Supporting information for

# Influence of F-position and solvent on coordination geometry and single ion magnet behavior of Co(II) complexes

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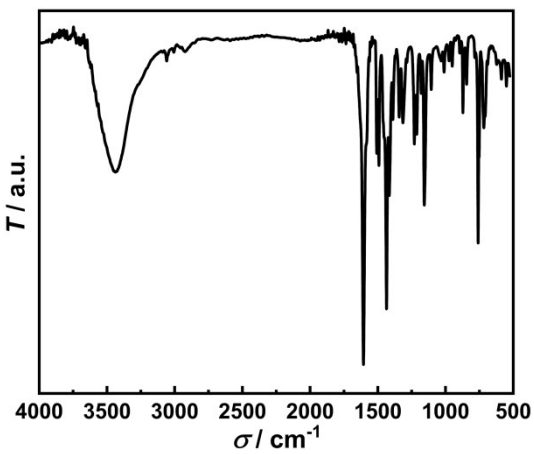
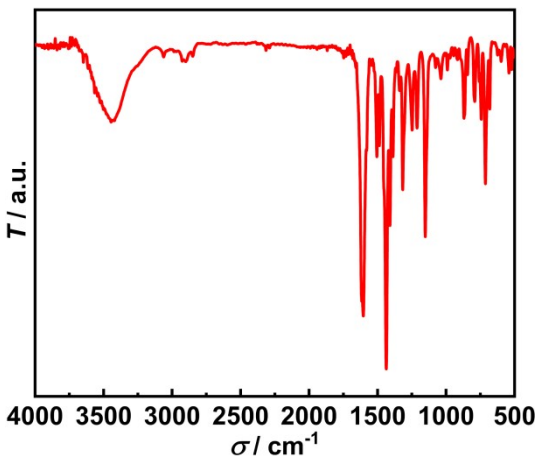
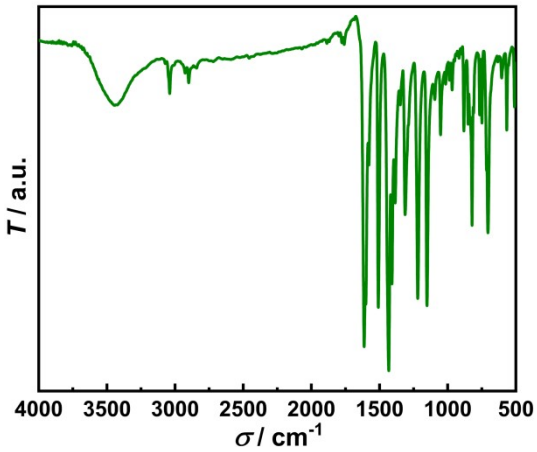



(a)

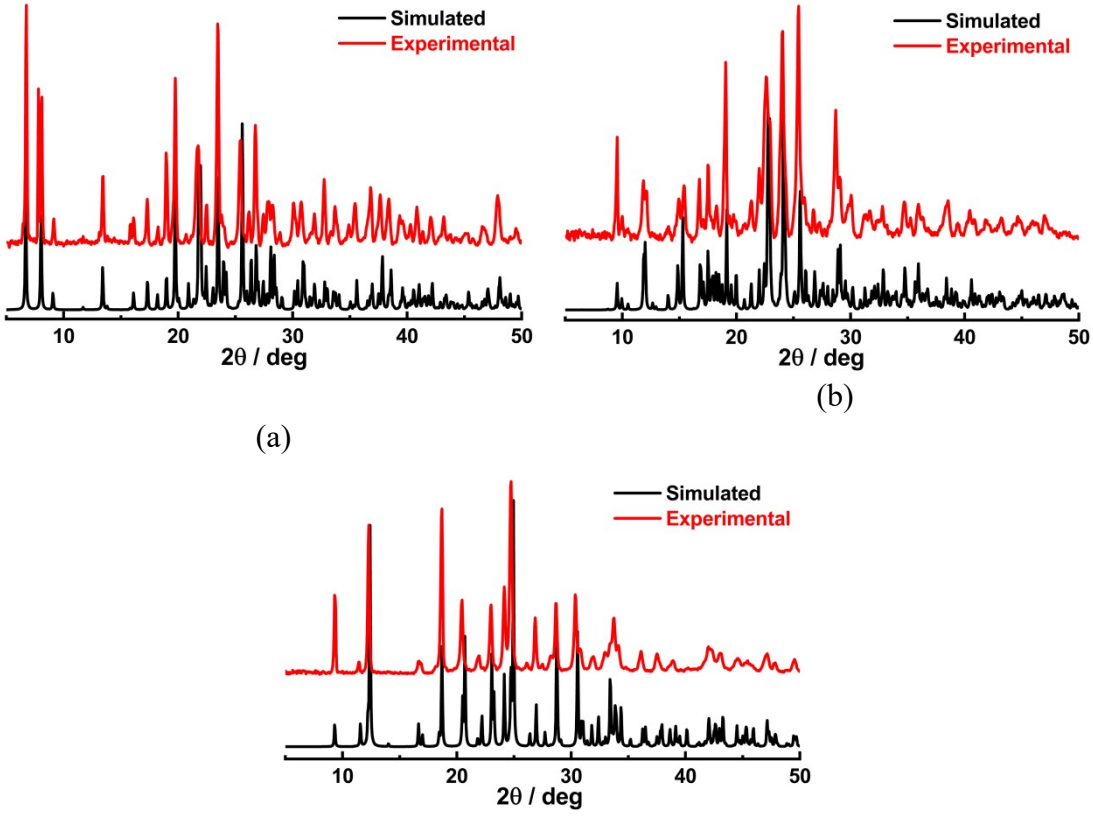



(b)




(c)

