Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Unprecedented Dawson Isomerism Induced by Central [WO_5] and Four 45°-rotated Belt Square Pyramids

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Preparation of $[NH_4]_{10}[W_{18}CuO_{60}(H_2O)]$ **(1)**: $(NH_4)_6H_6[H_3(WO_4)_6].H_2O$ (0.6 g, 0.37mmol) was dissolved in a mixture of DMF (7.5 mL), CH_3CN (6 mL) and H_2O (4.5 mL) at room temperature. pH value is adjusted to ~2 by adding 35% HCl dropwise, resulting in a colorless solution to which $Cu(CH_3CO_2)_2{\cdot}H_2O$ (0.50 g, 2.5 mmol) was added. The resulting blue solution was stirred at 50℃ for about 3h, giving a deep-green solution with white precipitate. The solution was filtered and evaporated to yield green crystals of **1** after seven days. The crystas are filtered, washed with ethanol and diethyl ether, and dried in air (yield, 55%). Calc. for $N_{10}H_{42}W_{18}CuO_{61}$: W 73.01, Cu 1.40; Found: W 73.90, Cu 1.29%.

Crystal data for **1**($H_{42}N_{10}O_{61}CuW_{18}$): M_r = 4531.28, 0.20×0.18×0.15 mm^3, green blocks; orthorhombic, space group: *I2mm*; a = 13.5226(9), b = 17.5596(12), c = 17.9569(13) Å, V = 4263.9(5) $Å^3$, Z = 2, ρ_{calcd} = 3.529 g cm^{-3}, λ (MoK\α) = 0.71073 Å, μ = 24.493 mm^{-1}, T = 295(2) K, $2\theta_{max}$ = 54.96°, 15987 reflections collected, 4922 independent reflections, R_{int} = 0.061, R_1 = 0.040, and R_2 = 0.077 for $I \geq 2\sigma(I)$; R_1 = 0.052 and R_2 = 0.081 for all data, GoF = 0.983.

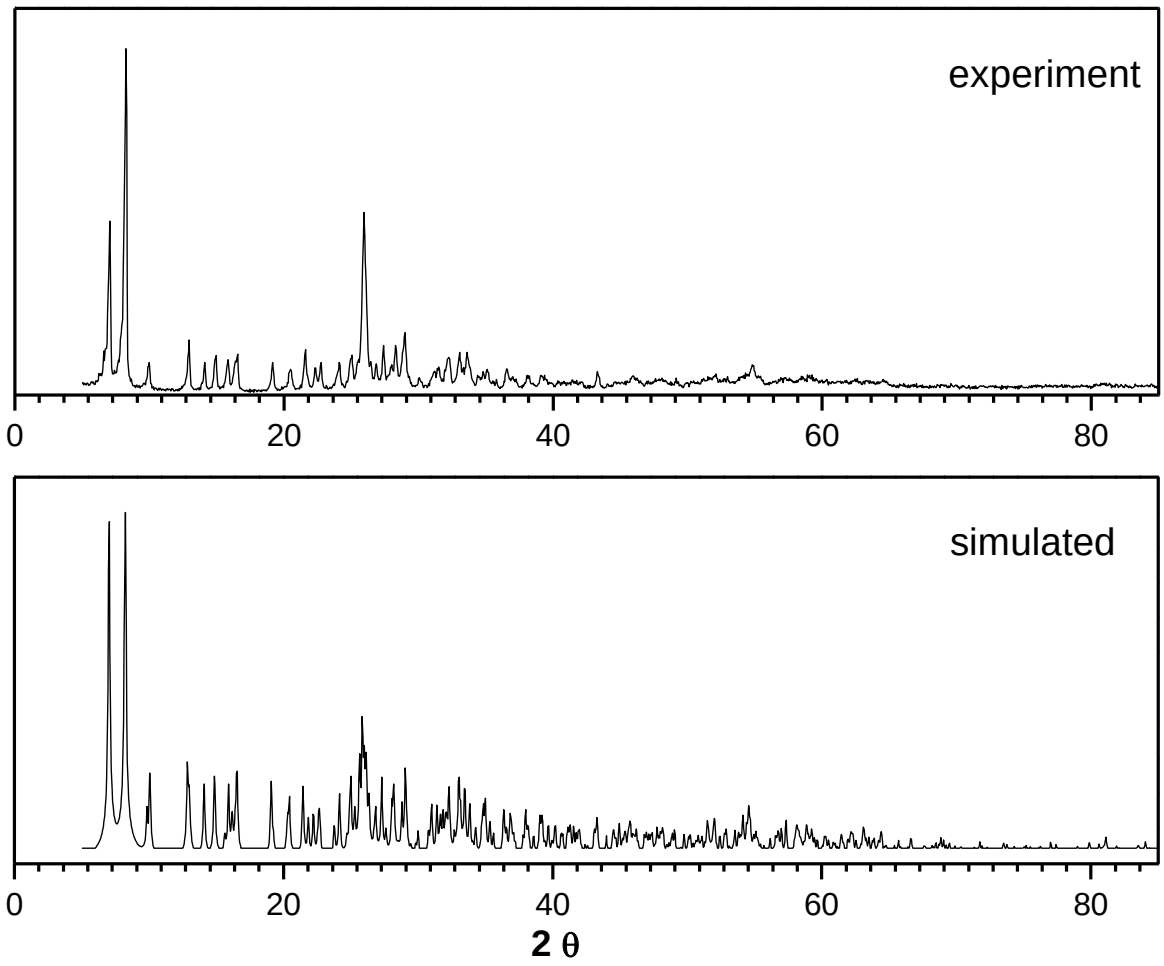


Figure **S1** Simulated and experimental XRPD of $[NH_4]_{10}[(WO_5)W_{17}Cu(H_2O)O_{55}]$ (**1**)

