCl₃ (77.10 ppm) or DMSO-*d*₆ (40.50 ppm). Elemental analysis of carbon, nitrogen andhydrogen was performed using an Elementary Vario ELanalyzer. Mass spectra were recorded on a LCT Premier XE Time of Flight mass spectrometer. Powder X-ray diffraction (XRD) patterns were obtained in the range of 5° < 2 θ < 60° at room temperature against the bulk crystalline samples on a Rigaku Dmax 2000 diffractometer with Cu K α radiation in a flat plate geometry.

Computational details. Complete active space second-order perturbation theory (CASPT2) considering the effect of the dynamical electronic correlation based on complete-active-space self-consistent field (CASSCF) using MOLCAS 8.0 program package⁵ was performed on the X-ray determined complete structures of **1**–**6**. For the first CASSCF calculation, the basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for magnetic center ion Co^{II} ; VTZ for close O atoms; 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. The effect of the dynamical electronic correlation was applied using CASPT2 based on the first CASSCF calculation. After that, the spin–orbit coupling was handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 10 active spaces considering 3d double shell effect include all seven 3d electrons, and the mixed spin-free states are 50 (all from 10 quadruplets; all from 40 doublets).

SI1.5 References

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SI2 ¹H NMR and ¹³C NMR spectra



Fig. S1 ¹H NMR spectrum of compound 1 (600 MHz) in CDCl₃ (10 mM).



Fig. S2 ¹H NMR spectrum of compound 2 (600 MHz) in CDCl₃ (10 mM).



Fig. S3 ¹H NMR spectrum of compound 3 (600 MHz) in DMSO- d_6 (10 mM).



Fig. S4 ¹³C NMR spectrum of compound 3 (100 MHz) in DMSO- d_6 (50 mM).



Fig. S5 ¹H NMR spectrum of compound 4 (400 MHz) in CDCl₃ (10 mM).



Fig. S6 ¹³C NMR spectrum of compound 4 (100 MHz) in CDCl₃ (10 mM).



Fig. S7 ¹H NMR spectrum of compound L^3 (600 MHz) in CDCl₃ (10 mM).



Fig. S8 ¹³C NMR spectrum of compound L³ (125 MHz) in CDCl₃ (50 mM).



Fig. S9 ¹H NMR spectrum of compound 5 (600 MHz) in DMSO- d_6 (10 mM).



Fig. S10 ¹³C NMR spectrum of compound 5 (125 MHz) in DMSO- d_6 (50 mM).



Fig. S11 ¹H NMR spectrum of compound 6 (600 MHz) in CDCl₃ (10 mM).



Fig. S12 ¹³C NMR spectrum of compound 6 (125 MHz) in CDCl₃ (10 mM).



Fig. S13 ¹H NMR spectrum of compound L^4 (600 MHz) in CDCl₃ (50 mM).



Fig. S14 ¹³C NMR spectrum of compound L⁴ (125 MHz) in CDCl₃ (50 mM).



Fig. S15 ¹H NMR spectrum of compound 7 (400 MHz) in DMSO- d_6 (10 mM).



Fig. S16 ¹³C NMR spectrum of compound 7 (100 MHz) in DMSO- d_6 (10 mM).



Fig. S17 ¹H NMR spectrum of compound 8 (600 MHz) in CDCl₃ (10 mM).



Fig. S18 ¹³C NMR spectrum of compound 8 (125 MHz) in CDCl₃ (30 mM).



Fig. S19 ¹H NMR spectrum of compound 9 (600 MHz) in CDCl₃ (10 mM).



Fig. S20 ¹³C NMR spectrum of compound 9 (125 MHz) in CDCl₃ (30 mM).



Fig. S21 ¹H NMR spectrum of compound L^5 (600 MHz) in CDCl₃ (10 mM).



Fig. S22 13 C NMR spectrum of compound L⁵ (125 MHz) in CDCl₃ (30 mM).

