Supporting Information (SI)

Remote substitutes and coordination anions effect on magnetic properties of Co(II) dimmer complexes

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Experimental

General information

All chemicals and solvents were obtained from commercial sources without further purification. All reactions were carried out under aerobic conditions. The elemental analyses (C, H, and N) were carried out using an Elementar Vario EL analyzer. Fourier transform IR spectra (4000 to 400 cm^{-1}) were measured on a Perkin-Elmer Spectrum GX spectrometer with samples prepared as KBr discs. Powder X-ray diffraction was carried out on a STOE STADI-P diffractometer, using Cu-Kα radiation with λ = 1.5406 Å. Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA2500 (TG/DTA) thermal analyzer under an inert atmosphere (maintained by a N_2 gas flow) at a heating rate of 10 °C min^{-1}.

X-ray crystal structures

The crystal structures were determined at room temperature on a Bruker diffractometer with graphite-monochromator Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELXTL program suite.

Physical measurements

Variable-temperature dc magnetic susceptibility measurements and ac magnetic susceptibility measurements were conducted on microcrystalline samples, suspended in eicosane to prevent torquing. Magnetic susceptibility data (2-300 K) were collected on powdered samples using a SQUID-based sample magnetometer, Quantum Design model MPMS-VSM instrument under a 1000 Oe applied magnetic field. Magnetization isotherms were collected at 1.8 K, 2 K, 5 K and 10 K between 0 and 7 T. Ac susceptibility measurements were carried out under an oscillating ac field of 2 Oe and ac frequencies ranging from 1 to 1000 Hz. Data were corrected for diamagnetism using Pascal constants and a sample holder correction.

Synthesis of Ligands

The two ligands were synthesized by same method, therefore only H_2L1 will be discussed in detail.

N, N′-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine (H_2L1)

An ethanol solution containing salicylaldehyde (10 mmol, 1.20 g) was mixed with 1,4-bis (3-aminopropyl) piperazine (5 mmol, 1.00 g) in ethanol. The yellow mixture was refluxed for 8 hours under stirring. The desire yellow product was obtained by slow evaporation of the solution. H_2L1 (N, N′-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine) Yield: 1.80 g (88% based on 1,4-bis (3-aminopropyl) piperazine). Anal. calc. (%) for $C_{24}H_{32}N_4O_2 \cdot 2H_2O$ (444.57): C, 64.84; H, 8.16; N, 12.60 wt %; found: C, 64.74; H, 8.23; N, 12.87wt %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.56 (s, 2H), 8.35 (s, 2H), 7.35-7.27 (m, 2H), 7.24 (dd, J = 7.7, 1.7 Hz, 2H), 6.96 (dd, J = 8.3, 1.0 Hz, 2H), 6.88 (td, J = 7.5, 1.1 Hz, 2H), 3.64 (td, J = 6.8, 1.2 Hz, 4H), 2.43 (d, J = 7.7 Hz, 12H), 1.89 (p, J = 6.9 Hz, 4H). FT-IR (KBr, cm^{-1}): 3742 (w), 3679 (w), 3054 (w), 2934 (m), 2809 (m), 1633 (vs), 1499 (m), 1453 (m), 1345 (w), 1280 (s), 1204 (w), 1144 (m), 970 (w), 889 (m), 755 (s), 640 (w).

N, N′-bis(2-hydroxy-5-bromobenzyl)-1,4-bis(3-iminopropyl)-piperazine (H_2L2)

The synthesis of H_2L2 is the same as that of H_2L1 by replacing the salicylaldehyde to 5-bromosalicylaldehyde Yield: 1.90 g (67% based on 1,4-bis (3-aminopropyl) piperazine). Anal. calc. (%) for $C_{24}H_{30}Br_2N_4O_2$ (566.33): C, 50.90; H, 5.34; N, 9.89 wt %; found: C, 50.90, H, 5.00; N, 10.10 wt %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.60 (s, 2H), 8.28 (s, 2H), 7.37 (dt, J = 5.5, 2.4 Hz, 4H), 6.86 (d, J = 8.7 Hz, 2H), 3.66 (t, J = 6.7 Hz, 4H), 2.89-2.21 (m,

12H), 1.94-1.82 (m, 4H). FT-IR (KBr, cm^{-1}): 3743 (s), 3676 (w), 3617 (w), 2934 (m), 2811 (m), 2765 (w), 1695 (w), 1636 (s), 1517 (w), 1478 (w), 1365 (m), 1274 (s), 1165 (w), 969 (w), 825 (s), 627 (w).

