*Supporting information for*

# Mixed-Valence Metallogrid [$Co^{III}_2Co^{II}_2$] with Unusual Electronic Structure and Single-Ion-Magnet Characterization

Wei Huang,[a] Feifei Pan,[a] Zhenxing Wang,[b] Yan Bai,[c] Xuejun Feng,*[a] Jiande Gu,[a] Zhong-Wen Ouyang[b] and Dayu Wu*[a]

[a] Key Laboratory of Advanced Catalytic Materials and Technology, Collaborative Innovation Center of Advanced Catalysis & Green Manufacturing, School of Petrochemical Engineering, Changzhou University, 213164, China

[b] Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, 430074 Wuhan, China

[c] Key Laboratory of Polyoxometalate Chemistry of Henan Province, School of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, People's Republic of China.

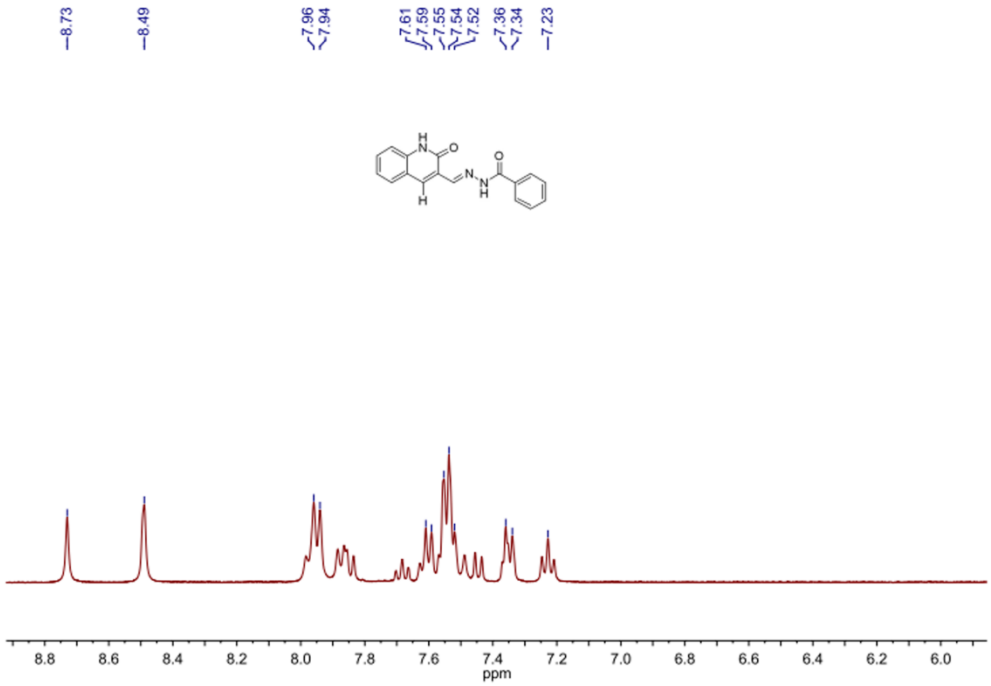


**Figure S1**. The $^{1}$H NMR spectra of ligand L in DMSO-$d^{6}$.

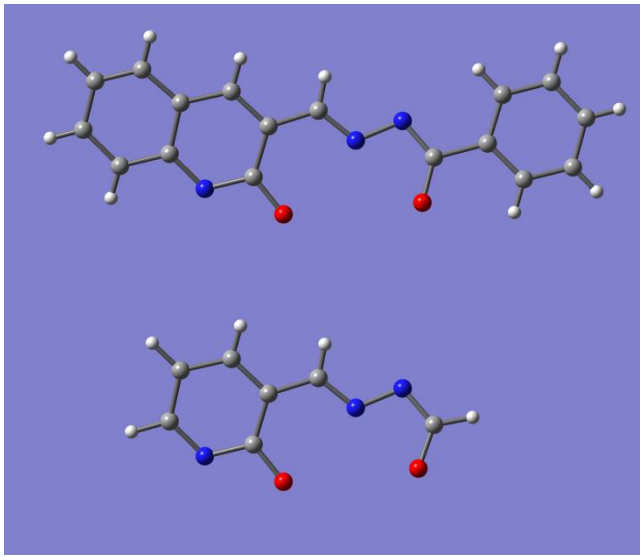

**Figure S2**. Ligand L and the simplified L. Color legend: red for O, grey for C, blue for N, and white for H.

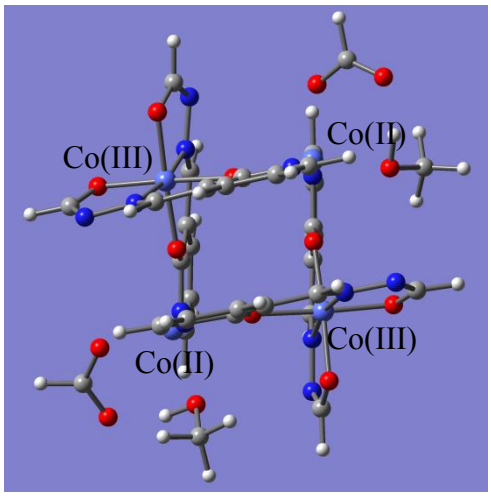