SI3 Structural details

	1	2	3	4	5	6
Formula	$C_{22}H_{22}Cl_{2}CoN_{6}O_{12} \\$	$C_{30}H_{38}Cl_{2}CoN_{6}O_{12} \\$	$C_{32}H_{41}Cl_{2}CoN_{7}O_{12} \\$	$C_{36}H_{34}N_6O_{12}Cl_2Co$	$C_{46}H_{53}Cl_2CoN_7O_{12}$	$C_{40}H_{48}Cl_{2}CoN_{8}O_{14} \\$
formula weight	692.28	804.49	845.55	872.52	1025.78	994.69
crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$	Pbca	Pbca	Pna2 ₁	$P2_1/n$	Fdd2
<i>a</i> , Å	15.9905(11)	13.8991(4)	16.987(3)	18.847(4)	16.0297(6)	25.736(3)
b, Å	10.9332(8)	19.9517(6)	19.242(4)	17.562(4)	16.8230(6)	75.453(7)
<i>c</i> , Å	16.8489(12)	25.3128(8)	22.838(5)	11.378(2)	19.7681(8)	9.3523(9)
α , deg	90	90	90	90	90	90
β , deg	102.5510(10)	90	90	90	109.7380(10)	90
γ, deg	90	90	90	90	90	90
<i>V</i> , Å ³	2875.3(4)	7019.5(4)	7465(3)	3766.1(13)	5017.6(3)	18161(3)
Ζ	4	8	8	4	4	16
<i>Т</i> , К	296(2)	180.0(1)	153.0(2)	153.0(6)	273.0(0)	296.15
<i>F</i> (000)	1412	3336	3512	1796	2140	8272
$D_{\rm C}, {\rm g} {\rm cm}^{-3}$	1.599	1.522	1.505	1.539	1.358	1.455
μ , mm ⁻¹	0.854	0.711	0.674	0.670	0.515	0.570
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal size, mm ³	$0.25\times0.15\times0.10$	$0.35 \times 0.33 \times 0.26$	$0.25 \times 0.24 \times 0.18$	$0.24\times0.23\times0.15$	$0.20\times0.19\times0.18$	$0.43 \times 0.36 \times 0.30$
T_{\min} and T_{\max}	0.815, 0.919	0.90957, 1.00000	0.6447, 1.0000	0.4997, 1.0000	0.6518, 0.7452	0.6712, 0.7455
$\theta_{\min}, \theta_{\max}, \deg$	2.24, 26.97	3.3150, 28.0200	1.1987, 27.4855	4.782, 52.738	2.19, 25.04	2.333, 19.907
no. total reflns.	9895	8397	9305	13273	38875	34526
no. uniq. reflns, R _{int}	5630, 0.0178	6896, 0.0411	7575, 0.0616	6487, 0.0470	8835, 0.0547	8535, 0.0566
no. obs. $[I \ge 2\sigma(I)]$	4915	5322	7306	5819	6394	6299
no. params	416	496	496	516	612	594
$R1 [I \ge 2\sigma(I)]$	0.0417	0.0672	0.0809	0.0526	0.0628	0.0629
wR2 (all data)	0.1281	0.1865	0.1423	0.1090	0.1923	0.1851
S	1.020	1.144	1.320	1.087	1.029	1.066
$\Delta \rho^a$, e/ Å ³	0.721, -0.491	1.596, -0.761	0.730, -0.736	0.330, -0.371	0.874, -0.888	0.671, -0.548
max. and mean Δ/σ^b	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000	0.000, 0.000	0.001, 0.000
CCDC	1477513	1477514	1477515	1477516	1552770	1477517

 Table S1. Crystal data, data collection, solution, and refinement information of compounds 1–6.

[a] Max and min residual density. [b] Max and mean shift/o.



Fig. S23 The powder XRD pattern of **1** and its simulated pattern from the single-crystal X-ray structure.



Fig. S24 The powder XRD pattern of **2** and its simulated pattern from the single-crystal X-ray structure.



Fig. S25 The powder XRD pattern of **3** and its simulated pattern from the single-crystal X-ray structure.



Fig. S26 The powder XRD pattern of **4** and its simulated pattern from the single-crystal X-ray structure.



Fig. S27 The powder XRD pattern of **5** and its simulated pattern from the single-crystal X-ray structure.



Fig. S28 The powder XRD pattern of **6** and its simulated pattern from the single-crystal X-ray structure.



Fig. S29 The strong π - π stacking of pyridine and *p*-tolyl rings between neighboring cationic complexes of **4**.



Fig. S30 The weak π - π stacking of pyridine ring between neighboring cationic complexes of 6.



Fig. S31 The packing crystal structure of 1 in one unit cell.



Fig. S32 The packing crystal structure of 2 in one unit cell.



Fig. S33 The packing crystal structure of 3 in one unit cell.



Fig. S34 The packing crystal structure of 4 in one unit cell.



Fig. S35 The packing crystal structure of 5 in one unit cell.