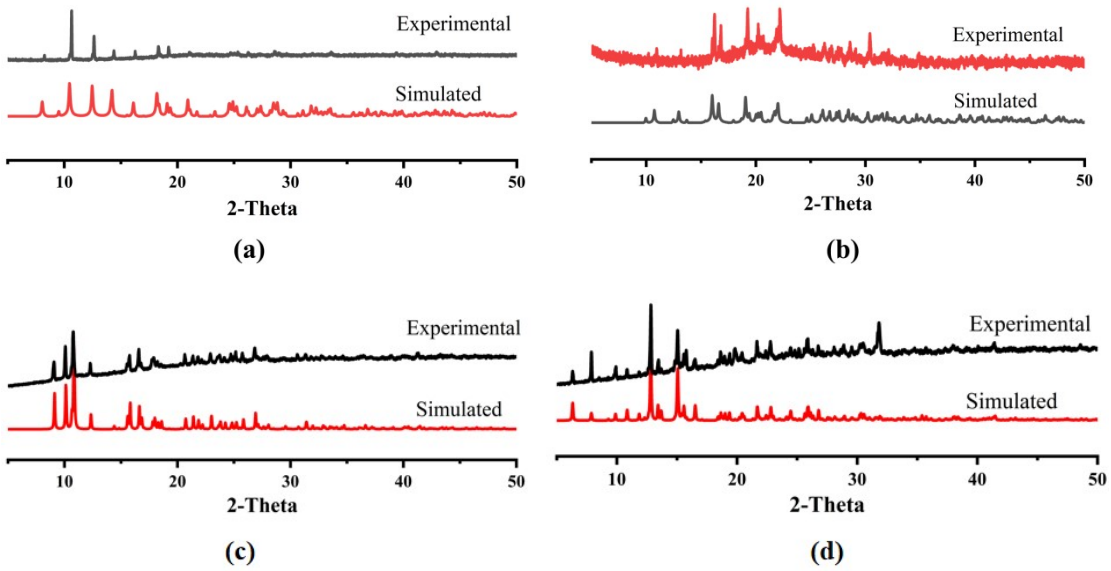

Fig. S1 Powder X-ray diffraction data for **1-4** (**a-d**).