**Figure S3**. The optimized structure of the model. Color legend: light blue for Co, others see Fig. S3.

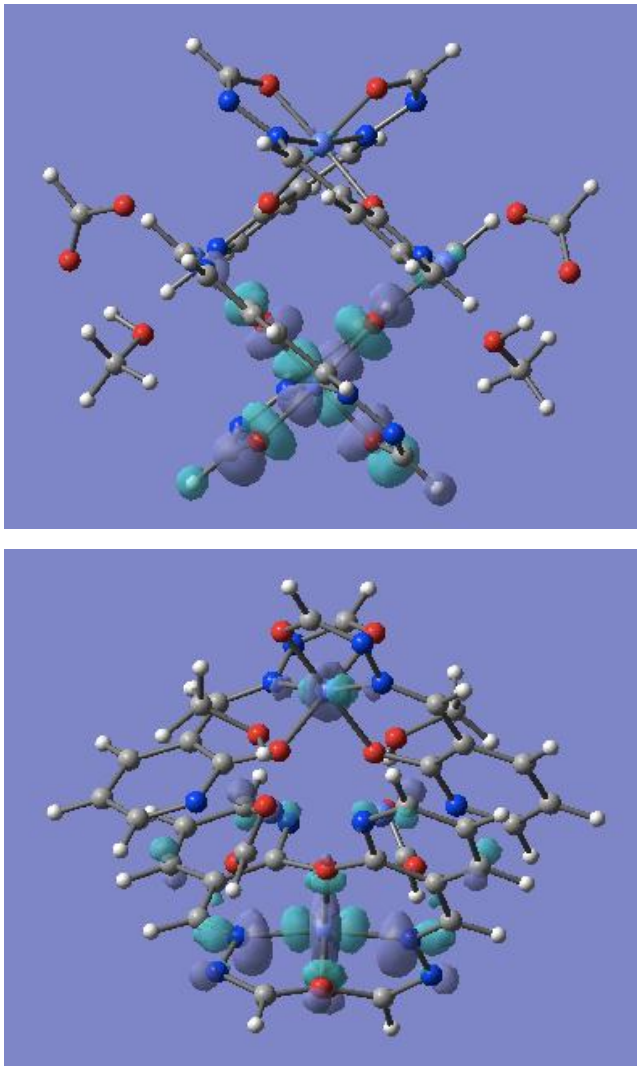

**Figure S4**. The unoccupied $dx^2$-$y^2$ (top) and $dz^2$ (below) MO of Co(III).

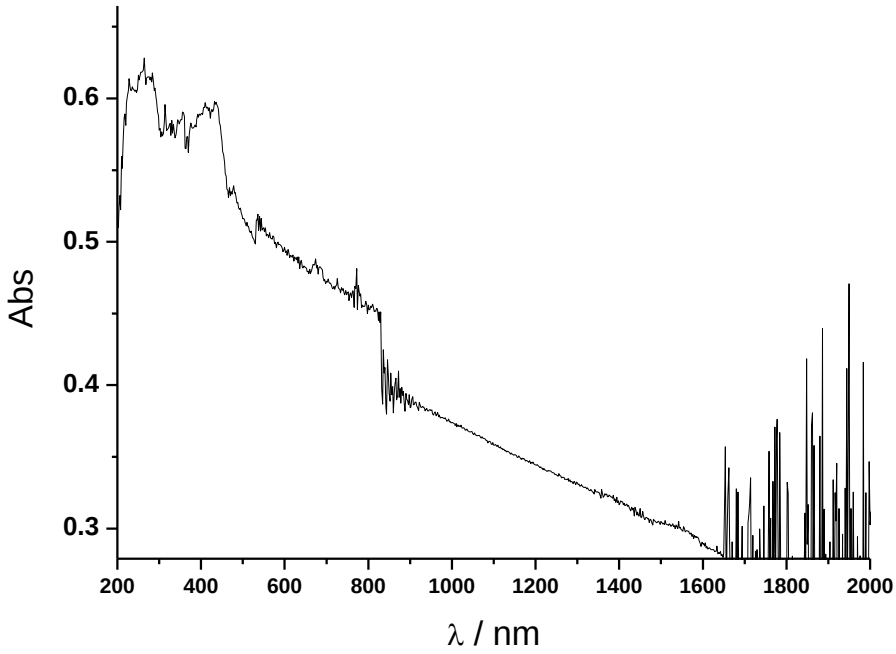


**Figure S5**. The UV-vis-NIR spectra of compound **1** in solid state.

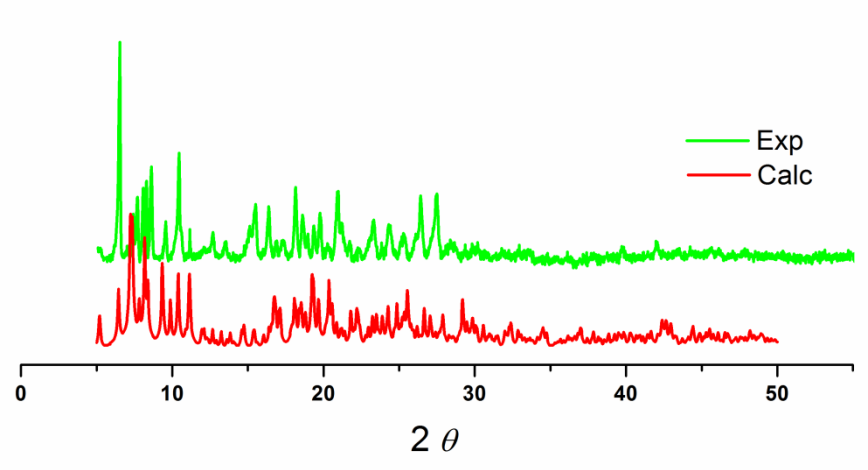