Fig. S36 The packing crystal structure of 6 in one unit cell.





Fig. S37 (a) $\chi_M T vs. T$ plots under a 1 kOe applied dc field at 2–300 K for **2**. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method. (b) Experimental and theoretical M vs. H/T plots at different temperatures.



Fig. S38 (a) $\chi_M T vs. T$ plots under a 1 kOe applied dc field at 2–300 K for **3**. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method. (b) Experimental and theoretical M vs. H/T plots at different temperatures.

Fig. S39 (a) $\chi_M T vs. T$ plots under a 1 kOe applied dc field at 2–300 K for 4. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method. (b) Experimental and theoretical M vs. H/T plots at different temperatures.

Fig. S40 (a) $\chi_M T vs. T$ plots under a 1 kOe applied dc field at 2–300 K for **5**. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method. (b) Experimental and theoretical M vs. H/T plots at different temperatures.

Fig. S41 (a) $\chi_M T vs. T$ plots under a 1 kOe applied dc field at 2–300 K for **6**. The red solid line represents the calculated magnetic susceptibilities by the CASPT2/RASSI/SINGLE-ANISO method. (b) Experimental and theoretical M vs. H/T plots at different temperatures.

Fig. S42 Temperature-dependent magnetic susceptibility data and fitting results on 1 kOe applied dc field at 2–300 K for (a–f) **1–6.** The red solid lines represent the best fits by *PHI*.

Fig. S43 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of 1 at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S44 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of **2** at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S45 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of **3** at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S46 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of 4 at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S47 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of **5** at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S48 Temperature dependence of in-phase (χ') and out-of-phase (χ'') of **6** at different frequencies in the absence of dc field, no obvious frequency dependence can be observed.

Fig. S49 Temperature dependence of in-phase (χ') of 1 at different frequencies under 2000 Oe dc field.

Fig. S50 Temperature dependence of in-phase (χ') of 2 at different frequencies under 2000 Oe dc field.

Fig. S51 Temperature dependence of in-phase (χ') of 3 at different frequencies under 2000 Oe dc field.

Fig. S52 Temperature dependence of in-phase (χ') of 4 at different frequencies under 2000 Oe dc field.

Fig. S53 Temperature dependence of in-phase (χ') of 5 at different frequencies under 2000 Oe dc field.

Fig. S54 Temperature dependence of in-phase (χ') of 6 at different frequencies under 2000 Oe dc field.

Fig. S55 Cole–Cole diagram of **1** under 2000 Oe dc field from 2 K to 6 K (ac frequencies from 100 Hz to 10000 Hz, 0.5 K interval).

Table S2 The p	arameters of	Cole-Col	e fitting of 1	1 under 2000) Oe dc field.
			<u> </u>		

<i>T</i> (K)	X_0	X_{t}	$\tau(s)$	α	R
2.0	0.03074	0.78718	0.00025	0.10014	7.82×10^{-4}
2.5	0.02620	0.82906	0.00015	0.05829	1.30×10^{-4}
3.0	0.03055	0.78569	0.00009	0.02901	5.63×10^{-5}
3.5	0.03617	0.71566	0.00006	0.01019	6.43×10^{-5}
4.0	0.03850	0.64411	0.00004	0.00486	3.54×10^{-5}
4.5	0.03992	0.58528	0.00003	0.00162	2.21×10^{-5}
5.0	0.03609	0.52904	0.00002	0.00067	4.21×10^{-5}
5.5	0.06096	0.48762	0.00001	0.00354	3.60×10^{-5}
6.0	0.06024	0.44807	0.00001	0.00017	2.38×10^{-5}

Fig. S56 Cole–Cole diagram of **2** under 2000 Oe dc field from 2 K to 8 K (ac frequencies from 100 Hz to 10000 Hz, 0.4 K interval).

