Toward Higher Nuclearity: Tetranuclear Cobalt(II) Metallogrid Exhibiting Spin Crossover

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General procedures: The reagents used are all purchased from commercial sources, including: $CoCl_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $NaClO_4$, 2,4-dichloropyrimidine, hydrazine, 6-bromo-pyridylaldehyde and 6-methyl-pyridylaldehyde.

Caution! *Perchlorate salts are potentially explosive and should only be used in small quantities and handled with precautions.*

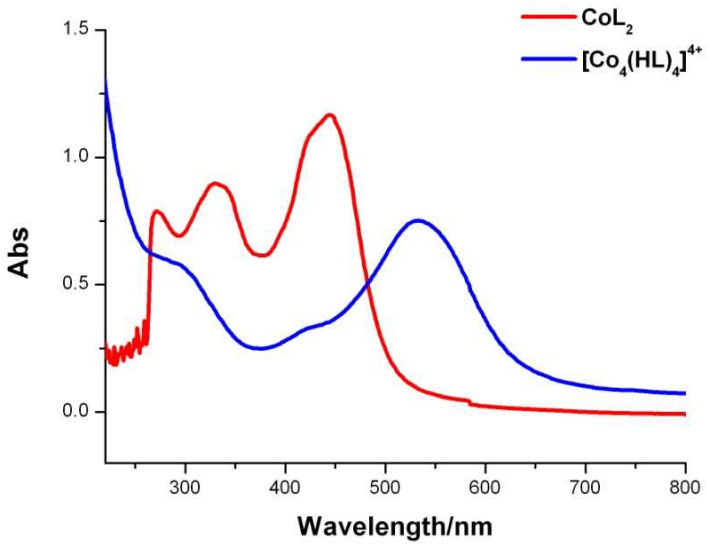


Figure S1. UV-vis Spectra of complexes **1** (CoL_2) and **3** ($Co_4(HL)_4$)

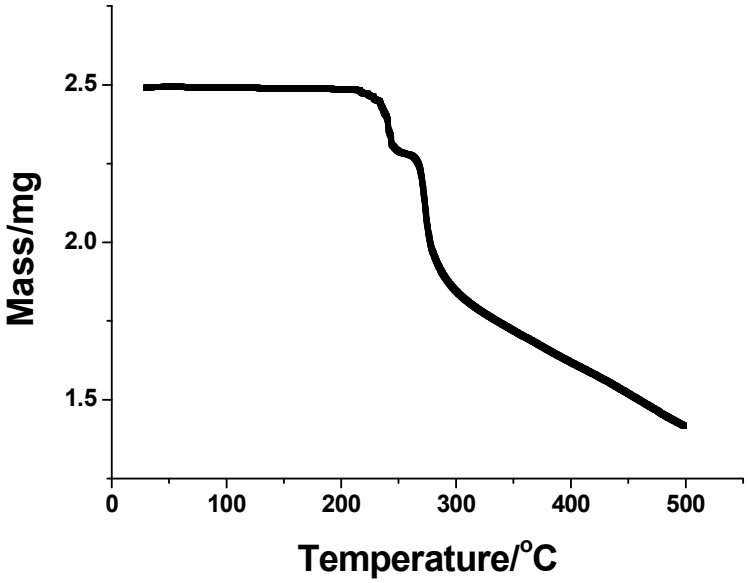
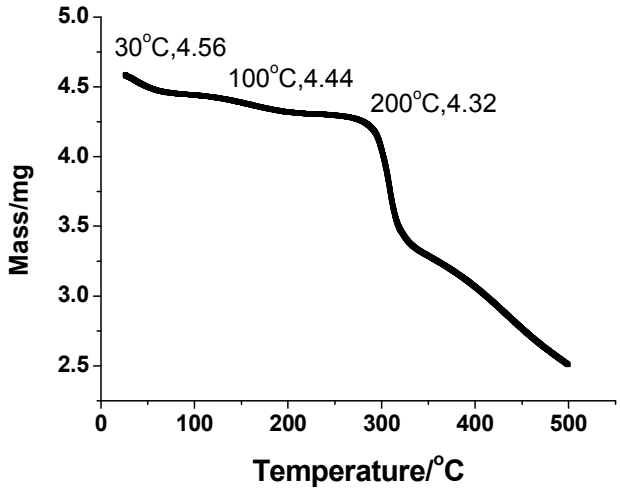


Figure S2. TGA plot for complex



1.