**Figure S6**. The experimental and calculated powder X-ray diffraction pattern of **1**.

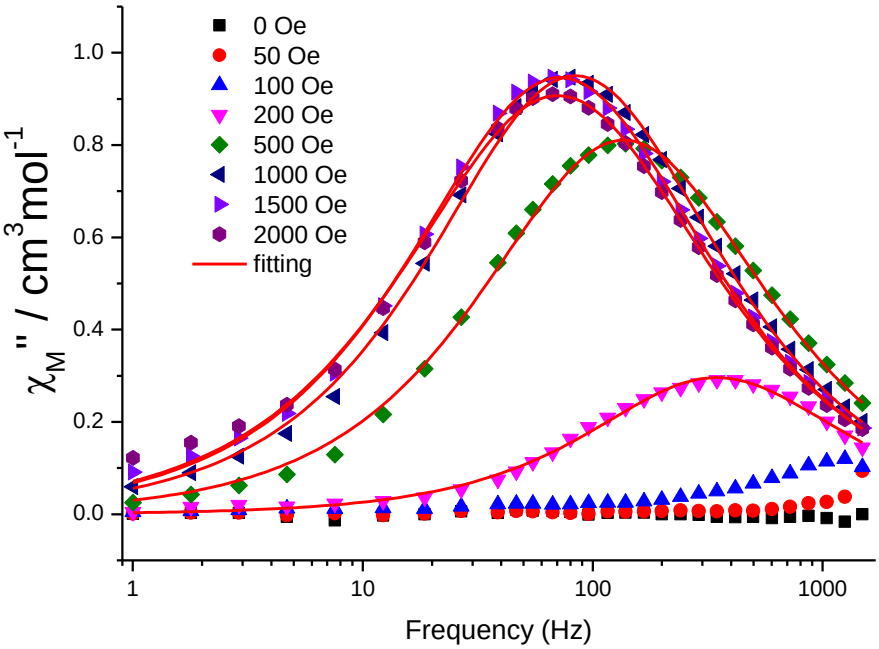


**Figure S7**. Frequency dependence of out-of-phase a*c* signal at different applied *dc* fields of **1**. The red lines are the best fit according to the generalized Debye model.

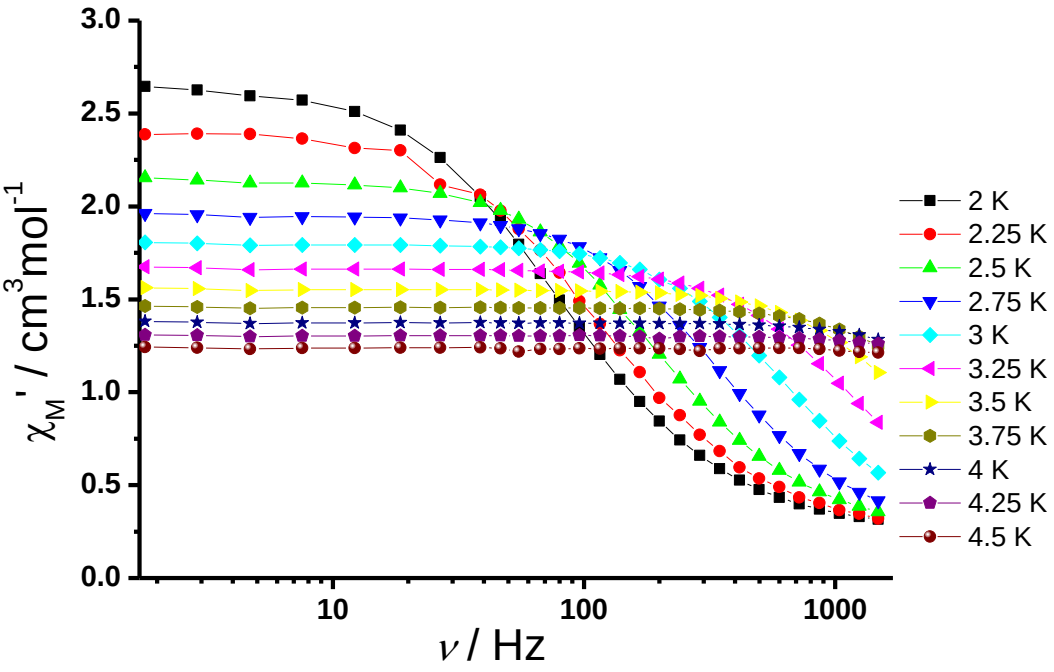


**Figure S8**. The in-phase $\chi'_M$ components of the ac magnetic susceptibility for **1** under 1000 Oe dc field. The solid lines are guided for eyes.

