Electronic Supplementary Information

Formation of a novel ferromagnetic end-to-end cyanate bridged homochiral helical copper(II) Schiff base complex via spontaneous symmetry breaking

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Details of Synthesis

All materials were commercially available, reagent grade and used as purchased from Sigma-Aldrich without further purification.

A methanol solution (10 mL) of *N,N*-dimethyl-1,2-diaminoethane (0.10 mL, 1 mmol) and 1-hydroxy-2-acetonaphthone (186 mg, 1 mmol) was refluxed for ca. 1 h to form the tridentate Schiff base *HL*. The ligand was not isolated. A methanol solution (5 mL) of copper(II) acetate monohydrate (200 mg, 1 mmol) was added into the methanol solution of the protonated ligand *HL* with constant stirring. A methanol:water solution (5 mL) of sodium cyanate (65 mg, 1 mmol) was added into the reaction mixture to get a dark green solution. The stirring was continued for ca. 2 additional hours. Dark blue single crystals, suitable for X-ray diffraction, were obtained after few days by slow evaporation of the solution in open atmosphere. Yield: 278 mg (77%). Anal. Calc. for $C_{17}H_{19}CuN_3O_2$ (360.89): C, 56.58; H, 5.31; N, 11.64 %. Found: C, 56.3; H, 5.1; N, 11.8 %. FT-IR (KBr, cm^{-1}): 1579 (C=N); 1414, 2186 (NCO). λ_{max} (nm) [ε_{max}(lit mol^{-1} cm^{-1})] (acetonitrile): 292 (3.98×10^4); 390 (2.15×10^4); 603 (3.63×10^2).

X-ray Crystallography

The structural analysis of the complex was performed on an Agilent SuperNova diffractometer with Atlas detector using mirror-monochromatized Mo-Kα (λ = 0.71073 Å) radiation at 170 K. CrysAlis^{PRO} program was used for data collection and processing.[S1] The intensities were corrected for absorption using the built-in absorption correction method.[S2] The structure was solved with the program Superflip[S3] and refined by full-matrix least squares on F^2 using the WinGX[S4] software equipped with SHELXL-97.[S5] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 larger than the respective host atoms. CCDC reference number is 1019456.

Crystal data: Formula = $C_{17}H_{19}CuN_3O_2$; Formula Weight = 360.89; Temperature (K) = 170(2); Crystal System = Orthorhombic; Space group = $P2_12_12_1$; a(Å) = 8.2090(5); b(Å) = 9.1718(6); c(Å) = 20.3772(17); Z = 4; d_{calc} (g cm^{-3}) = 1.562; μ(mm^{-1}) = 1.437; F(000) = 748; Total Reflections = 4550; Unique Reflections = 3262; Observed data [$I > 2\sigma(I)$] = 3107; No. of parameters = 211; R(int) = 0.022; $R1$, $wR2$ (all data) = 0.0334, 0.0715; $R1$, $wR2$ [$I > 2\sigma(I)$] = 0.0311, 0.0688.

Details of Instrumentation

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectrum in KBr (4500-500 cm^{-1}) was recorded with a Perkin-Elmer Spectrum Two spectrophotometer. Electronic spectrum in acetonitrile was recorded on a Perkin-Elmer lamda 35 UV-visible spectrophotometer. Fluorescence spectrum in acetonitrile was obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Solid state (KBr pellets) circular dichroism (CD) spectrum was recorded on a JASCO J-810 spectropolarimeter.

The variable-temperature magnetization data were acquired on polycrystalline samples obtained from crushed crystals with a Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) magnetometer over a temperature range of 2 to 300 K at the constant field of 1 T. Each raw data set was corrected for the diamagnetic contribution of both the sample holder and the complex to the susceptibility. The molar diamagnetic corrections were calculated on the basis of Pascal constants.[S6,S7] Magnetization measurements at 2 K from 0 to 5 T were carried out to check the existence of important cooperative phenomena.

References

S1. CrysAlisPro, 2013, Agilent Technologies. Version 1.171.136.128.

S2. R. C. Clark, J. S. Reid, *Acta Cryst.* 1995, *A51*, 887-897.

S3. L. Palatinus, G. Chapuis, *J. Appl. Cryst.* 2007, *40*, 786-790.

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S5. G. M. Sheldrick, *Acta Cryst.* 2008, *A64*, 112-122.

S6. P. Pascal, *Ann. Phys. Chim.* 1910, *19*, 5*; Ann*. *Phys. Chim.* 1912, *25*, 289*; Ann. Phys. Chim.* 1913, *28*, 218.

S7. G. A. Bain, J. F. Berry, *J. Chem. Educ*. 2008, *85*, 532-536.