Figure S3. TGA plot for complex **3**.

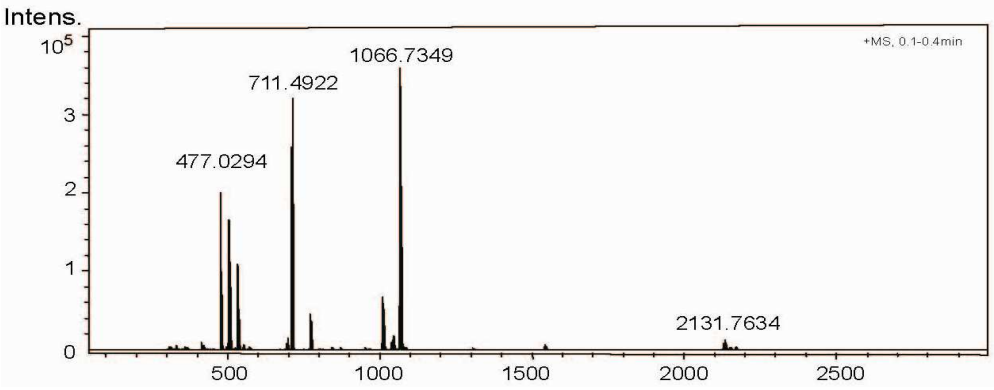


Figure S4. The mass spectrum of complex **3** in MeOH.

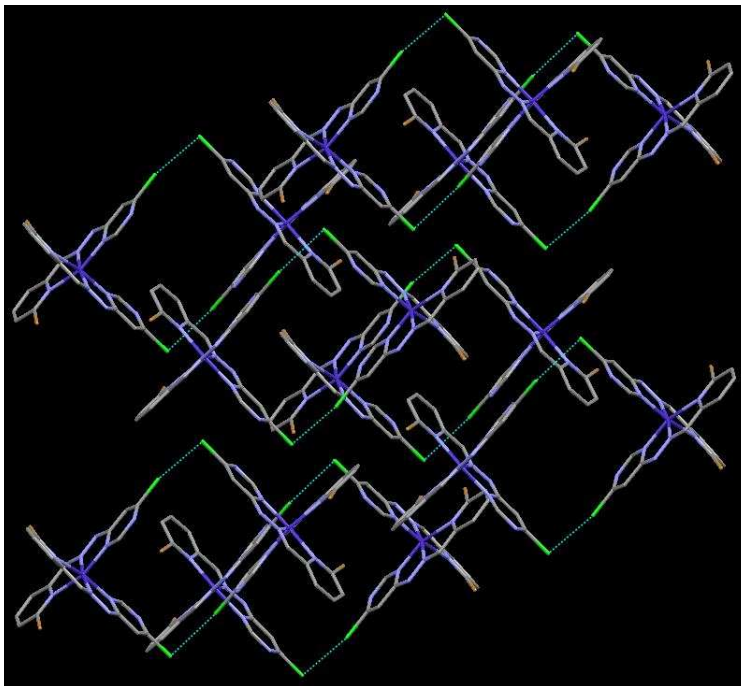


Figure S5. Supramolecular dimers of complex **1** via Cl---Cl contacts (dotted lines).

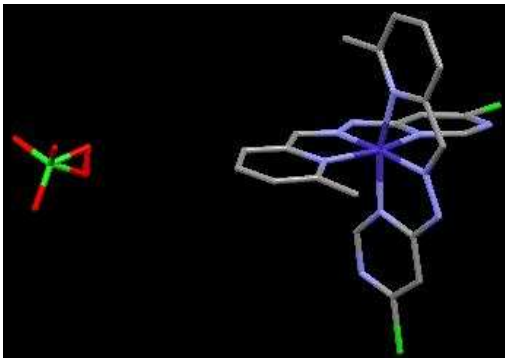


Figure S6. Molecular structure for complex **2** (H atoms are omitted for clarity). One oxygen atom of the perchlorate anion experiences serious disorder and is split into two atoms with the occupancy of 0.5.