Table S1. Selected bond lengths(Å) and bond angles(°) in complex **1**

| | | | |
|---|---|---|---|
| Co1-O3 | 1.856(4) | Co1-N11 | 1.860(4) |
| Co1-N5 | 1.892(4) | Co1-O4 | 1.899(3) |
| Co1-O7 | 1.876(3) | Co1-O8 | 1.917(4) |
| Co2-O12 | 1.985(4) | Co2-N6 | 2.033(4) |
| Co2-N7 | 2.044(4) | Co2-O14 | 2.065 (4) |
| Co2-O4 | 2.354(3) | Co3-N9 | 1.878(4) |
| Co3-O1 | 1.885(4) | Co3-N2 | 1.892(4) |
| Co3-O6 | 1.886(3) | Co3-O2 | 1.8947(16) |
| Co3-O5 | 1.914(3) | Co4-O9 | 1.981(4) |
| Co4-O10 | 2.007(2) | Co4-N12 | 2.028(5) |
| Co4-N3 | 2.032(4) | O3-Co1-N11 | 88.53(9) |
| O3-Co1-O7 | 93.38(8) | N11-Co1-O7 | 83.27(9) |
| O3-Co1-N5 | 83.14(9) | N11-Co1-N5 | 169.68(9) |
| O7-Co1-N5 | 91.12(9) | O3-Co1-O4 | 178.11(9) |
| N11-Co1-O4 | 92.72(9) | O4-Co1-O7 | 88.18(8) |
| N5-Co1-O4 | 95.76(9) | O3-Co1-O8 | 89.64(9) |
| N11-Co1-O8 | 94.84(10) | O7-Co1-O8 | 176.39(7) |
| N5-Co1-O8 | 91.21(9) | O4-Co1-O8 | 88.84(8) |
| O12-Co2-N6 | 97.78(9) | O12-Co2-N7 | 111.17(9) |
| N6-Co2-N7 | 138.69(10) | O12-Co2-O14 | 94.67(8) |
| N6-Co2-O14 | 107.45(9) | N7-Co2-O14 | 99.11(8) |
| O12-Co2-O4 | 88.46(7) | N6-Co2-O4 | 59.63(8) |
| N7-Co2-O4 | 91.42(8) | O14-Co2-O4 | 167.05(8) |
| N9-Co3-O1 | 90.80(9) | N9-Co3-N2 | 171.27(9) |
| O1-Co3-N2 | 84.37(9) | N9-Co3-O6 | 82.46(9) |
| O1-Co3-O6 | 90.15(8) | N2-Co3-O6 | 90.27(9) |
| N9 Co3 O2 | 90.10(9) | O1-Co3-O2 | 177.78(9) |
| N2-Co3-O2 | 94.99(9) | O6-Co3-O2 | 91.98(8) |
| N9-Co3-O5 | 96.07(9) | O1-Co3-O5 | 88.88(8) |
| N2-Co3-O5 | 91.11(9) | O6-Co3-O5 | 178.23(8) |
| O2-Co3-O5 | 89.01(8) | O9-Co4-O10 | 93.44(10) |
| O9-Co4-N12 | 112.01(10) | O10-Co4-N12 | 95.54(10) |
| O9-Co4-N3 | 100.73(11) | O10-Co4-N3 | 112.91(10) |
| N12-Co4-N3 | 135.00(11) | | |

Table S2. The total energy (in Hartree) and the cartesian coordinates for the optimised structure of the complex **1**.