**Fig. S1** IR spectra of complexes **1** (a), **2** (b) and **3** (c).

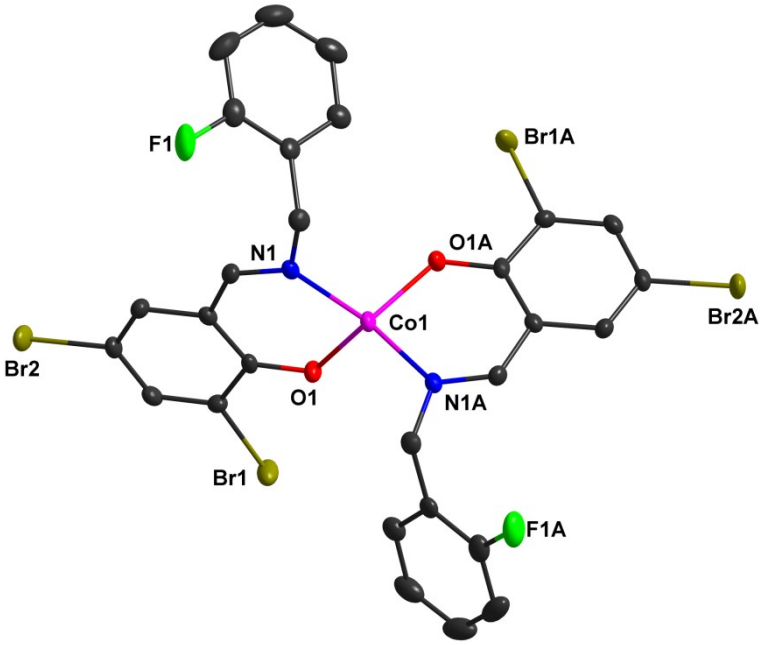



(a)

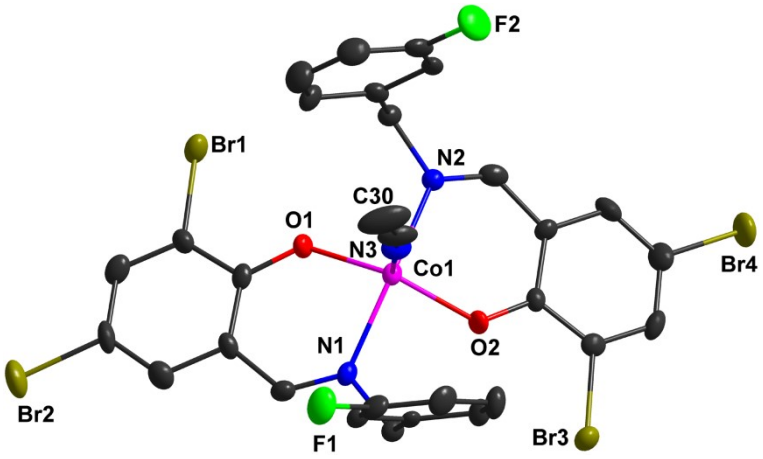
(b)

(c)

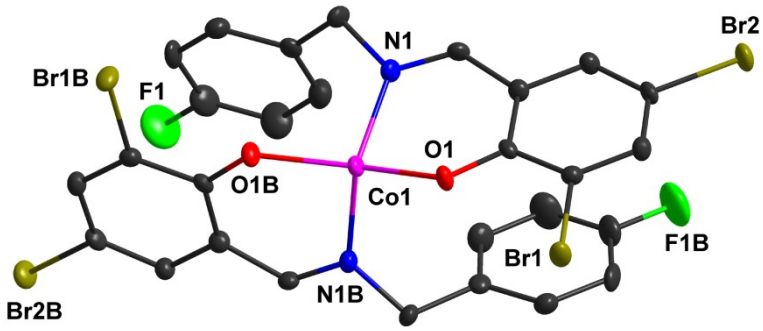
**Fig. S2** Measured (red) and simulated (black) PXRD patterns of complexes **1** (a), **2** (b) and **3** (c).




(a)




(b)




(c)

**Fig. S3** ORTEP views of complexes **1**-**3** (a-c) with displacement ellipsoids drawn at the 50% probability level. C30 in the structure of **2** (b) is severely disordered and was split by OLEX 2. [S1] Symmetric codes: A 1.5-x, y, 0.5-z; B 1-x, y, -z.

**Table S1** Continuous shape measures (CShM) for complexes **1-3**

| | 1 | 3 | | 2 |
|---|---|---|---|---|
| SP-4 | 20.549 | 15.971 | PP-5 | 32.996 |
| T-4 | **3.065** | 4.754 | vOC-5 | 2.889 |
| SS-4 | 4.945 | **3.764** | TBPY-5 | **1.535** |
| vTBPY-4 | 5.759 | 7.252 | SPY-5 | **1.536** |
| | | | JTBPY-5 | 3.305 |
| SP-4 = Square, T-4 = Tetrahedron, SS-4 = Seesaw, vTBPY-4 = Vacant trigonal bipyramid<br>PP-5 = Pentagon, vOC-5 = Vacant octahedron, TBPY-5 = Trigonal bipyramid, SPY-5 = Spherical square pyramid, JTBPY-5 = Johnson trigonal bipyramid J12 | | | | |