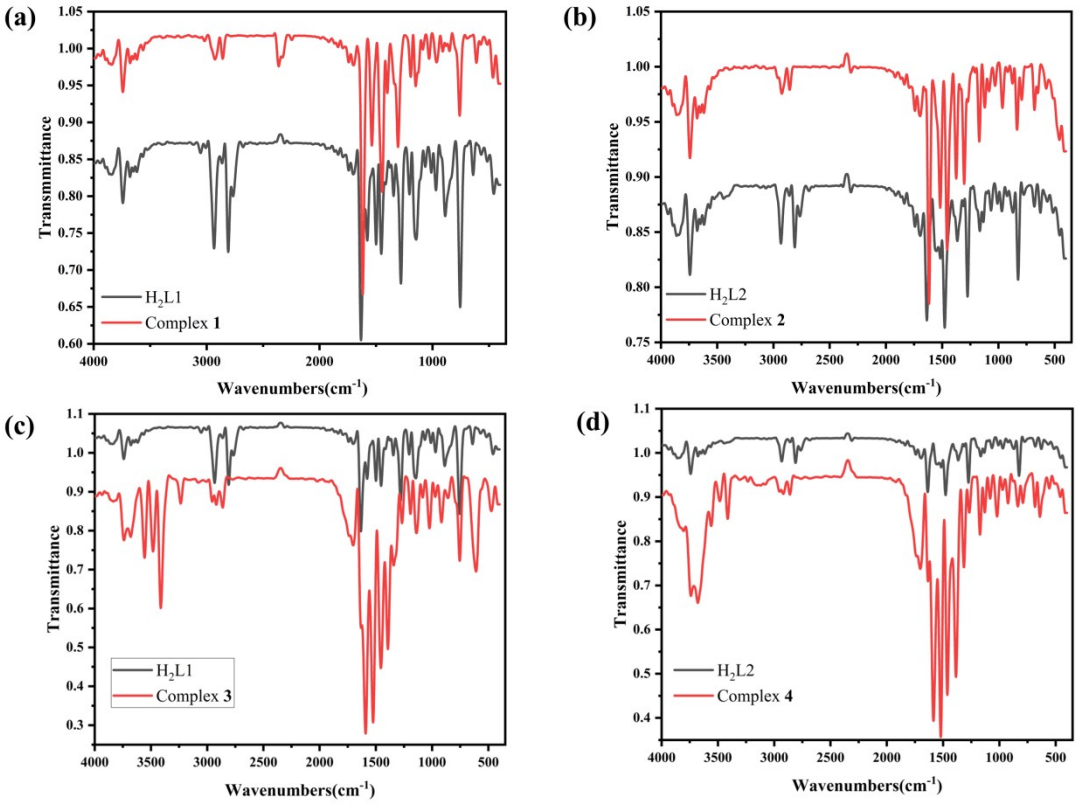

Fig. S2 IR spectroscopy of complexes **1-4** (**a-d**)

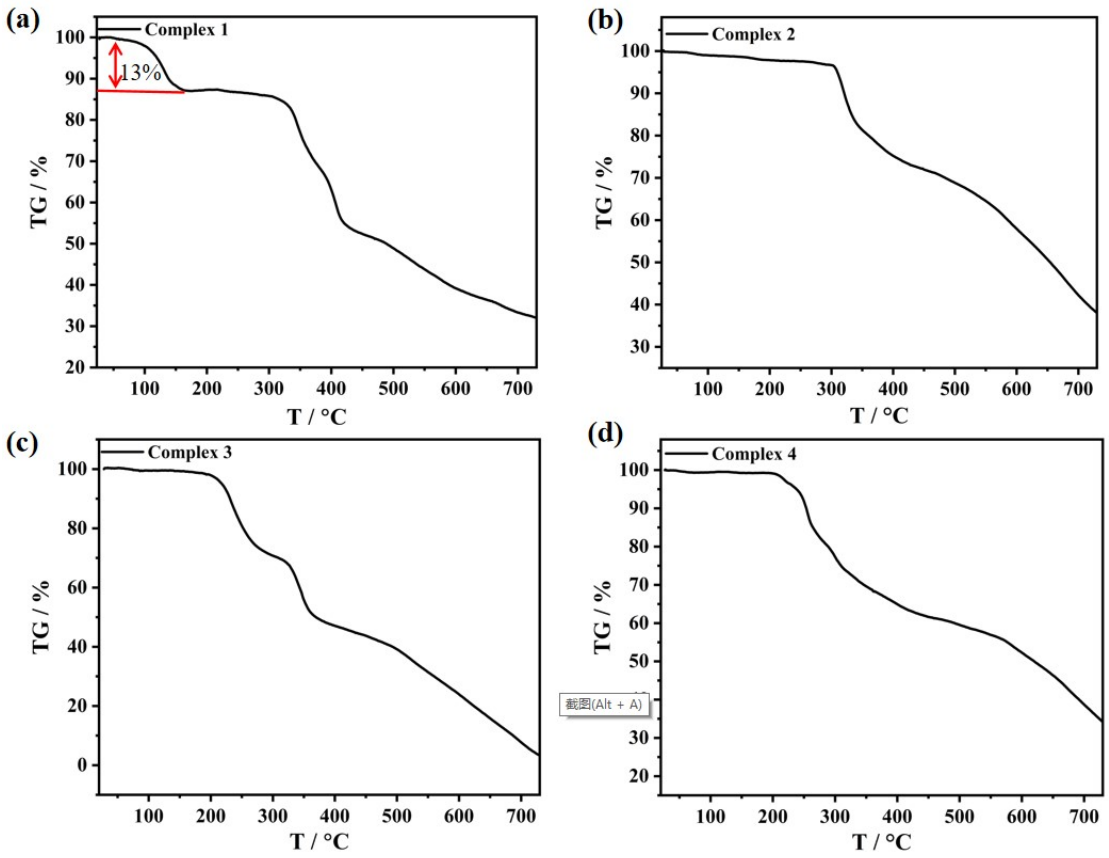

Fig.S3. TGA plots of complexes **1-4** (**a-d**).

Table 3. Continuous Shape Measures (CShMs) of the coordination geometry for Co(II) ion in complexes **1-4**.