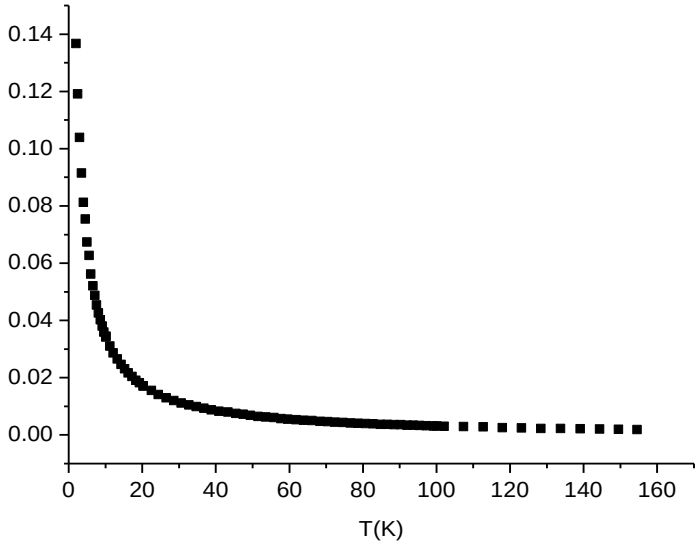


Figure **S2** Temperature-dependent magnetic susceptibility of $[NH_4]_{10}[(WO_5)W_{17}Cu(H_2O)O_{55}]$ (1)

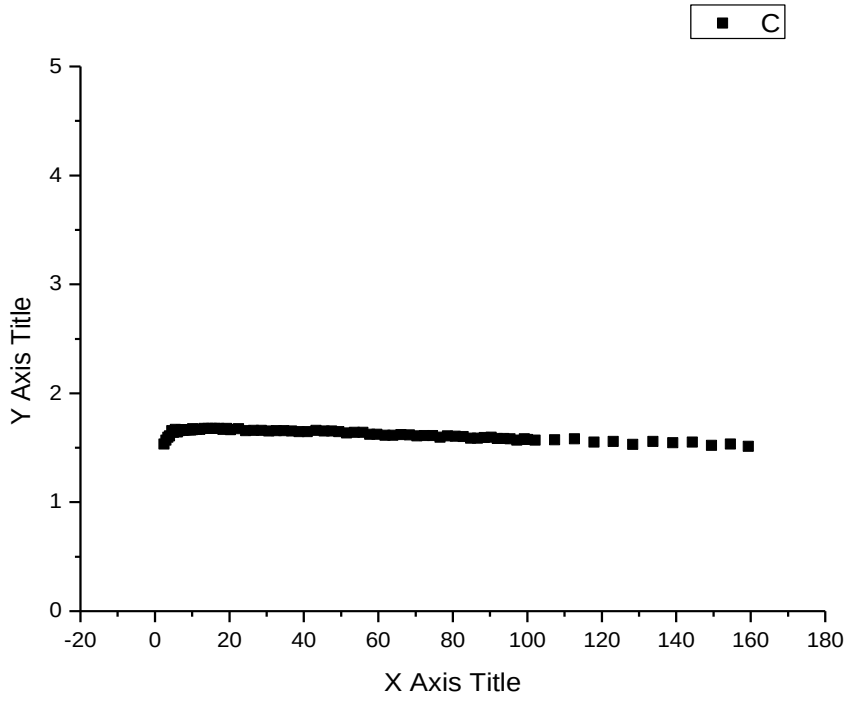
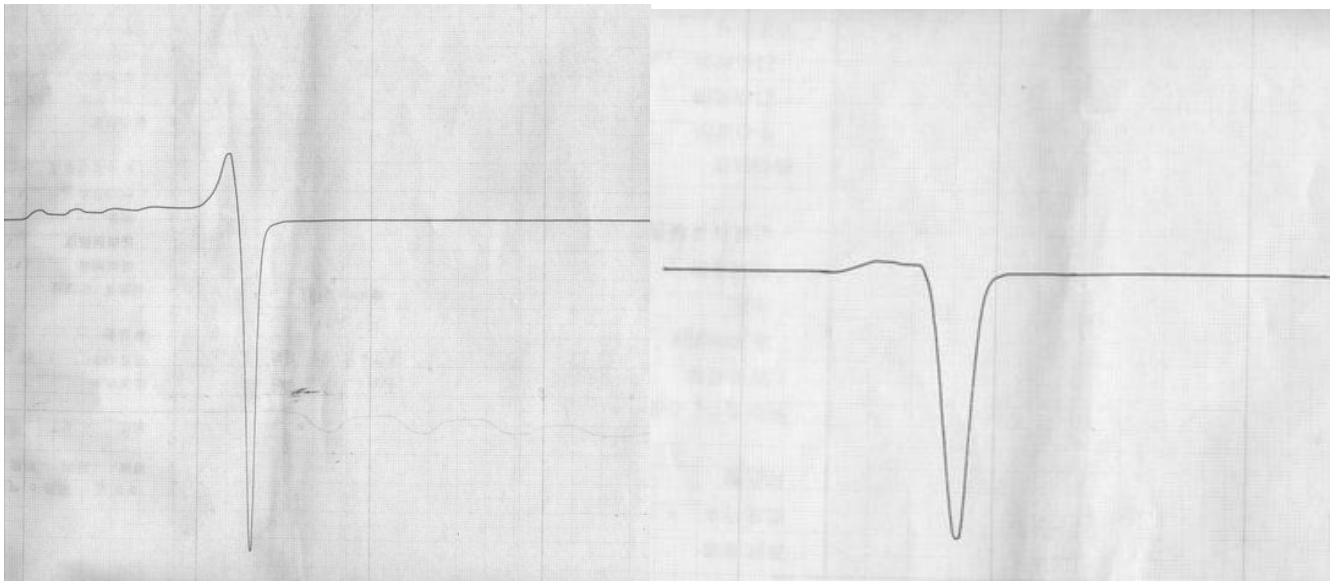


