

Mutual structure-direction effects of a non-interpenetrated square grid coordination polymer and its complementary complex anion net

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Experimental:

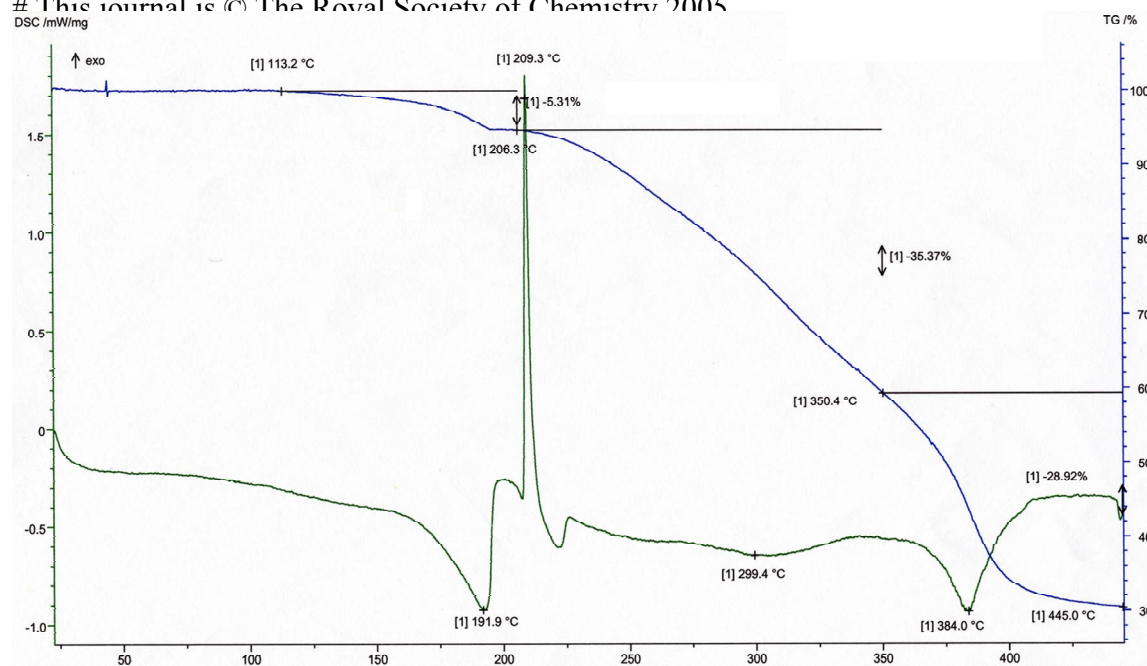
Synthesis of $trans$ -[Cu(L2)₂(H₂O)₄]

Cu(NO₃)₂ and two equivalents of 4-pyridine sulfonic acid (L2)* were stirred in water for 4 hrs at room temperature. The aqueous solution was then precipitated into ice-cold tetrahydrofuran and placed in the freezer overnight. The product was isolated by vacuum filtration the following day, subsequently washed with tetrahydrofuran and allowed to dry. X-ray quality crystals were isolated by vapour diffusion of tetrahydrofuran into an aqueous solution of $trans$ -[Cu(L2)₂(H₂O)₄]. Yield; 82%. EA; anal. calcd for [Cu(L2)₂(H₂O)₄] (451.9134 g/mol): C 26.58, H 3.57, N 6.20. Found: C 27.22, H 3.21, N 6.16. IR (KBr pellet); ν (cm⁻¹) 3435(s,br), 3102(s), 3048(s), 1605(s), 1417(s), 1381(w), 1320(w), 1252(s), 1218(s), 1138(s), 1038(s), 1026(m), 985(w), 832(m), 749(m), 619(s), 574(s), 552(w). DSC/TGA: 28 – 79 °C (62 °C, endo), 79 – 142 °C (104 °C, endo; 126 °C, endo), 171 – 238 °C (222 °C, endo; 231 °C, exo), 318 – 346 °C (333 °C, endo), 346 – 425 °C (362 °C, endo; 420 °C, endo).