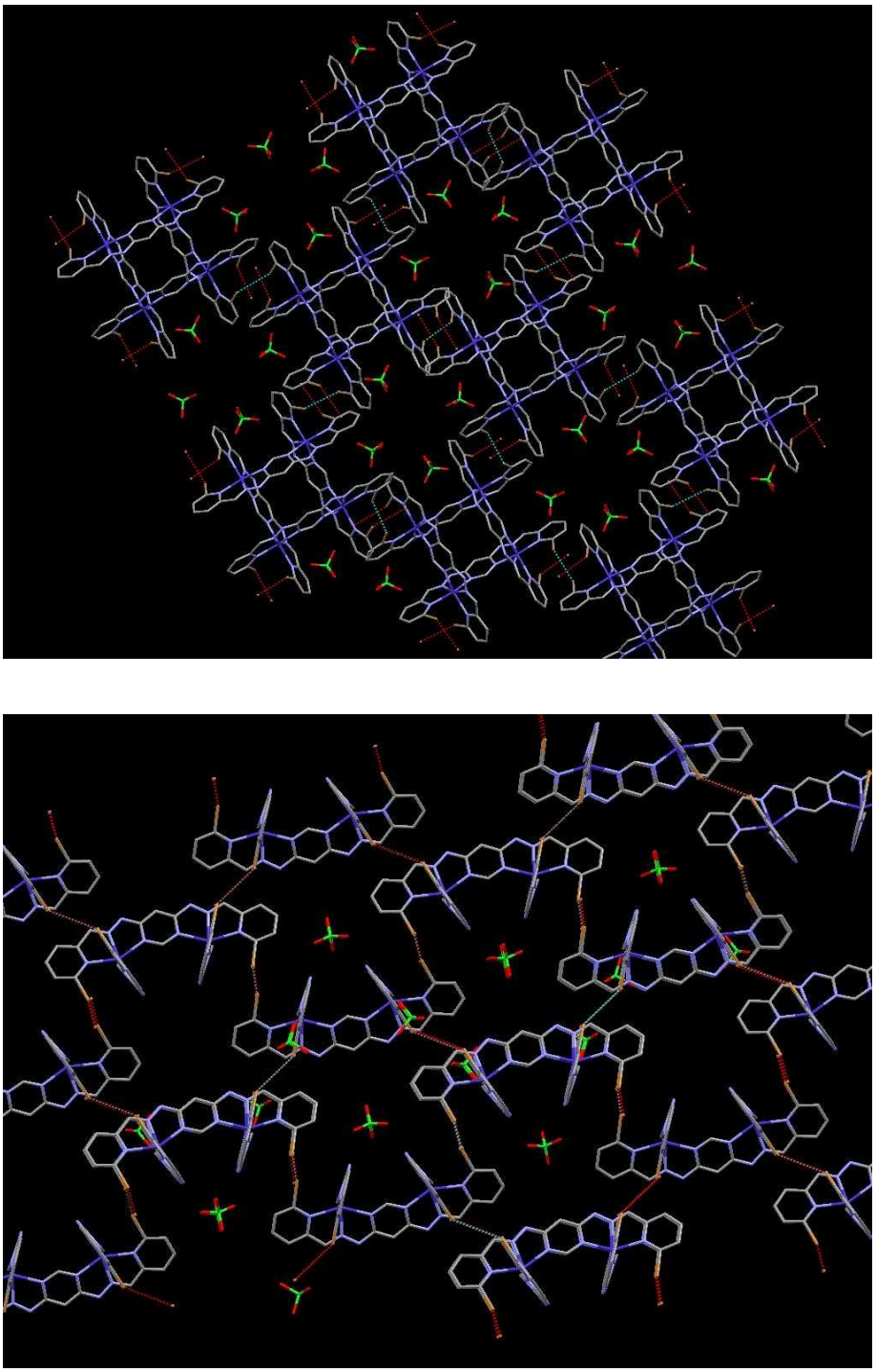


Figure S7. Br---Br interaction (dotted lines) yielding a 3D layer for complex **3**.

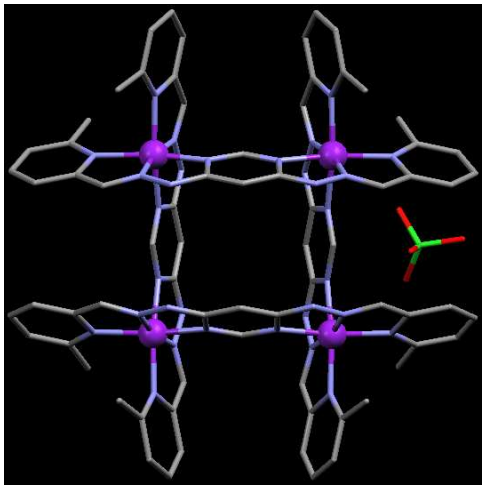


Figure S8. Molecular structure for complex **4** (H atoms and solvents are omitted for clarity).