Complexes	Label	Shape	Symmetry	Distortion
1	SP-4	Square	D_{4h}	25.2098
	T-4	Tetrahedron	T_d	2.0319
	SS-4	Seesaw	C_{2V}	7.1444
2	SP-4	Square	D_{4h}	27.3930
	T-4	Tetrahedron	T_d	1.7353
	SS-4	Seesaw	C_{2V}	7.8209
3	PP-5	Pentagon	D_{5h}	34.03126
	vOC-5	Vacant octahedron	C_{4V}	5.75785
	TBPY-5	Trigonal bipyramid	D_{3h}	0.36928
	SPY-5	Spherical square pyramid	C_{4V}	3.77594
	JTBPY-5	Johnson trigonal bipyramid J12	D_{3h}	3.18736
4	PP-5	Pentagon	D_{5h}	33.28680
	vOC-5	Vacant octahedron	C_{4V}	3.87570
	TBPY-5	Trigonal bipyramid	D_{3h}	1.04673
	SPY-5	Spherical square pyramid	C4V	2.36315
	JTBPY-5	Johnson trigonal bipyramid J12	D3h	3.52584

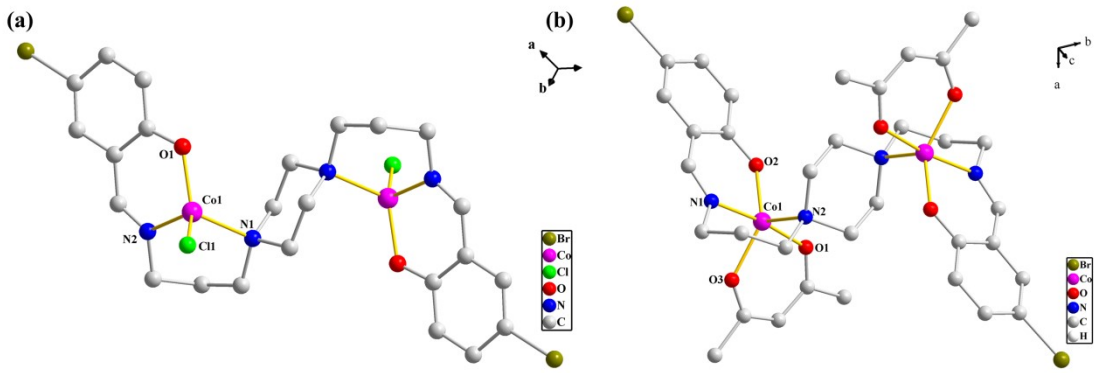

Fig. S3 Molecular structures of complexes **2** and **4** (left and right)

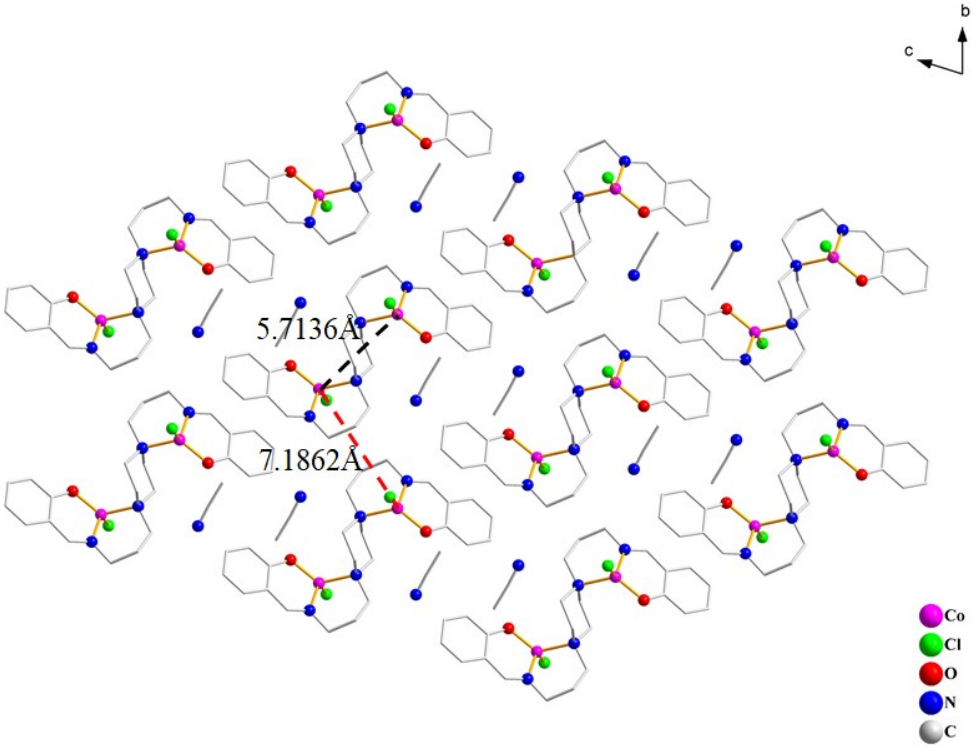

Fig. S5 Packing of complex **1**. dash lines are the intramolecular Co-Co distances (black dash line) and intermolecular Co-Co (red dash line) distances withing the complex.