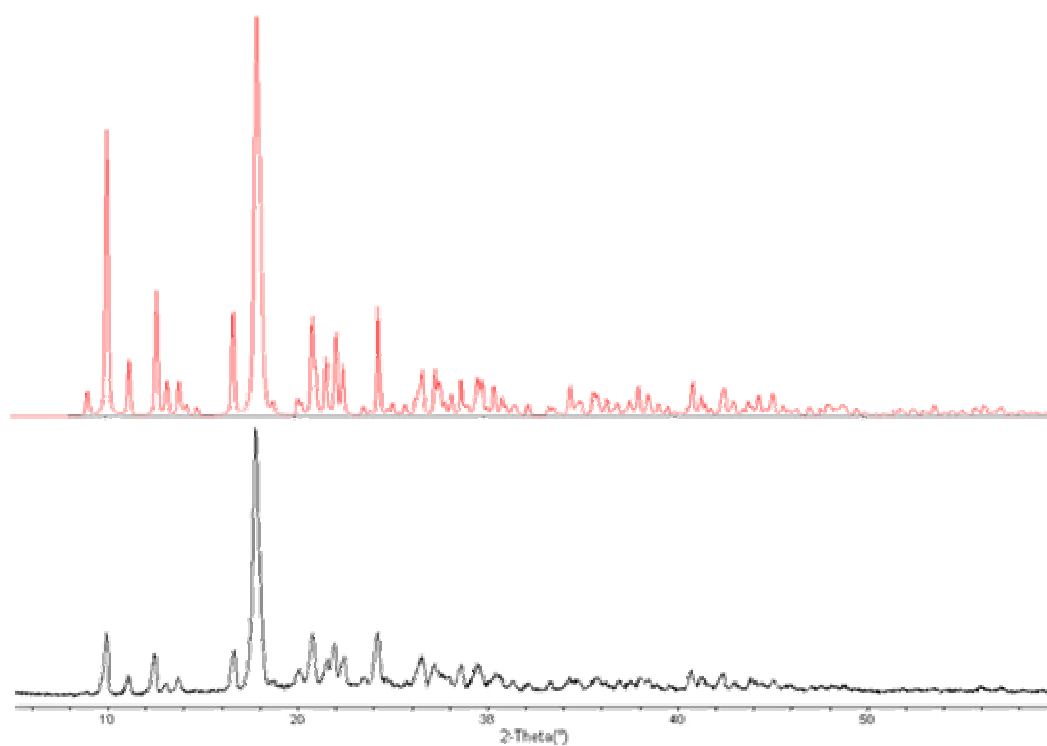
* L2 synthesis adapted from R. F. Evans and H. C. Brown, *J. Org. Chem.*, 1962, **27**, 1329.

*Synthesis of {[Cu(L1)₂(H₂O)₂]_n[Cu(L2)₄(H₂O)₂]}_n, **1***

An aqueous solution of $trans$ -[Cu(L2)₂(H₂O)₄] and two equivalents of 1,2-bis(4-pyridyl)ethane (L1) was stirred at room temperature overnight. The resulting solid was isolated by vacuum filtration, washed with tetrahydrofuran and dried. X-ray quality crystals were isolated by vapour diffusion of tetrahydrofuran into an aqueous solution of **1**. Yield; 45%. EA; Anal. Calcd for {[Cu(L1)₂(H₂O)₂]_n[Cu(L2)₄(H₂O)₂]}_n (1200.2522 g/mol): C 44.03, H 4.03, N 9.34. Found: C 43.86, H 3.73, N 9.11. IR (KBr pellet); ν (cm⁻¹) 3386(s,br), 3101(w), 3076(w), 3047(w), 2934(w), 2860(w), 1669(w), 1615(s), 1607(m), 1556(w), 1506(w), 1429(m), 1415(m), 1252(s), 1219(s), 1202(s), 1137(m), 1095(w), 1066(m), 1034(s), 881(w), 840(m), 824(m), 749(m), 668(w), 619(s), 571(m), 554(m). DSC/TGA: 113 – 206 °C (192 °C, endo), 206 – 350 °C (209 °C, exo), 350 – 445 °C (384 °C, endo).



TGA (blue) and DSC (green) curves for $\{[\text{Cu}(\text{L1})_2(\text{H}_2\text{O})_2]_n[\text{Cu}(\text{L2})_4(\text{H}_2\text{O})_2]\}$, **1**



Experimental (bottom) and simulated (top) PXRD patterns for $\{[\text{Cu}(\text{L1})_2(\text{H}_2\text{O})_2]_n[\text{Cu}(\text{L2})_4(\text{H}_2\text{O})_2]\}$, **1**