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 ºC (62 ºC, endo), 79 – 142 ºC (104 ºC, endo; 126 ºC, endo), 171 – 238 ºC (223 ºC, endo, 231 ºC, exo), 318 – 346 ºC (333 ºC, endo), 346 – 425 ºC (362 ºC, endo; 420 ºC, endo).


Synthesis of [Cu(L1)2(H2O)2][Cu(L2)4(H2O)2], 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][Cu(L2)4(H2O)2] (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 ºC (192 ºC, endo), 206 – 350 ºC (209 ºC, exo), 350 – 445 ºC (384 ºC, endo).
TGA (blue) and DSC (green) curves for $\{[\text{Cu}(L1)_2(H_2O)_2][\text{Cu}(L2)_n(H_2O)_2]\}$, 1

Experimental (bottom) and simulated (top) PXRD patterns for $\{[\text{Cu}(L1)_2(H_2O)_2][\text{Cu}(L2)_n(H_2O)_2]\}$, 1