**Table S2** Selected bond lengths (Å) and angles (°) for complexes **1-3**

| **1** | | | |
|---|---|---|---|
| Co(1)-O(1)#1 | 1.9235(17) | Co(1)-O(1) | 1.9236(17) |
| Co(1)-N(1)#1 | 2.002(2) | Co(1)-N(1) | 2.002(2) |
| O(1)#1-Co(1)-O(1) | 122.81(11) | O(1)#1-Co(1)-N(1)#1 | 93.15(8) |
| O(1)-Co(1)-N(1)#1 | 109.86(8) | O(1)#1-Co(1)-N(1) | 109.86(8) |
| O(1)-Co(1)-N(1) | 93.15(8) | N(1)#1-Co(1)-N(1) | 131.31(12) |
| **2** | | | |
| Co(1)-O(2) | 1.955(4) | Co(1)-O(1) | 1.957(4) |
| Co(1)-N(3) | 2.049(5) | Co(1)-N(2) | 2.111(4) |
| Co(1)-N(1) | 2.125(5) | O(2)-Co(1)-O(1) | 139.09(16) |
| O(2)-Co(1)-N(3) | 109.45(17) | O(1)-Co(1)-N(3) | 111.42(17) |
| O(2)-Co(1)-N(2) | 89.67(16) | O(1)-Co(1)-N(2) | 86.34(16) |
| N(3)-Co(1)-N(2) | 97.99(17) | O(2)-Co(1)-N(1) | 88.16(16) |
| O(1)-Co(1)-N(1) | 88.20(16) | N(3)-Co(1)-N(1) | 92.97(18) |
| N(2)-Co(1)-N(1) | 168.93(16) | | |
| **3** | | | |
| Co(1)-O(1)#2 | 1.936(4) | Co(1)-O(1) | 1.936(4) |
| Co(1)-N(1)#2 | 2.021(5) | Co(1)-N(1) | 2.021(5) |
| O(1)#2-Co(1)-O(1) | 144.3(3) | O(1)#2-Co(1)-N(1)#2 | 93.10(19) |

| | | | |
|---|---|---|---|
| O(1)-Co(1)-N(1)#2 | 103.72(19) | O(1)#2-Co(1)-N(1) | 103.72(19) |
| O(1)-Co(1)-N(1) | 93.10(19) | N(1)#2-Co(1)-N(1) | 123.3(3) |
| Symmetry codes: #1 -x+3/2, y, -z+1/2; #2 -x+1, y, -z | | | |

**Table S3** Zero field splitting parameters for complexes **1-3** extracted from magnetic data and theoretic calculations.

| | | $D$ / cm$^{-1}$ | $E$ / cm$^{-1}$ | $g_x$ | $g_y$ | $g_z$ | TIP×10$^5$ / cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Experimental | **1** | -27.5 | -2.2 | 2.038 | 2.038 | 2.685 | 66.7 |
| | **2** | -50.9 | 17.3 | 2.133 | 2.133 | 2.573 | - |
| | **3** | -36.9 | 7.0 | $g_{iso}$ = 2.297 | | | 76.1 |
| Theoretic (CASPT2) | **1** | –36.5 | 2.7 | 2.103 | 2.180 | 2.595 | - |
| | **2** | –41.3 | 12.5 | 1.995 | 2.221 | 2.504 | - |
| | **3** | –43.7 | 9.5 | 2.064 | 2.320 | 2.710 | - |
| Theoretic (NEVPT2) | **1** | –34.7 | –2.5 | 2.103 | 2.175 | 2.557 | - |
| | **2** | –44.3 | –14.2 | 1.990 | 2.232 | 2.542 | - |
| | **3** | –46.8 | –7.7 | 2.068 | 2.286 | 2.700 | - |

**Table S4** Calculated spin-free energies (cm$^{-1}$) of the lowest ten terms ($S$ = 3/2) of the Co$^{II}$ ion of complexes **1**−**3** using CASPT2/RASSI-SO with MOLCAS 8.4.

| spin-free states | **1** | **2** | **3** |
|---|---|---|---|
| | $E$/cm$^{-1}$ | $E$/cm$^{-1}$ | $E$/cm$^{-1}$ |
| 1 | 0.0 | 0.0 | 0.0 |
| 2 | 1893.2 | 1969.8 | 1416.6 |
| 3 | 5680.4 | 2400.4 | 2752.1 |
| 4 | 7179.8 | 5186.2 | 4950.7 |
| 5 | 7764.7 | 7453.4 | 5999.5 |
| 6 | 9340.1 | 12273.6 | 10054.6 |
| 7 | 9641.9 | 16890.8 | 10819.2 |
| 8 | 18842.9 | 19328.3 | 17697.9 |

| | | | |
|---|---|---|---|
| 9 | 21643.4 | 20683.4 | 20647.2 |
| 10 | 22628.5 | 24904.7 | 24369.5 |

**Table S5** Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of complexes **1**–**3** using CASPT2/RASSI-SO with MOLCAS 8.4.

| | Spin-orbit states | Energy ($cm^{-1}$) | Spin-free states, Spin, Weights | | | | |
|---|---|---|---|---|---|---|---|
| **1** | 1 | 0.0 | 1,1.5,0.9404 | 2,1.5,0.0548 | 3,1.5,0.0027 | 6,1.5,0.0006 | 4,1.5,0.0003 |
| | 2 | 73.6 | 1,1.5,0.9836 | 2,1.5,0.0075 | 3,1.5,0.0048 | 6,1.5,0.0022 | 17,0.5,0.0007 |
| **2** | 1 | 0.0 | 1,1.5,0.9610 | 2,1.5,0.0234 | 4,1.5,0.0077 | 3,1.5,0.0037 | 5,1.5,0.0020 |
| | 2 | 93.3 | 1,1.5,0.9863 | 2,1.5,0.0050 | 3,1.5,0.0031 | 5,1.5,0.0027 | 4,1.5,0.0018 |
| **3** | 1 | 0.0 | 1,1.5,0.9073 | 2,1.5,0.0771 | 3,1.5,0.0123 | 5,1.5,0.0010 | 4,1.5,0.0005 |
| | 2 | 93.4 | 1,1.5,0.9665 | 2,1.5,0.0156 | 3,1.5,0.0130 | 6,1.5,0.0020 | 5,1.5,0.0008 |

**Table S6** Calculated ZFS parameters $D$, $E$ ($cm^{-1}$) and $\boldsymbol{g}$ ($g_x$, $g_y$, $g_z$) tensors of complexes **1**–**3** using CASPT2 and NEVPT2 with MOLCAS 8.4 and ORCA 4.2, respectively.