Figure **S3** Temperature-dependent magnetic moments of $[NH_4]_{10}[(WO_5)W_{17}Cu(H_2O)O_{55}]$ (1)



(298K) 77K

Figure **S4** Electronic Paramagnetic Resonance Spectrum of $[NH_4]_{10}[(WO_5)W_{17}Cu(H_2O)O_{55}]$ (1)

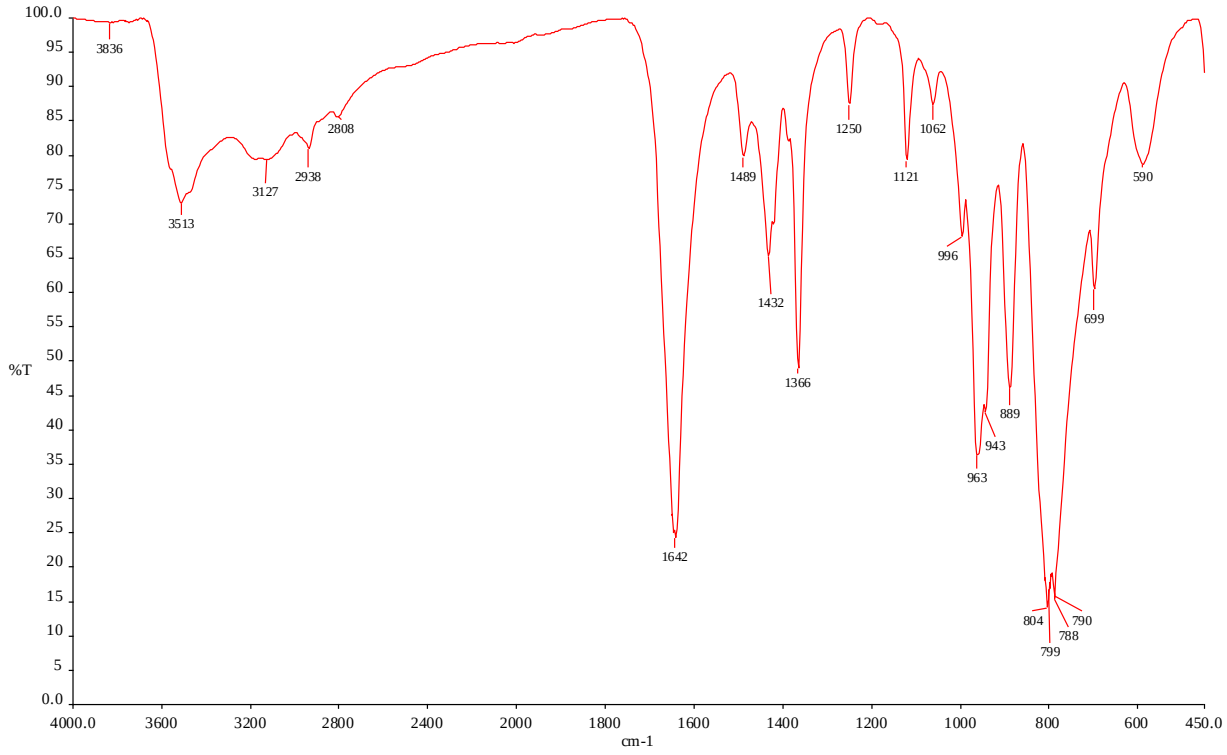


Figure **S5** IR spectrum of $[NH_4]_{10}[(WO_5)W_{17}Cu(H_2O)O_{55}]$ (1)

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