HF=-8478.10516

| | | | |
|---|---|---|---|
| Co | 0.000000 | -0.000000 | -2.729199 |
| Co | -0.149746 | -2.875575 | -0.101214 |
| Co | 0.149746 | 2.875575 | -0.101214 |
| C | -2.997926 | -0.530874 | 1.463494 |
| C | -4.284356 | -0.889979 | 1.041079 |
| H | -5.130815 | -0.306448 | 1.404123 |
| C | -4.483626 | -1.947705 | 0.163186 |
| C | -3.366064 | -2.637702 | -0.295089 |
| C | -1.919239 | -1.316042 | 0.975086 |
| C | 2.808628 | -0.584642 | 2.341622 |
| H | 3.674855 | -1.175144 | 2.651836 |
| C | 2.997926 | 0.530874 | 1.463494 |
| C | 4.284356 | 0.889979 | 1.041079 |
| C | 5.130815 | 0.306448 | 1.404123 |
| C | 4.483626 | 1.947705 | 0.163186 |
| C | 3.366064 | 2.637702 | -0.295089 |
| C | 1.919239 | 1.316042 | 0.975086 |
| C | 2.849814 | 0.275706 | -2.491388 |
| H | 3.767899 | 0.782583 | -2.799969 |
| C | 2.937290 | -0.885793 | -1.657319 |
| C | 4.189104 | -1.388934 | -1.278750 |
| H | 5.083200 | -0.891728 | -1.656270 |
| C | 4.297579 | -2.479838 | -0.427270 |
| C | 3.125111 | -3.063636 | 0.042617 |
| C | 1.798008 | -1.563058 | -1.148912 |
| C | -0.564538 | -2.062091 | -4.213946 |
| C | -2.849814 | -0.275706 | -2.491388 |
| H | -3.767899 | -0.782583 | -2.799969 |
| C | -2.937290 | 0.885793 | -1.657319 |
| C | -4.189104 | 1.388934 | -1.278750 |
| C | -4.297579 | 2.479838 | -0.427270 |
| C | -3.125111 | 3.063636 | 0.042617 |
| C | -1.798008 | 1.563058 | -1.148912 |
| C | -1.183008 | -4.487715 | 2.247831 |
| H | -0.930167 | -5.148406 | 3.086356 |
| H | -1.842231 | -5.025097 | 1.550600 |
| H | -1.709419 | -3.610023 | 2.635924 |
| C | 0.331302 | -5.540803 | -1.045793 |
| N | -2.128829 | -2.328135 | 0.100142 |
| N | 1.651294 | -0.931553 | 2.812852 |
| N | 2.128829 | 2.328135 | 0.100142 |
| N | 1.725971 | 0.772391 | -2.903317 |
| N | 1.918574 | -2.615335 | -0.311135 |
| N | -1.760275 | -1.898186 | -3.697004 |
| N | -1.725971 | -0.772391 | -2.903317 |
| N | -1.918574 | 2.615335 | -0.311135 |
| O | -0.655656 | -1.177146 | 1.264905 |
| O | 0.655656 | 1.177146 | 1.264905 |
| O | -0.461125 | 1.307683 | -4.015869 |
| O | 0.542894 | -1.265012 | -1.380028 |
| O | 0.461125 | -1.307683 | -4.015869 |
| O | -0.542894 | 1.265012 | -1.380028 |
| O | 0.000000 | -4.031942 | 1.608964 |

| | | | |
|---|---|---|---|
| H | 0.452459 | -4.821361 | 1.166472 |
| O | 0.918290 | -5.870155 | 0.001411 |
| O | -0.319509 | -4.463451 | -1.269964 |
| O | -0.000000 | 4.031942 | 1.608964 |
| Co | -0.000000 | 0.000000 | 2.632395 |
| C | -0.398127 | 2.045111 | 4.197728 |
| C | -2.808628 | 0.584642 | 2.341622 |
| H | -3.674855 | 1.175144 | 2.651836 |
| C | 0.398127 | -2.045111 | 4.197728 |
| N | -1.604047 | 1.993379 | 3.686726 |
| N | -1.651294 | 0.931553 | 2.812852 |
| N | 1.604047 | -1.993379 | 3.686726 |
| O | 0.581058 | 1.248347 | 3.934017 |
| O | -0.581058 | -1.248347 | 3.934017 |
| C | 1.183008 | 4.487715 | 2.247831 |
| H | 1.842231 | 5.025097 | 1.550600 |
| H | 1.709419 | 3.610023 | 2.635924 |
| H | 0.930167 | 5.148406 | 3.086356 |
| C | 0.564538 | 2.062091 | -4.213946 |
| C | -0.331302 | 5.540803 | -1.045793 |
| N | 1.760275 | 1.898186 | -3.697004 |
| O | -0.918290 | 5.870155 | 0.001411 |
| O | 0.319509 | 4.463451 | -1.269964 |
| H | -0.452459 | 4.821361 | 1.166472 |
| H | -5.083200 | 0.891728 | -1.656270 |
| H | -0.432200 | -2.912268 | -4.886810 |
| H | -3.131428 | 3.918766 | 0.717283 |
| H | -5.265610 | 2.874959 | -0.132675 |
| H | -0.340474 | 6.252052 | -1.896999 |
| H | 0.340474 | -6.252052 | -1.896999 |
| H | -5.479564 | -2.229937 | -0.166422 |
| H | -3.438468 | -3.457849 | -1.009098 |
| H | -0.208801 | 2.839052 | 4.924894 |
| H | 0.208801 | -2.839052 | 4.924894 |
| H | 0.432200 | 2.912268 | -4.886810 |
| H | 5.479564 | 2.229937 | -0.166422 |
| H | 3.438468 | 3.457849 | -1.009098 |
| H | 5.265610 | -2.874959 | -0.132675 |
| H | 3.131428 | -3.918766 | 0.717283 |