	1	U			
<i>T</i> (K)	X_0	X _t	$\tau(s)$	α	R
2.0	0.02925	0.71633	0.00136	0.10398	5.45×10^{-4}
2.4	0.02402	0.67248	0.00090	0.09049	2.29×10^{-4}
2.8	0.02939	0.60350	0.00056	0.04948	5.62×10^{-4}
3.2	0.02197	0.55888	0.00039	0.06587	1.15×10^{-4}
3.6	0.01869	0.51520	0.00026	0.05123	8.51×10^{-5}
4.0	0.01659	0.47356	0.00017	0.05904	9.64×10^{-5}
4.4	0.02257	0.43165	0.00011	0.01834	8.07×10^{-5}
4.8	0.02242	0.39249	0.00007	0.01108	1.38×10^{-4}
5.2	0.01746	0.37094	0.00005	0.03080	6.25×10^{-5}
5.6	0.01573	0.34514	0.00004	0.02509	1.32×10^{-4}
6.0	0.01578	0.32211	0.00002	0.02131	5.14×10^{-5}
6.4	0.01848	0.30392	0.00002	0.00960	4.76×10^{-5}
6.8	0.01755	0.28537	0.00001	0.00848	7.77×10^{-5}
7.2	0.00982	0.26918	0.00001	0.00840	9.06×10^{-5}
7.6	0.01226	0.25693	0.00001	0.01844	5.94×10^{-5}
8.0	0.01420	0 24803	0.00001	0 11283	1.90×10^{-4}

Table S3 The parameters of Cole-Cole fitting of 2 under 2000 Oe dc field.

Fig. S57 Cole–Cole diagram of **3** under 2000 Oe dc field from 2 K to 6 K (ac frequencies from 100 Hz to 10000 Hz, 0.4 K interval).

	-	-				
<i>T</i> (K)	X_0	X _t	$\tau(s)$	α	R	
2.0	0.01905	0.74683	0.00038	0.09285	1.02×10^{-4}	
2.4	0.01906	0.71182	0.00030	0.08547	6.08×10^{-5}	
2.8	0.02102	0.65609	0.00023	0.07496	1.12×10^{-4}	
3.2	0.02194	0.60835	0.00017	0.06350	1.42×10^{-4}	
3.6	0.02245	0.55721	0.00013	0.06324	1.58×10^{-4}	
4.0	0.02027	0.50207	0.00009	0.03910	9.48×10^{-5}	
4.4	0.02849	0.46514	0.00007	0.01565	6.53×10^{-5}	
4.8	0.02906	0.42943	0.00005	0.01808	5.09×10^{-5}	
5.2	0.03000	0.39728	0.00003	0.00039	9.96×10^{-5}	
5.6	0.02252	0.37050	0.00002	0.02030	5.59×10^{-5}	
60	0 02980	0 34856	0.00002	0.00722	3.51×10^{-5}	

Table S4 The parameters of Cole-Cole fitting of 3 under 2000 Oe dc field.

<i>T</i> (K)	X_0	Xt	$\tau(s)$	α	R
2.0	0.03156	0.50094	0.00227	0.03850	4.70×10^{-3}
2.4	0.02980	0.58971	0.00192	0.02935	2.79×10^{-3}
2.8	0.02358	0.67433	0.00161	0.07902	6.10×10^{-4}
3.2	0.02998	0.65930	0.00102	0.05682	9.63×10^{-4}
3.6	0.02310	0.61849	0.00060	0.07290	2.72×10^{-4}
4.0	0.02326	0.55339	0.00034	0.04360	1.34×10^{-4}
4.4	0.02276	0.51086	0.00021	0.02442	9.39×10^{-5}
4.8	0.01759	0.47071	0.00013	0.03106	2.62×10^{-5}
5.2	0.01789	0.43586	0.00009	0.01768	8.72×10^{-5}
5.6	0.01505	0.41054	0.00006	0.03830	6.28×10^{-5}
6.0	0.01860	0.38096	0.00004	0.00924	5.19×10^{-5}
6.4	0.01682	0.36190	0.00003	0.03192	6.50×10^{-5}
6.8	0.01562	0.34223	0.00002	0.03373	1.03×10^{-4}
7.2	0.02741	0.31817	0.00002	0.00441	9.82×10^{-5}
7.6	0.02444	0.30601	0.00001	0.00023	1.44×10^{-4}
8.0	0.03510	0.29005	0.00001	0.00009	4.36×10^{-5}

 Table S5 The parameters of Cole-Cole fitting of 4 under 2000 Oe dc field.

Fig. S58 Cole–Cole diagram of **5** under 2000 Oe dc field from 2 K to 7 K (ac frequencies from 100 Hz to 10000 Hz, 0.4 K interval).