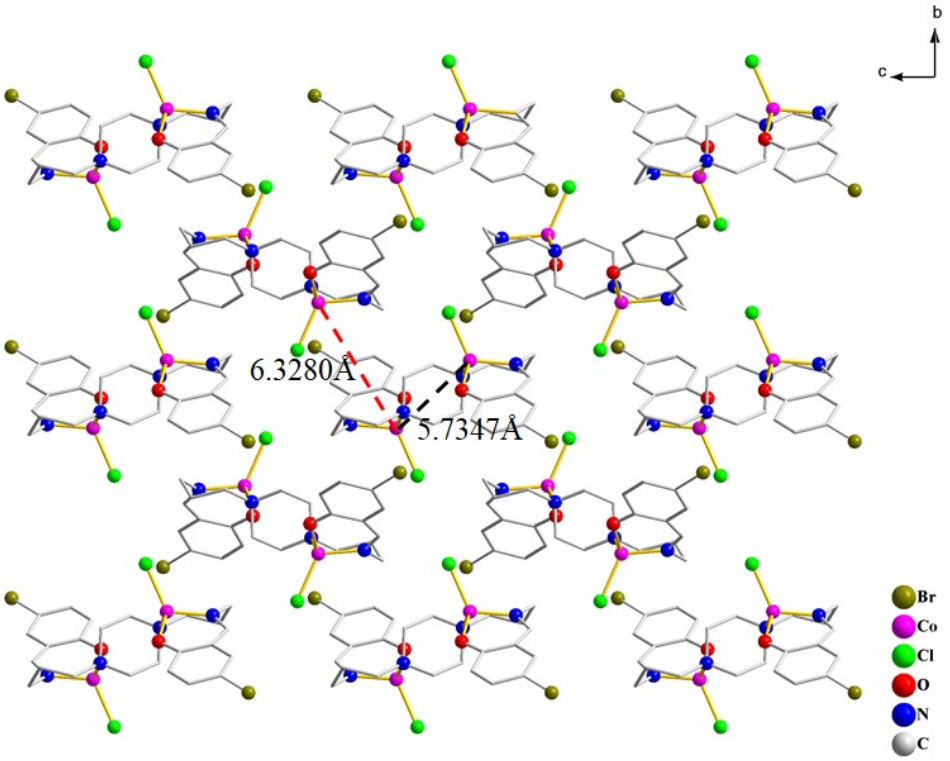

Fig. S6 Packing of complex **2**. dash lines are the intramolecular Co-Co distances (black dash line) and intermolecular Co-Co (red dash line) distances withing the complex.