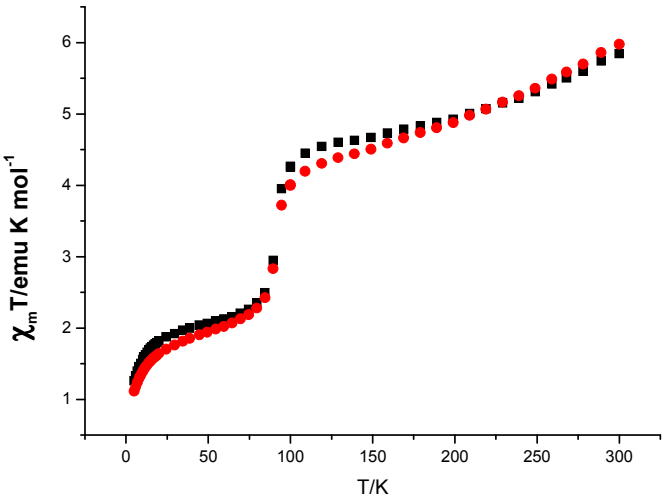


Figure S9. Temperature dependence of $\chi_m T$ per Co_4 for complex **3**. Black: Before heated; Red: After heated in vacuum for 5 hr at 400 K. The magnetic properties remains nearly unchanged after the desolvent process.

Computational Details

DFT calculations were performed by the Gaussian09 suite of program using spin-unrestricted Kohn-Sham equation.[1] The hybrid B3LYP functional[2] has been employed throughout calculation of ligands, and corresponding anions. We have used 6-311++G (2d, 2p) basis set for Br atom and 6-311++G (d, p) basis set for other atoms during geometric optimization and calculation of ligand HL^1, HL^2, $(L^1)^-$, and $(L^2)^-$.[3] Mulliken charges of coordinating N atoms are listed in Table 1.

Table S1. Mulliken charges of coordinating N atoms

	HL^1	HL^2	$(L^1)^-$	$(L^2)^-$
N_{py}	0.312	0.175	0.295	0.134
N_{imi}	0.069	0.044	-0.210	-0.243
N_{pym}	-0.146	-0.152	-0.119	-0.126

M06L functional[4] has been employed for theoretical study of complexes. We have used LANL2DZ basis[5] for Co atom and 6-311G (d, p) for other atoms.[3] The X-ray structure of complex **1** at 123 K was subject to DFT calculation.[6] Obtained anisotropic *g* values are 2.07, 2.03 and 2.02, consistent with the experimental values. Optimization of high spin state $[Co(L^1)_2]$ at room temperature was carried out to obtain structural details and g-tensor. The isotropic *g* value was 2.33, corresponding to a $\chi_m T$ value of 2.55 emu K mol^{-1}. The optimized structure is showed in Figure 1. The experimental structure at room temperature is also showed.

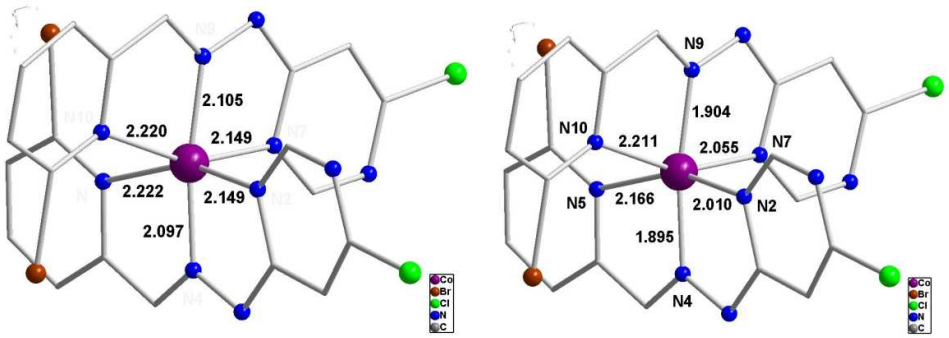


Figure S10. (Left) optimized structure with HS Co(II), and (Right) experimental structure of complex **1** at room temperature.

REFERENCES

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