| complexes | CASPT2 | | | | | NEVPT2 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $D_{cal}$ | $E_{cal}$ | $g_x$ | $g_y$ | $g_z$ | $D_{cal}$ | $E_{cal}$ | $g_x$ | $g_y$ | $g_z$ |
| **1** | –36.5 | 2.7 | 2.103 | 2.180 | 2.595 | –34.7 | –2.5 | 2.103 | 2.175 | 2.557 |
| **2** | –41.3 | 12.5 | 1.995 | 2.221 | 2.504 | –44.3 | –14.2 | 1.990 | 2.232 | 2.542 |
| **3** | –43.7 | 9.5 | 2.064 | 2.320 | 2.710 | –46.8 | –7.7 | 2.068 | 2.286 | 2.700 |

**Table S7** Contribution of the excited states (with relative energy E, $cm^{-1}$) to $D$ values ($cm^{-1}$) for complexes **1**–**3** using NEVPT2 with ORCA 4.2.

| complexes | State No. | Mult | Energy, $cm^{-1}$ | Contribution, $cm^{-1}$ |
|---|---|---|---|---|
| | | | | $D$ |
| **1** | 1 | 4 | 1728.4 | –51.3 |
| | 2 | 4 | 4651.6 | 8.7 |
| | 4 | 4 | 7756.1 | 5.8 |
| **2** | 1 | 4 | 1571.8 | –13.5 |

| | | | | |
|---|---|---|---|---|
| | 3 | 4 | 3904.7 | –12.2 |
| | 4 | 4 | 6388.6 | –8.2 |
| **3** | 1 | 4 | 1396.9 | –55.1 |
| | 2 | 4 | 2406.6 | 3.9 |
| | 5 | 4 | 8483.1 | 5.4 |

**Table S8** Relative energies ($cm^{-1}$) of ligand field one-electron states (in the basis of d-AOs) of complexes **1**–**3** from AILFT analysis using NEVPT2 with ORCA 4.2.

| complexes | No. | LF one-electron state | Energy, $cm^{-1}$ |
|---|---|---|---|
| **1** | 1 | $-0.95\ d_{z2} - 0.31\ d_{x2-y2}$ | 0.0 |
| | 2 | $0.90\ d_{x2-y2} - 0.31\ d_{z2} + 0.30\ d_{xy}$ | 1537.8 |
| | 3 | $-1.0\ d_{yz}$ | 1694.6 |
| | 4 | $1.0\ d_{xz}$ | 5607.6 |
| | 5 | $0.95\ d_{xy} - 0.30\ d_{x2-y2}$ | 9215.8 |
| **2** | 1 | $0.99\ d_{yz}$ | 0.0 |
| | 2 | $-0.99\ d_{xz}$ | 1482.5 |
| | 3 | $0.99\ d_{xy}$ | 2767.6 |
| | 4 | $0.91\ d_{x2-y2} + 0.39\ d_{z2}$ | 4715.0 |
| | 5 | $0.91\ d_{z2} - 0.40\ d_{x2-y2}$ | 11317.4 |
| **3** | 1 | $-0.97\ d_{z2} - 0.25\ d_{x2-y2}$ | 0.0 |
| | 2 | $0.74\ d_{yz} - 0.68\ d_{xz}$ | 1852.5 |
| | 3 | $-0.79\ d_{xy} - 0.59\ d_{x2-y2}$ | 2562.7 |
| | 4 | $-0.74\ d_{xz} - 0.68\ d_{yz}$ | 4181.6 |
| | 5 | $0.77\ d_{x2-y2} - 0.61\ d_{xy}$ | 11253.6 |