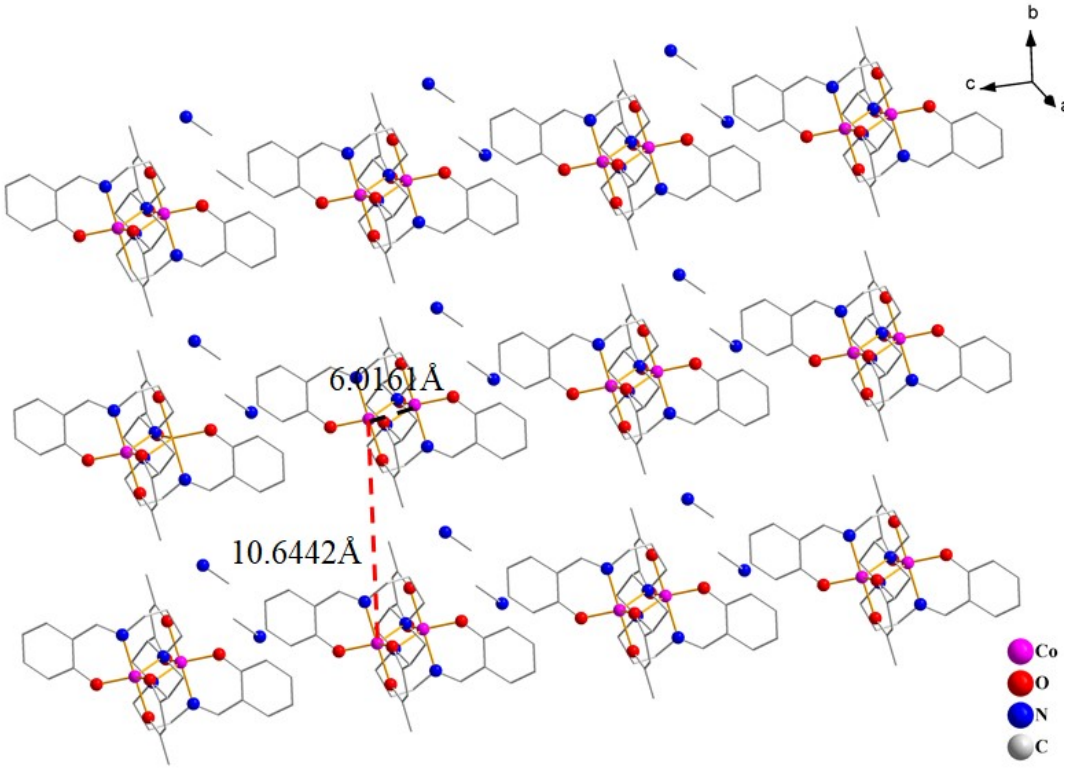

Fig. S7 Packing of complex **3**. dash lines are the intramolecular Co-Co distances (black dash line) and intermolecular Co-Co (red dash line) distances withing the complex.

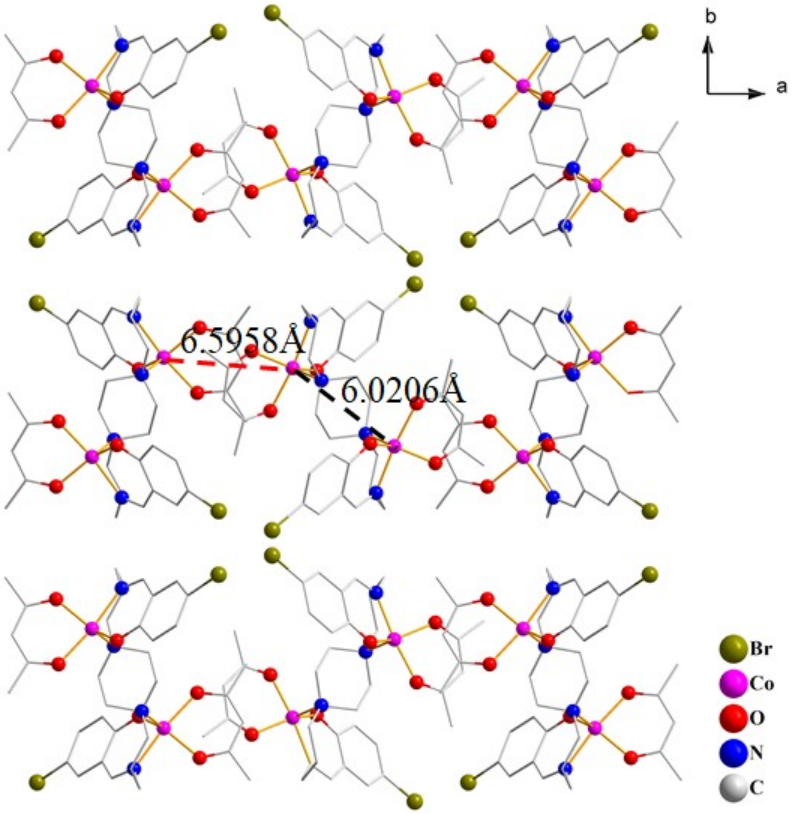

Fig. S8 Packing of complex **4**. dash lines are the intramolecular Co-Co distances (black dash line) and intermolecular Co-Co (red dash line) distances withing the complex.