Table S6 The parameters	of Cole-Cole fitting	of 5 under 2000	Oe dc field.
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<i>T</i> (K)	X_0	X_{t}	τ	α	R
2.0	0.03462	0.80223	0.00073	0.05493	5.45×10^{-4}
2.25	0.03332	0.75608	0.00055	0.04995	4.27×10^{-4}
2.5	0.03086	0.72440	0.00042	0.05822	3.12×10^{-4}
2.75	0.02978	0.67159	0.00031	0.05037	2.27×10^{-4}
3	0.02727	0.63446	0.00024	0.05009	1.49×10^{-4}
3.25	0.02680	0.59252	0.00018	0.03762	1.20×10^{-4}
3.5	0.02459	0.56247	0.00015	0.04580	8.53×10^{-5}
3.75	0.02084	0.53011	0.00011	0.05007	3.70×10^{-5}
4	0.01960	0.50016	0.00009	0.03696	3.50×10^{-5}
4.25	0.01855	0.47546	0.00007	0.05022	7.47×10^{-5}
4.5	0.01827	0.44790	0.00006	0.03332	4.55×10^{-5}
4.75	0.01764	0.42595	0.00005	0.03249	4.79×10^{-5}
5	0.01665	0.40605	0.00004	0.03496	4.91×10^{-5}
5.25	0.01775	0.38794	0.00003	0.03233	4.79×10^{-5}
5.5	0.01767	0.37396	0.00003	0.04175	5.68×10^{-5}
5.75	0.01530	0.35600	0.00002	0.03199	5.00×10^{-5}
6	0.01582	0.34207	0.00002	0.03736	4.45×10^{-5}
6.25	0.01112	0.32908	0.00002	0.03765	9.52×10^{-5}
6.5	0.01734	0.31583	0.00001	0.01407	5.56×10^{-5}
6.75	0.02121	0.30677	0.00001	0.05216	6.87×10^{-5}
7	0.02731	0.29548	0.00001	0.03035	6.24×10^{-5}

Fig. S59 Cole–Cole diagram of **6** under 2000 Oe dc field from 2 K to 5.5 K (ac frequencies from 100 Hz to 10000 Hz, 0.25 K interval).

$T(\mathbf{K})$	X_0	X_{t}	$\tau(s)$	α	R
2.0	0.02251	0.79621	0.00009	0.07637	1.21×10^{-4}
2.25	0.02592	0.74741	0.00007	0.05779	1.12×10^{-4}
2.5	0.02179	0.70354	0.00006	0.06296	9.24×10^{-5}
2.75	0.02542	0.65095	0.00004	0.05045	6.59×10^{-5}
3.0	0.02670	0.61041	0.00004	0.05031	5.35×10^{-5}
3.25	0.02405	0.57261	0.00003	0.05252	3.27×10^{-5}
3.5	0.02452	0.53620	0.00003	0.04680	7.17×10^{-5}
3.75	0.02500	0.51000	0.00002	0.05010	$6.45 \times 10-5$
4	0.03544	0.47398	0.00002	0.01259	1.34×10^{-4}
4.25	0.02019	0.45980	0.00002	0.07135	1.59×10^{-4}
4.5	0.02042	0.42814	0.00001	0.04674	9.90×10^{-5}
4.75	0.01245	0.41339	0.00001	0.08167	1.50×10^{-4}
5	0.01492	0.39148	0.00001	0.06083	8.62×10^{-5}
5.25	0.02738	0.36915	0.00001	0.05358	6.40×10^{-5}
5.5	0.02353	0.35579	0.00001	0.09624	8.16×10^{-5}

Table S7 The parameters of Cole-Cole fitting of 6 under 2000 Oe dc field.

Fig. S60 Arrhenius plots for compounds 1–6 obtained from ac susceptibility measurements under 2000 Oe dc field.

Fig. S61 Field dependence of the magnetic relaxation time at 2 K for 1–6 (a–f).

SI5 Theoretical calculation details

Tab	ole S8	Calculat	ted spin-fi	ree energi	$es(cm^{-1})$	of the lowe	st ten term	s(S = 3/2)	of complex	es 1–6.
1	0.0	918.7	1090.8	8791.5	8973.0	11544.1	19958.7	21089.5	21769.7	22141.7
2	0.0	882.4	1063.8	8469.4	8652.1	11560.1	19617.3	20747.4	21838.1	21961.9
3	0.0	691.0	957.6	7845.8	8297.2	10873.2	18394.3	20076.5	21446.8	21765.7
4	0.0	586.1	2229.2	8242.9	8474.1	10317.7	17716.9	20193.1	21209.6	21986.9
5	0.0	701.2	751.5	7913.6	8052.0	11045.7	18535.3	20062.3	21525.2	21776.5
6	0.0	897.7	980.2	8219.4	8240.8	11525.7	19604.2	20739.6	21694.9	21829.1

Table S8 Calculated spin-free energies (cm⁻¹) of the lowest ten terms (S = 3/2) of complexes 1–6.