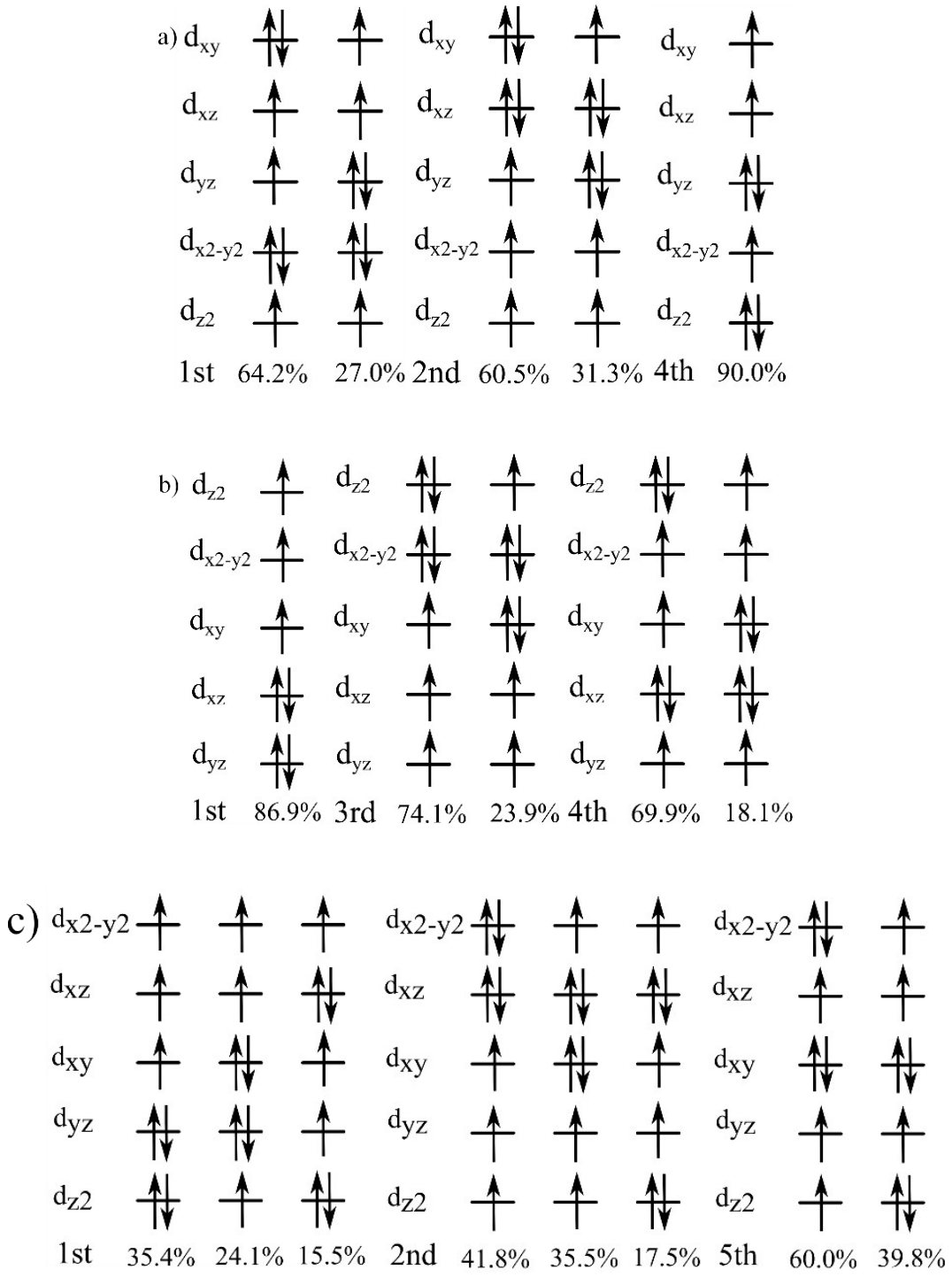
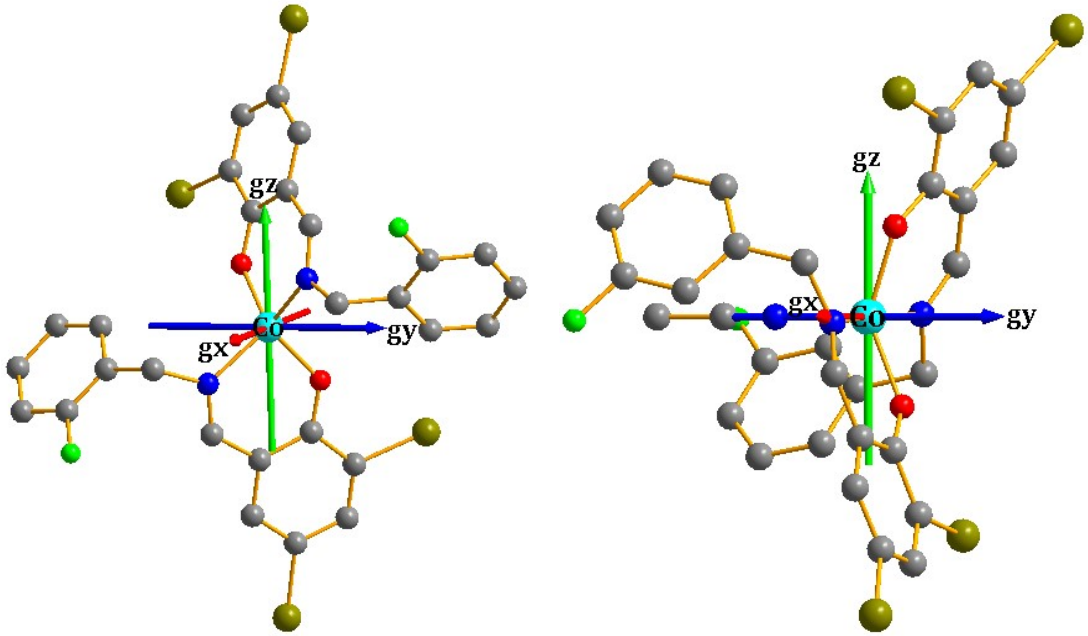
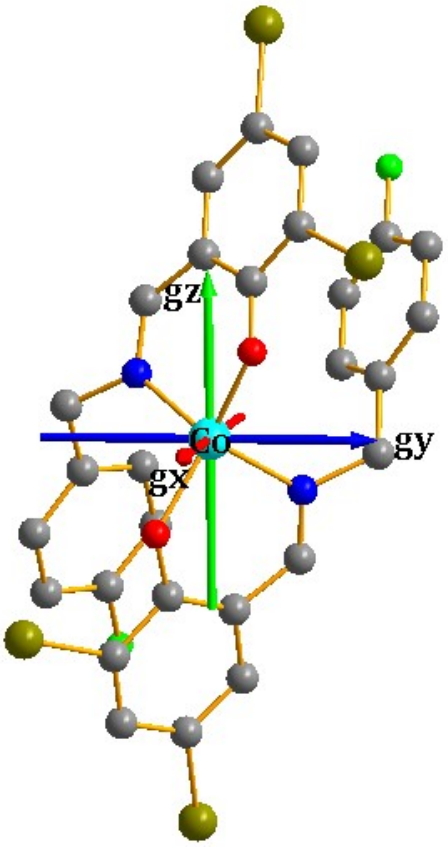



**Fig. S4** (a-c) Multi-determinant wavefunction of the selected excited states having important contributions to *D* tensor for complex **1**–**3**. The computed CI coefficients that are larger than 10% are shown above.

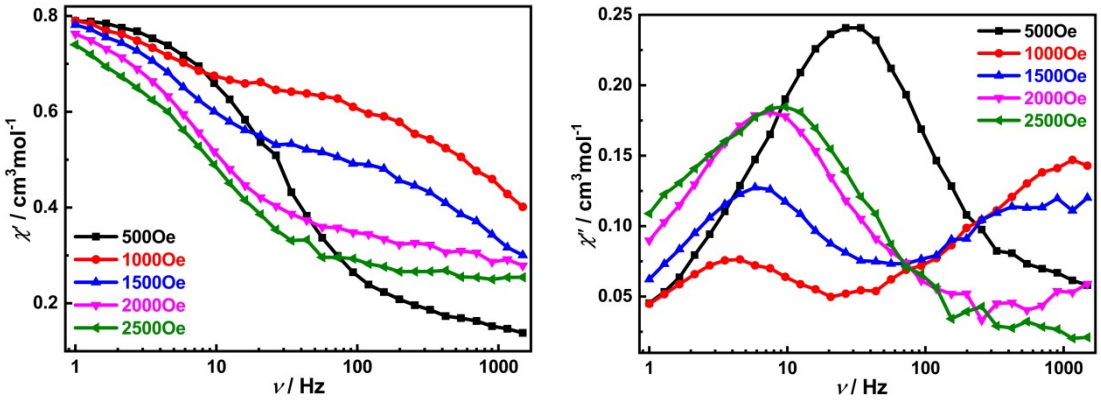



(a) (b)