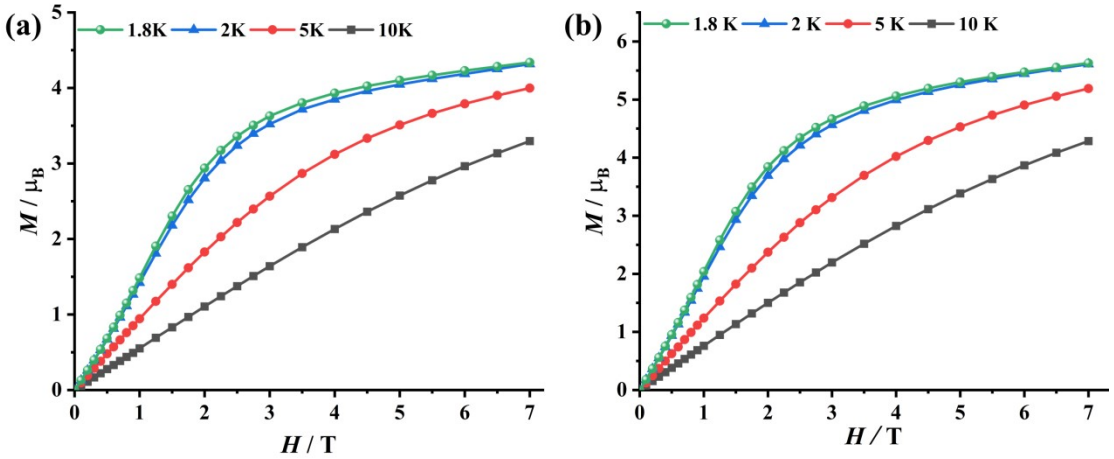

Fig. S9 Plots of *M* vs *H* at different temperature for complexes **1** and **2**(left to right)

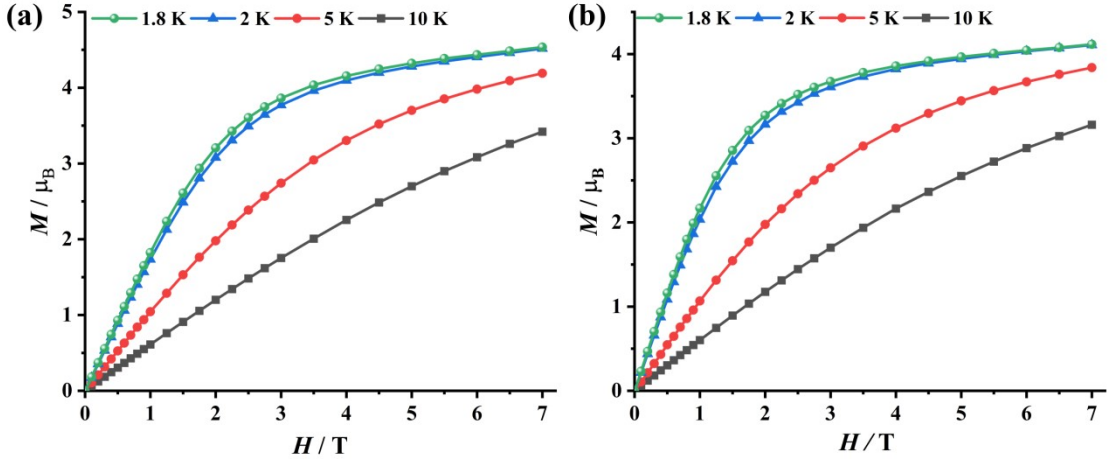

Fig. S10 Plots of M vs H at different temperature for complexes **3** and **4**(left to right)

