Spin canting magnetization in a 3D Cu(II) complex based on molybdate oxid cluster and 5-triazole isophthalic acid

Min Zhu,[a,b] Sheng-Qun Su[a,b], Xue-Zhi Song[a,b], Zhao-Min Hao[a,b], Shu-Yan Song[a] and Hong-Jie Zhang*[a]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

Tel: +86-431-85262127; Fax: +86-431-85698041; E-mail: hongjie@ciac.jl.cn

[b] Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China

A mixture of $Na_2MoO_4\cdot 2H_2O$ (0.8 g, 3.31 mmol), $CuCl_2\cdot 2H_2O$ (0.23 g, 1.35 mmol), H_2**L** (0.02 g, 0.08mmol) and H_2O (30 mL) was stirred for an hour. The pH was adjusted to 3.7–4.7 with 2 M HCl, then sealed in a 50 mL Teflon-lined reactor and heated at 160 °C for 3 days. After the reactor was slowly cooled to room temperature over a period of 10 °C/h, blue block crystals were filtered, washed with water, and dried at room temperature (yield 56%, based on Mo). $C_{20}H_{16}Cu_2N_6O_{23}Mo_4$ (1219.2): Calc: C, 19.70%; H, 1.32%; N, 6.89%. Found: C, 19.26%; H, 1.09%; N, 6.95%. IR (solid KBr pellet, cm^{-1}): 3518 (w), 3417 (w), 3097 (s), 3066 (w), 1714 (s), 1571 (s), 1537 (m), 1458 (m), 1411 (m), 1377 (s), 1307 (m), 1251 (w), 1066 (s), 1001 (m), 958 (s), 893 (s), 761 (s), 649 (m), 572 (w), 536 (w).

5-Triazole isophthalic acid was synthesized as described previously.[1] Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The IR spectrum was obtained on Bruker TENSOR 27 Fourier Transform Infrared Spectrometer with KBr pellet in the 400–4000 cm^{-1} region. The TG analysis was performed on a Perkin–Elmer Thermal Analysis Pyris Diamond TG/DTA instrument in flowing N_2 at a heating rate of 10 °C/min. The XRPD pattern was obtained with a Bruker D8-ADVANCE diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA), and the scanning rate is 5°/min, 2θ ranging from

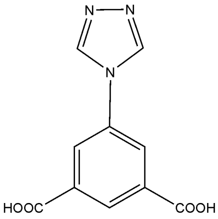
5–40°. Magnetic susceptibility measurement was obtained on finely grounded polycrystalline sample of **1** with the use of a Quantum Design SQUID magnetometer MPMS-XL. Experimental data measured were corrected for the sample holder. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[2] The structure was solved by the directed methods and refined by full matrix least-squares on F2 using the SHELXTL crystallographic software package.[3]

Reference:

1 T. Panda, P. Pachfule and R. Banerjee, *Chem. Commun.*, 2011, **47**, 7674.

2 *Theory and Applications of Molecular Paramagnetism*, ed. E. A. Boudreaux and L. N. Mulay, John Wiley & Sons, New York, 1976.

3 (*a*) Sheldrick, G. M. SHELX-97, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997; (*b*) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Solution; University of Göttingen: Germany, 1997.



Scheme S1 The molecular structure of 5-triazole isopthalic acid used in compound **1**.

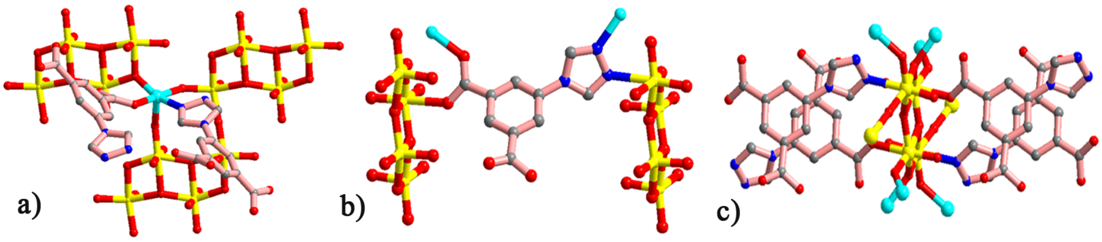


Figure S1. View of the coordination environments for Cu(II) ions, H**L**$^-$ ligand and molybdate oxide cluster (from left to right).

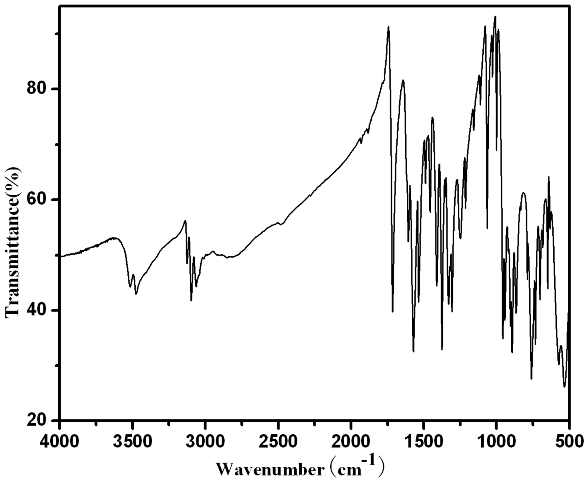


Figure S2. IR spectrum of compound **1**.