Table S9 Calculated weights of the five most important spin-orbit-free states for the lowest two spinorbit states of complexes 1–6.

Complex	Spin-orbit state	Energy(cm ⁻¹)		Spin-t	free states, Spin, V	Weights	
1	1	0.0	1, 1.5, 0.8446	2, 1.5, 0.0905	3, 1.5, 0.0607	4, 1.5, 0.0012	5, 1.5, 0.0010
1	2	139.0	1, 1.5, 0.9385	2, 1.5, 0.0322	3, 1.5, 0.0256	5, 1.5, 0.0012	4, 1.5, 0.0012
2	1	0.0	1, 1.5, 0.8374	2, 1.5, 0.0924	3, 1.5, 0.0661	4, 1.5, 0.0011	5, 1.5, 0.0011
2	2	135.2	1, 1.5, 0.9372	2, 1.5, 0.0321	3, 1.5, 0.0266	5, 1.5, 0.0015	4, 1.5, 0.0013
2	1	0.0	1, 1.5, 0.7795	2, 1.5, 0.1392	3, 1.5, 0.0777	4, 1.5, 0.0010	5, 1.5, 0.0009
3	2	146.2	1, 1.5, 0.9214	2, 1.5, 0.0465	3, 1.5, 0.0269	5, 1.5, 0.0020	4, 1.5, 0.0016
4	1	0.0	1, 1.5, 0.7750	2, 1.5, 0.2100	3, 1.5, 0.0125	5, 1.5, 0.0007	22, 0.5, 0.0005
4	2	147.6	1, 1.5, 0.9342	2, 1.5, 0.0491	3, 1.5, 0.0104	5, 1.5, 0.0025	4, 1.5, 0.0015
5	1	0.0	1, 1.5, 0.7623	2, 1.5, 0.1252	3, 1.5, 0.1083	4, 1.5, 0.0012	5, 1.5, 0.0011
3	2	170.3	1, 1.5, 0.9137	2, 1.5, 0.0428	3, 1.5, 0.0392	5, 1.5, 0.0016	4, 1.5, 0.0015
6	1	0.0	1, 1.5, 0.8336	2, 1.5, 0.0888	3, 1.5, 0.0730	4, 1.5, 0.0013	5, 1.5, 0.0012
6	2	144.5	1, 1.5, 0.9331	2, 1.5, 0.0335	3, 1.5, 0.0294	5, 1.5, 0.0014	4, 1.5, 0.0013

Table S10 The bond lengths between Co^{II} and its close N.

		0					
Bo	ond	1	2	3	4	5	6
	Co-N1	2.145	2.165	2.178	2.150	2.194	2.187
long	Co-N3	2.161	2.182	2.191	2.152	2.225	2.173
distance	Co-N4	2.168	2.158	2.187	2.145	2.204	2.171
	Co-N6	2.173	2.201	2.233	2.185	2.186	2.183
short	Co-N2	2.067	2.052	2.061	2.080	2.057	2.063
distance	Co-N5	2.060	2.062	2.072	2.077	2.070	2.055

Atoms		1	2	3	4	5	6
Со		1.300	1.392	1.396	1.396	1.396	1.393
long distance	N1	-0.429	-0.450	-0.451	-0.452	-0.445	-0.443
	N3	-0.428	-0.443	-0.442	-0.447	-0.439	-0.449
	N4	-0.427	-0.442	-0.444	-0.446	-0.436	-0.433
	N6	-0.437	-0.445	-0.441	-0.441	-0.447	-0.441
short distance	N2	-0.296	-0.330	-0.332	-0.340	-0.334	-0.334
	N5	-0.304	-0.331	-0.333	-0.348	-0.332	-0.333
	N4 N6 N2 N5	$-0.427 \\ -0.437 \\ -0.296 \\ -0.304$	-0.442 -0.445 -0.330 -0.331	$-0.444 \\ -0.441 \\ -0.332 \\ -0.333$	-0.446 -0.441 -0.340 -0.348	$-0.436 \\ -0.447 \\ -0.334 \\ -0.332$	$-0.43 \\ -0.44 \\ -0.33 \\ -0.33$

Table S11 Natural Bond Order (NBO) charges per atoms in the ground state of complexes 1-6calculated within CASPT2.