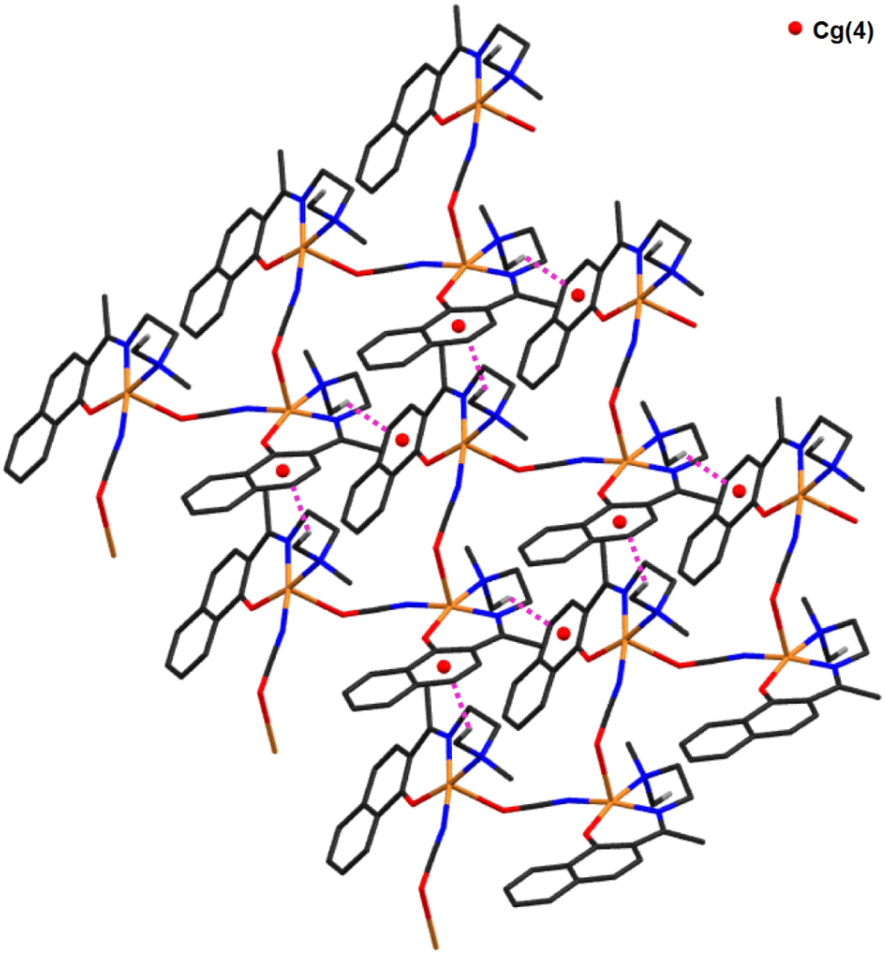

Figure S1: Two-dimensional sheet structure formed by the inter-molecular C-H···π interactions in the complex.

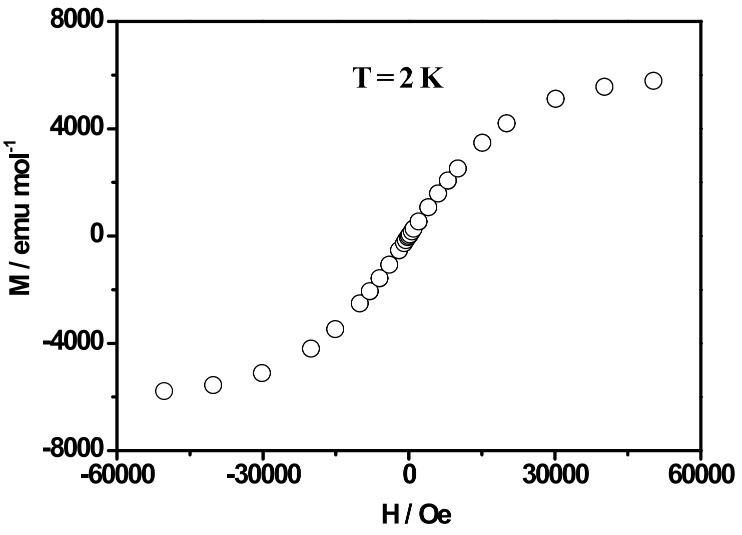

Figure S2: Magnetization measurements at 2 K between 5 and -5 T.

Table S1: Selected angles (º) for the complex.

O(1)-Cu(1)-N(1)	91.28(9)
O(1)-Cu(1)-N(2)	169.24(9)
O(1)-Cu(1)-N(3)	89.84(9)
O(1)-Cu(1)-O(2)*	94.89(7)
N(1)-Cu(1)-N(2)	85.10(9)
N(1)-Cu(1)-N(3)	169.19(11)
O(2)*-Cu(1)-N(1)	94.89(9)
N(2)-Cu(1)-N(3)	91.85(9)
O(2)*-Cu(1)-N(2)	95.51(8)

Table S2: Magnetic interactions and Cu-N-C and Cu-O-C angles in one-dimensional cyanate-copper(II) complexes.

Complex	**Cu-N-C angle (º)**	**Cu-O-C angle (º)**	**Δ (º)**	**Magnetic interactions**	**Reference**
$[Cu(L)(\mu_{1,3}\text{-}NCO)]_n$	134.75	131.23	3.52	Ferromagnetic	This work
$[CuL^1(\mu_{1,3}\text{-}NCO)]_n\cdot 2nH_2O$	149.77	125.07	24.7	Ferromagnetic	18
$\{[CuL^2(NCO)][ClO_4]\}_n$	169.0 170.2	119.9 116.3	49.1 53.9	Antiferromag.	21
$[CuL^3(\mu_{1,3}\text{-}NCO)]_n$	167.55	117.50	50.05	Antiferromag.	22