Table S3. The Mullican charge and spin for the optimised structure of the complex **1**.

| | | Charge | SPIN |
|---|---|---|---|
| 1 | Co | 1.186789 | 0.020614 |
| 2 | Co | 1.128336 | 2.807811 |
| 3 | Co | 1.128336 | 2.807811 |
| 4 | C | 0.041890 | 0.001626 |
| 5 | C | -0.169325 | -0.017909 |
| 6 | H | 0.184066 | 0.001287 |
| 7 | C | -0.253163 | 0.010145 |
| 8 | C | 0.041428 | -0.019574 |
| 9 | C | 0.665470 | -0.005490 |
| 10 | C | 0.041061 | 0.001522 |
| 11 | H | 0.194109 | 0.000045 |
| 12 | C | 0.041890 | 0.001626 |
| 13 | C | -0.169325 | -0.017909 |
| 14 | H | 0.184066 | 0.001287 |
| 15 | C | -0.253163 | 0.010145 |
| 16 | C | 0.041428 | -0.019574 |
| 17 | C | 0.665470 | -0.005490 |
| 18 | C | 0.044365 | 0.001912 |
| 19 | H | 0.191301 | -0.000055 |
| 20 | C | 0.043118 | 0.000215 |
| 21 | C | -0.168234 | -0.013596 |
| 22 | H | 0.182463 | 0.001012 |
| 23 | C | -0.253795 | 0.008178 |
| 24 | C | 0.051039 | -0.014913 |
| 25 | C | 0.688231 | -0.001001 |
| 26 | C | 0.328463 | -0.000501 |
| 27 | C | 0.044365 | 0.001912 |
| 28 | H | 0.191301 | -0.000055 |
| 29 | C | 0.043118 | 0.000215 |
| 30 | C | -0.168234 | -0.013596 |
| 31 | C | -0.253795 | 0.008178 |
| 32 | C | 0.051039 | -0.014913 |
| 33 | C | 0.688231 | -0.001001 |
| 34 | C | -0.254297 | -0.001799 |
| 35 | H | 0.181868 | 0.002348 |
| 36 | H | 0.179082 | 0.002038 |
| 37 | H | 0.183269 | 0.001051 |
| 38 | C | 0.438049 | -0.005048 |
| 39 | N | -0.633062 | 0.026139 |
| 40 | N | -0.373347 | -0.001159 |
| 41 | N | -0.633062 | 0.026139 |
| 42 | N | -0.376379 | -0.001615 |
| 43 | N | -0.626247 | 0.023888 |
| 44 | N | -0.287770 | 0.000128 |
| 45 | N | -0.376379 | -0.001615 |
| 46 | N | -0.626247 | 0.023888 |
| 47 | O | -0.717678 | 0.014173 |
| 48 | O | -0.717678 | 0.014173 |
| 49 | O | -0.539887 | 0.002420 |
| 50 | O | -0.739657 | 0.016082 |
| 51 | O | -0.539887 | 0.002420 |
| 52 | O | -0.739657 | 0.016082 |
| 53 | O | -0.726391 | 0.049892 |
| 54 | H | 0.512353 | -0.000782 |