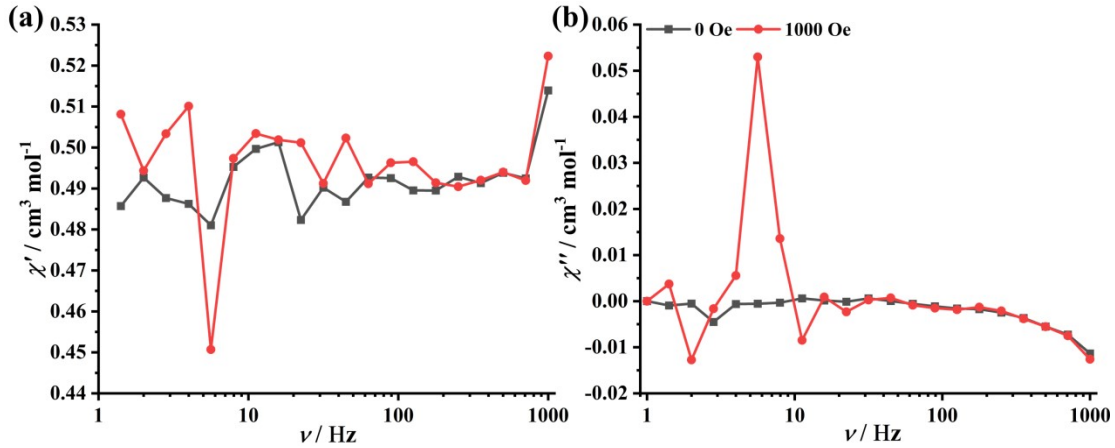

Fig. S11 Plots of χ' (left) and χ'' (right) vs frequencies at 2 K in different dc fields for complex **2**

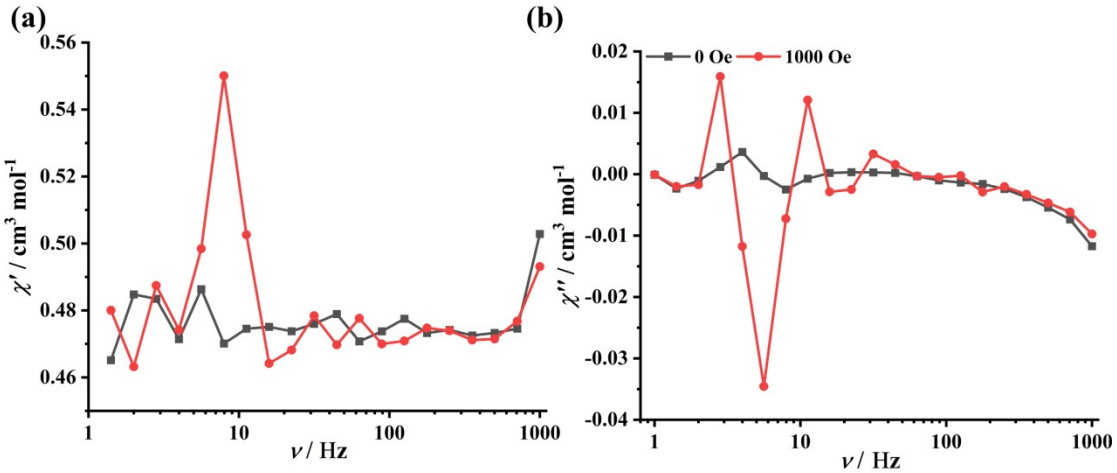

Fig. S12 Plots of χ' (left) and χ'' (right) vs frequencies at 2 K in different dc fields for complex **3**

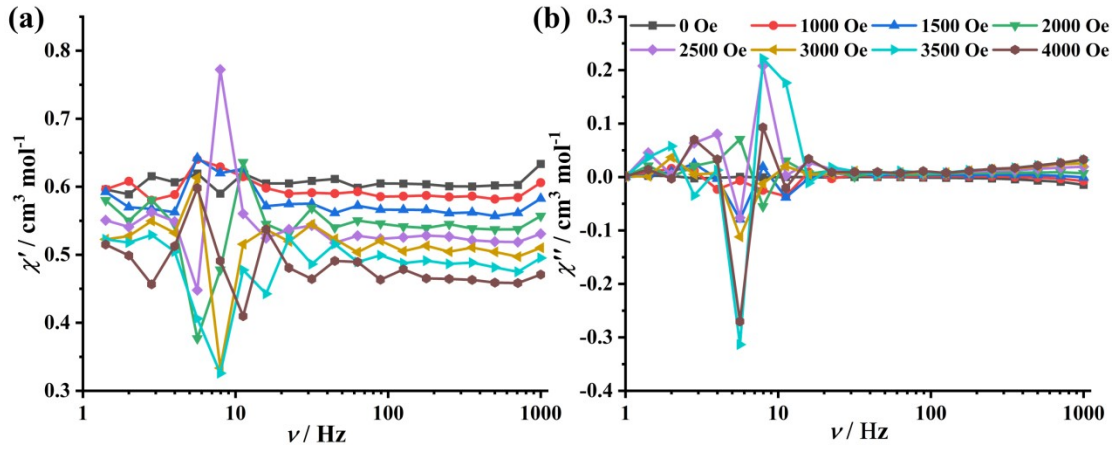

Fig. S13 Plots of χ' (left) and χ'' (right) vs frequencies at 2 K in different dc fields for complex **4**