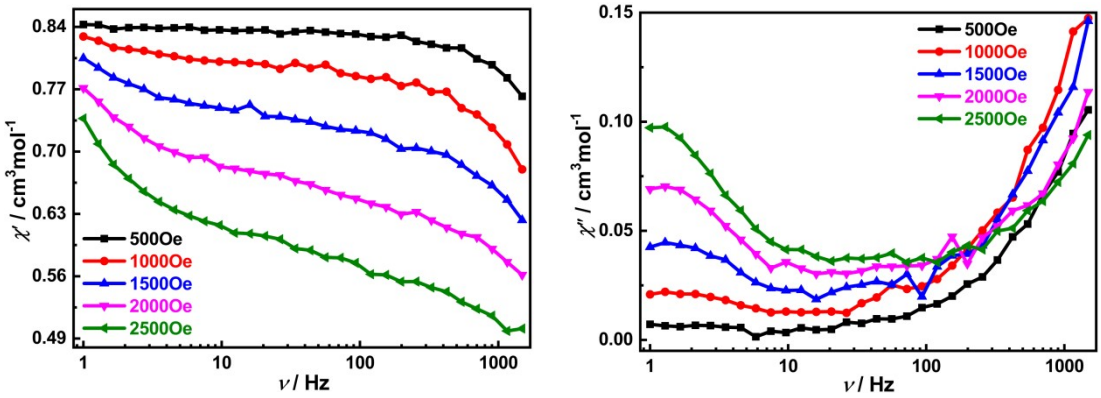

(c)

**Fig. S5** Orientations of the local magnetic axes (red: $g_x$; blue: $g_y$; green: $g_z$) on Co(II) ions of **1**–**3** in their ground spin-orbit states.



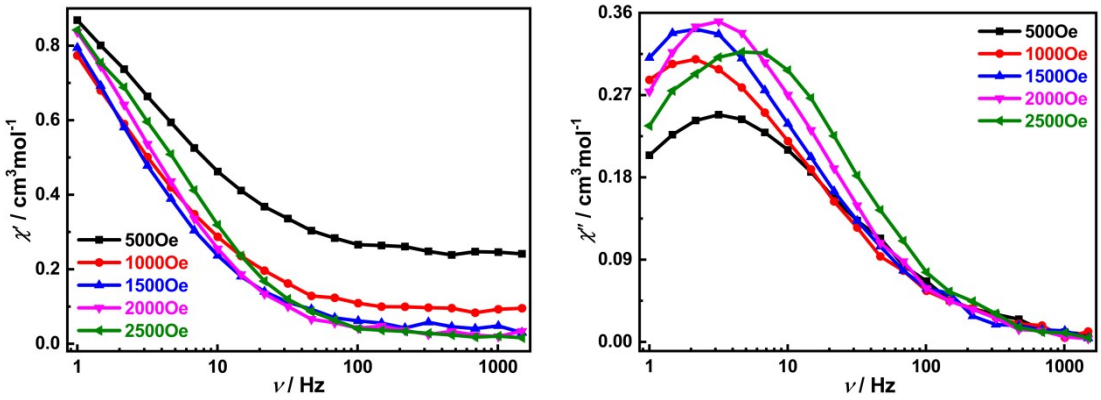

(a) (b)

**Fig. S6** Frequency dependence of in-phase (a) and out-of-phase (b) ac susceptibility under various dc fields at 2 K for **1**.




(a) (b)

**Fig. S7** Frequency dependence of in-phase (a) and out-of-phase (b) ac susceptibility under various dc fields at 2 K for **2**.




(a) (b)

**Fig. S8** Frequency dependence of in-phase (a) and out-of-phase (b) ac susceptibility under various dc fields at 2 K for **3**.

**Table S9** Cole-Cole parameters of **1** at 1000 Oe dc field

| T / K | $\chi_S$ / $cm^{-3}mol^{-1}$ | $\Delta\chi_1$ / $cm^{-3}mol^{-1}$ | $\tau_1$ / s | $\alpha_1$ | $\Delta\chi_2$ / $cm^{-3}mol^{-1}$ | $\tau_2$ / s | $\alpha_2$ | $R$ |
|---|---|---|---|---|---|---|---|---|
| 2 | 1.64E-01 | 5.20E-01 | 1.16 E-04 | 3.71 E-01 | 1.58E-01 | 4.52 E-02 | 8.83E-02 | 3.40E-04 |
| 2.3 | 8.89E-02 | 5.22E-01 | 8.38 E-05 | 3.96 E-01 | 1.56E-01 | 3.21 E-02 | 8.47E-02 | 1.25E-03 |
| 2.6 | 1.24E-07 | 5.65E-01 | 5.31 E-05 | 4.86 E-01 | 1.26E-01 | 1.89 E-02 | 7.61E-15 | 4.90E-04 |
| 2.9 | 2.30E-07 | 5.07E-01 | 5.52 E-05 | 4.56 E-01 | 1.30E-01 | 9.20 E-03 | 2.64E-15 | 4.30E-04 |
| 3.2 | 3.06E-07 | 4.51E-01 | 5.33 E-05 | 4.22 E-01 | 1.36E-01 | 4.16 E-03 | 4.03E-15 | 4.19E-04 |
| 3.5 | 2.12E-08 | 3.92E-01 | 4.16 E-05 | 3.78 E-01 | 1.54E-01 | 1.90 E-03 | 1.32E-14 | 1.04E-03 |
| 3.8 | 1.70E-08 | 3.39E-01 | 3.60 E-05 | 3.25 E-01 | 1.70E-01 | 9.95 E-04 | 2.35E-14 | 4.22E-04 |
| 4.1 | 2.45E-08 | 2.97E-01 | 3.03 E-05 | 2.82 E-01 | 1.81E-01 | 5.70 E-04 | 3.41E-14 | 6.65E-04 |
| 4.4 | 5.04E-08 | 2.67E-01 | 2.68 E-05 | 2.72 E-01 | 1.84E-01 | 3.39 E-04 | 3.63E-14 | 3.09E-04 |
| 4.7 | 7.44E-08 | 2.46E-01 | 2.45 E-05 | 2.00 E-01 | 1.79E-01 | 2.28 E-04 | 6.24E-14 | 5.22E-04 |