| | | | |
|---|---|---|---|
| 55 | O | -0.557265 | 0.006164 |
| 56 | O | -0.589508 | 0.071970 |
| 57 | O | -0.726391 | 0.049892 |
| 58 | Co | 1.183994 | 0.016567 |
| 59 | C | 0.322752 | -0.000418 |
| 60 | C | 0.041061 | 0.001522 |
| 61 | H | 0.194109 | 0.000045 |
| 62 | C | 0.322752 | -0.000418 |
| 63 | N | -0.275312 | 0.000280 |
| 64 | N | -0.373347 | -0.001159 |
| 65 | N | -0.275312 | 0.000280 |
| 66 | O | -0.545834 | 0.002181 |
| 67 | O | -0.545834 | 0.002181 |
| 68 | C | -0.254297 | -0.001799 |
| 69 | H | 0.179082 | 0.002038 |
| 70 | H | 0.183269 | 0.001051 |
| 71 | H | 0.181868 | 0.002348 |
| 72 | C | 0.328463 | -0.000501 |
| 73 | C | 0.438049 | -0.005048 |
| 74 | N | -0.287770 | 0.000128 |
| 75 | O | -0.557265 | 0.006164 |
| 76 | O | -0.589508 | 0.071970 |
| 77 | H | 0.512353 | -0.000782 |
| 78 | H | 0.182463 | 0.001012 |
| 79 | H | 0.180773 | 0.000057 |
| 80 | H | 0.205642 | 0.002261 |
| 81 | H | 0.192922 | 0.000345 |
| 82 | H | 0.109431 | 0.006688 |
| 83 | H | 0.109431 | 0.006688 |
| 84 | H | 0.192220 | 0.000342 |
| 85 | H | 0.206999 | 0.002972 |
| 86 | H | 0.171058 | 0.000100 |
| 87 | H | 0.171058 | 0.000100 |
| 88 | H | 0.180773 | 0.000057 |
| 89 | H | 0.192220 | 0.000342 |
| 90 | H | 0.206999 | 0.002972 |
| 91 | H | 0.192922 | 0.000345 |
| 92 | H | 0.205642 | 0.002261 |

Table S4. The parameters of $\chi_T$, $\chi_S$, $\tau$, and $\alpha$ used in the analyses by Debye model for complex **1** under the different fields at 2 K.

| | $\chi_T$ | $\chi_S$ | $\alpha$ | $\tau$(s) |
|---|---|---|---|---|
| **200 Oe** | 1.59 | 0.91 | 0.09 | 0.00046 |
| **500 Oe** | 2.52 | 0.47 | 0.15 | 0.00117 |
| **1000 Oe** | 2.72 | 0.28 | 0.16 | 0.00190 |
| **1500 Oe** | 2.74 | 0.26 | 0.17 | 0.00221 |
| **2000 Oe** | 2.72 | 0.28 | 0.18 | 0.00226 |

Table S5. The parameters of $\chi_T$, $\chi_S$, $\tau$, and $\alpha$ used in the analyses by Debye model for complex **1** under 1000 Oe field.

| | $\chi_T$ | $\chi_S$ | $\alpha$ | $\tau$ |
|---|---|---|---|---|
| **2.0 K** | 2.75 | 0.38 | 0.19 | 0.00189 |
| **2.25 K** | 2.48 | 0.35 | 0.19 | 0.00129 |
| **2.5 K** | 2.15 | 0.33 | 0.12 | 0.00079 |
| **2.75 K** | 1.93 | 0.31 | 0.06 | 0.00045 |
| **3.0 K** | 1.78 | 0.31 | 0.04 | 0.00024 |
| **3.25 K** | 1.66 | 0.38 | 0.04 | 0.00014 |
| **3.5 K** | 1.54 | 0.31 | 0.04 | 0.00008 |
| **3.75 K** | 1.45 | 0.46 | 0.002 | |
| **4.0 K** | 1.37 | 0.53 | 0.005 | |

Equation S1.

$$\chi''(\chi') = -\frac{\chi_T - \chi_S}{2\tan[1/2\pi(1-\alpha)]}\{[\frac{\chi_T - \chi_S}{2}]^2 - [\frac{\chi_T - \chi_S}{2\tan[1/2\pi(1-\alpha)]}]^2 - [\chi' - \frac{\chi_T + \chi_S}{2}]^2\}^{1/2}$$