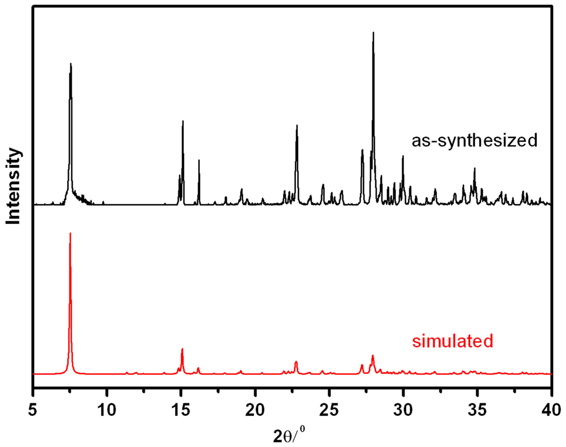


Figure S3. Powder X-ray diffraction pattern of compound **1**.

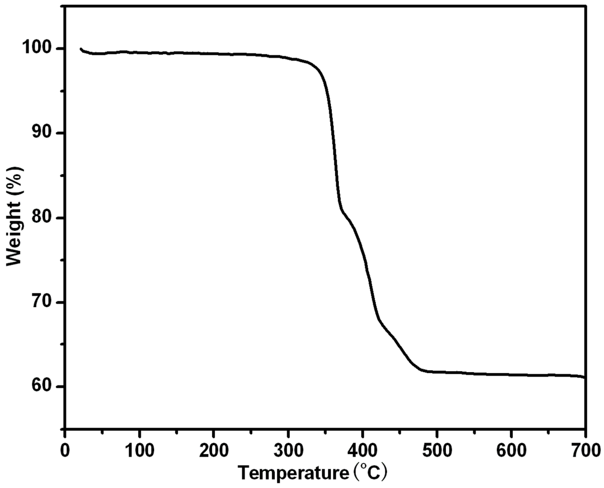


Figure S4.TG curve of compound **1**.

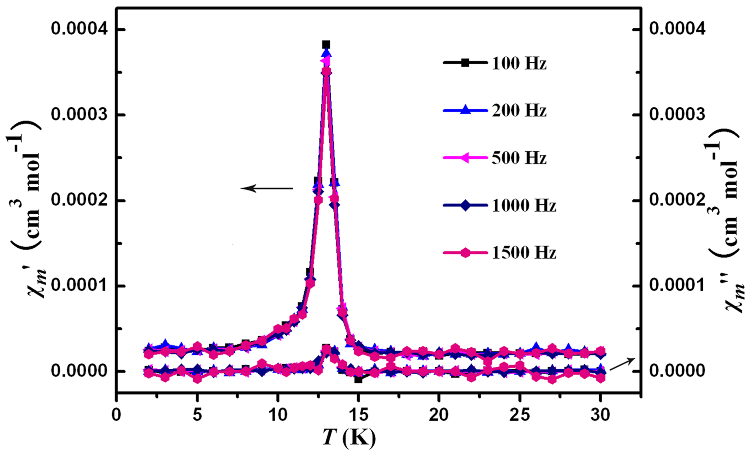


Figure S5. The in-phase χ_m' and out-of-phase χ_m'' components of the ac susceptibility of **1** measured at different frequencies (100, 200, 500, 1000, 1500 Hz) in an applied ac field of 3 Oe.

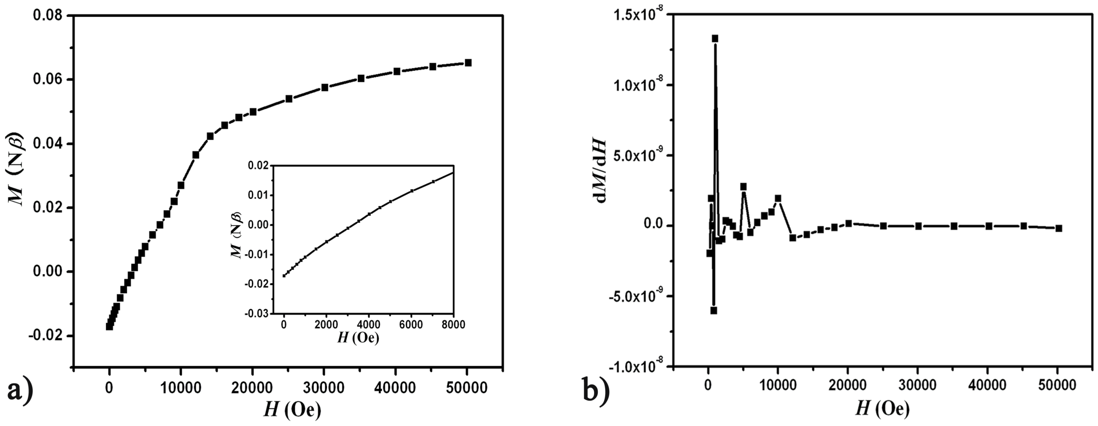


Figure S6. a) The field dependent isothermal magnetization for **1** at 2 K from 0 to 5 T; insert: showing in low field range; (b) d*M*/d*H* *vs*. *H* plot in the range of 0 to 5 T.

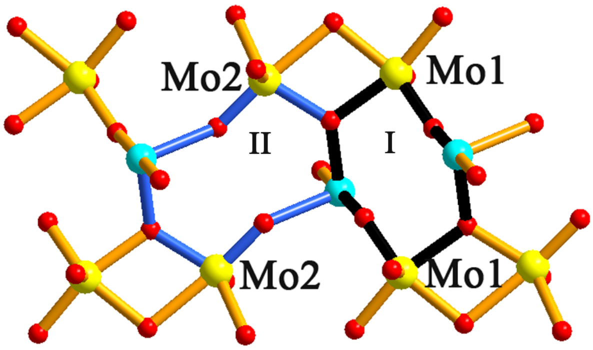


Figure S7. View of the magnetic Cu(II) centers bridged by oxygen atoms from two pathways: [Mo1O$_5$] and [Mo2O$_5$] polyhedra.