**Table S10** Cole-Cole parameters of **3** at 1500 Oe dc field

| $T$ / K | $\chi_S$ / $cm^{-3}mol^{-1}$ | $\chi_T$ / $cm^{-3}mol^{-1}$ | $\tau$ / s | $\alpha$ | $R$ |
|---|---|---|---|---|---|
| 1.9 | 2.86E-02 | 1.29E+00 | 8.35E-02 | 2.77E-01 | 1.47E-03 |
| 2.2 | 2.36E-02 | 1.09E+00 | 5.89E-02 | 2.62E-01 | 1.35E-03 |
| 2.5 | 2.70E-02 | 9.37E-01 | 4.18E-02 | 2.29E-01 | 2.44E-03 |
| 2.8 | 2.85E-02 | 8.29E-01 | 2.84E-02 | 1.99E-01 | 1.75E-03 |
| 3.1 | 2.97E-02 | 7.32E-01 | 1.82E-02 | 1.54E-01 | 1.51E-03 |
| 3.4 | 3.01E-02 | 6.62E-01 | 1.11E-02 | 1.17E-01 | 1.87E-03 |
| 3.7 | 2.47E-02 | 6.03E-01 | 6.49E-03 | 8.45E-02 | 1.32E-03 |

| | | | | | |
|---|---|---|---|---|---|
| 4 | 3.02E-02 | 5.56E-01 | 3.86E-03 | 5.25E-02 | 1.12E-03 |
| 4.3 | 2.72E-02 | 5.19E-01 | 2.32E-03 | 4.15E-02 | 1.11E-03 |
| 4.6 | 2.64E-02 | 4.86E-01 | 1.42E-03 | 3.28E-02 | 7.07E-04 |
| 4.9 | 2.60E-02 | 4.58E-01 | 8.92E-04 | 3.11E-02 | 5.43E-04 |
| 5.2 | 2.15E-02 | 4.33E-01 | 5.68E-04 | 2.72E-02 | 6.59E-04 |
| 5.5 | 2.43E-02 | 4.10E-01 | 3.81E-04 | 1.94E-02 | 7.31E-04 |
| 5.8 | 1.95E-02 | 3.90E-01 | 2.46E-04 | 2.49E-02 | 1.15E-03 |
| 6.1 | 2.00E-02 | 3.72E-01 | 1.68E-04 | 3.29E-02 | 7.23E-04 |
| 6.4 | 6.14E-03 | 3.54E-01 | 1.15E-04 | 3.56E-02 | 5.31E-04 |
| 6.7 | 7.68E-06 | 3.40E-01 | 8.04E-05 | 3.80E-02 | 3.82E-04 |
| 7 | 2.74E-15 | 3.25E-01 | 5.87E-05 | 2.05E-02 | 5.71E-04 |
| 7.3 | 4.97E-15 | 3.13E-01 | 4.54E-05 | 1.01E-14 | 1.53E-03 |
| 7.6 | 7.88E-15 | 3.00E-01 | 3.17E-05 | 1.32E-14 | 4.84E-04 |

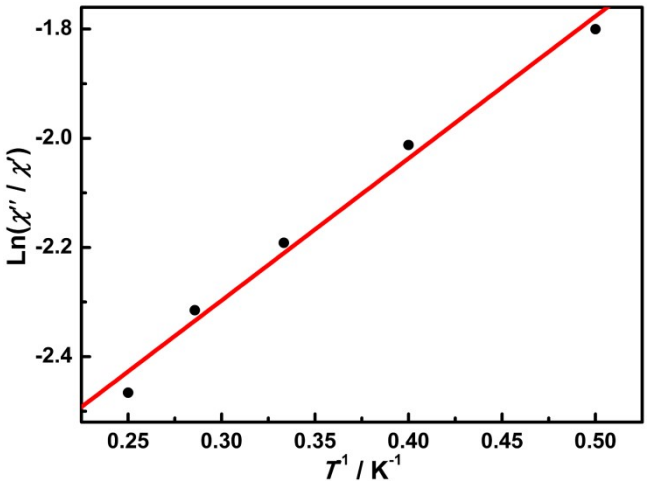



**Fig. S9** Ln($\chi''/\chi'$) versus $T^{-1}$ plots of **2** at frequency of 901Hz. The solid line is the best-fit curve.

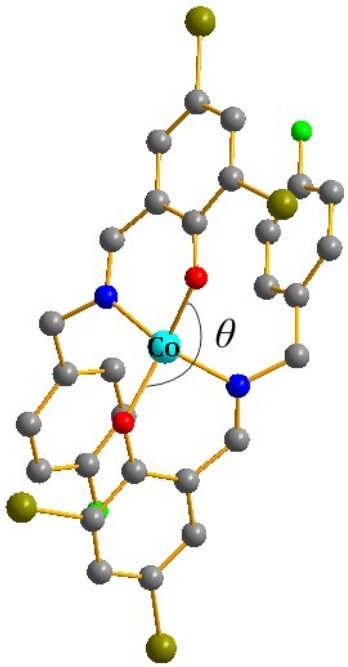



**Fig. S10** Included $\theta$ angle between $Co^{II}$ and O atoms.

**Table S11** Calculated ZFS parameters $D$, $E$ ($cm^{-1}$) and $\boldsymbol{g}$ ($g_x$, $g_y$, $g_z$) tensors of complex **3** with the angle of O-Co-O ranging from 144 to 180 degrees using CASPT2/RASSI-SO with MOLCAS 8.4.

| $\theta$ | $D_{cal}$ | $E_{cal}$ | $g_x$ | $g_y$ | $g_z$ |
|---|---|---|---|---|---|
| 144° | –43.7 | 9.5 | 2.064 | 2.320 | 2.710 |
| 150° | –42.2 | 8.3 | 2.063 | 2.304 | 2.688 |
| 160° | –45.4 | 8.4 | 2.054 | 2.311 | 2.710 |
| 170° | –50.3 | 9.4 | 2.042 | 2.329 | 2.763 |
| 180° | –60.1 | 11.0 | 2.024 | 2.347 | 2.873 |

**Table S12** Coordination environment and magnetic parameters of four coordinated Co(II) complexes with both N and O donors.

| Compound | Donor set | Geometry | $D$ / $cm^{-1}$ | $E$ / $cm^{-1}$ | Dc field / Oe | $U_{eff}$ / K | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | $CoN_2O_2$ | tetrahedron | -27.5 | -2.2 | 1000 | 28.4 | This work |
| 3 | $CoN_2O_2$ | seesaw | -36.9 | 7.0 | 1500 | 48.9 | |
| $[Co(L_1)_2]$ | $CoN_2O_2$ | tetrahedron | -49.9 | 6.3 | 2000 | 54.9 | S2 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[Co(L_1)_2]\cdot C_2H_5OH$ | $CoN_2O_2$ | tetrahedron | -19.3 | -0.05 | 0 | 48 | S3 |
| $[Co(L_2)_2]\cdot C_2H_5OH$ | $CoN_2O_2$ | tetrahedron | -19.2 | 1.2 | 0 | 42 | |
| $[Co(L^1)_2]$ | $CoN_2O_2$ | tetrahedron | -41 | / | 400 | 49 | S4 |
| | | | | | 1000 | 89 | |
| $[Co(L^2)_2]$ | $CoN_2O_2$ | tetrahedron | -35 | / | / | / | |
| $[Co(L^{Br})_2]$ | $CoN_2O_2$ | tetrahedron | -36.7 | / | 400 | 52 | S5 |
| $[Co(L^{Ph})_2]\cdot CH_2Cl_2$ | $CoN_2O_2$ | tetrahedron | -39.8 | / | 400 | 62 | |
| $Co(hpbdti)_2\cdot 3CH_3OH$ | $CoN_2O_2$ | tetrahedron | / | / | 2000 | 56.7 | S6 |
| $Co(BrL)_2\cdot 3CH_3OH$ | $CoN_2O_2$ | tetrahedron | -44 | ≤0.01 | 2000 | 18.4 | S7 |
| $Co(PL)_2\cdot 2CH_3OH$ | $CoN_2O_2$ | tetrahedron | -50 | ≤0.01 | 400 | 50.4 | |
| $[Co(L^{Sal,2\text{-}Ph})_2]$ | $CoN_2O_2$ | tetrahedron | -25.1 | / | 400 | 48 | S8 |
| $[Co(L^{Nph,2\text{-}Ph})_2]$ | $CoN_2O_2$ | tetrahedron | -31.4 | / | 400 | 76 | |
| $[Co(Himl)_2]\cdot CH_3OH$ | $CoN_2O_2$ | tetrahedron | -42 | / | 1400 | / | S9 |
| $[Co(Himn)_2]$ | $CoN_2O_2$ | tetrahedron | -38 | / | 0 | / | |
| $[Co(Hthp)_2]$ | $CoN_2O_2$ | tetrahedron | -35 | / | 0 | 89 | |

**Table S13** Coordination environment and magnetic parameters of five coordinated Co(II) complexes with intermediate coordination geometry in between trigonal bipyramid and square pyramid.

| Compound | Donor set | Addision parameter ($\tau$) | $D$ / $cm^{-1}$ | $E$ / $D$ | Dc field / Oe | $U_{eff}$ / K | Ref. |
|---|---|---|---|---|---|---|---|
| 2 | $CoN_3O_2$ | 0.497 | -50.9 | 0.334 | 1000 | 2.6 | This work |
| $[CoCl_2L^{C12}]_\infty$ | $CoN_3Cl_2$ | 0.41 | 46.8 | / | 2000 | 40.5 | S10 |
| [Co(terpy)(NCS)$_2$] | $CoN_5$ | 0.43 | / | / | 5600 | 17 | S11 |
| $[Co(L3A)Cl_2]$ | $CoN_3Cl_2$ | 0.38 | 45.7 | 0.24 | / | / | S12 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| [Co(pypz)(NCO)$_2$] | $CoN_5$ | 0.46 | 30 | / | 2000 | 25.3 | S13 |
| [Co(dpt)(NCS)$_2$] | $CoN_5$ | 0.46 | 36.2 | 0.33 | 3000 | / | S14 |
| [Co(L)$Cl_2$] | $CoN_3Cl_2$ | 0.46 | 26 | 0.333 | 1500 | 18.9 | S15 |
| [Co(L)$Br_2$] | $CoN_3Br_2$ | 0.41 | 39.2 | 0.333 | 500/1250 | 19.1/20.1 | S15 |
| [Co(phen)(DMSO)$Cl_2$] | $CoN_2OCl_2$ | 0.54 | -17 | 0.24 | 1000 | 40.3 | S16 |
| [Co(dmbpy)$_2$($H_2O$)](ClO4)$_2$ | $CoN_4O$ | 0.44 | 35.8 | / | 1000/2500 | / | S17 |
| [Co($Me_4$cyclam)$N_3$]$ClO_4$ | CoN5 | 0.48 | 20-60 | ≤ 0.2 | / | / | S18 |

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