Electronic Supplementary Material for CrystEngComm

Transforming the cube: A tetranuclear cobalt(II) cubane cluster and its transformation to dimer of dimers

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Synthesis of $[Co_4\{(py)_2C(OH)O\}_4(NO_3)_3(H_2O)]NO_3$ (**1**)

$Co(NO_3)_2{\cdot}6H_2O$ (0.074 g, 0.25 mmol) and $(py)_2CO$ (0.046 g, 0.25 mmol) were dissolved in actonitrile (20 mL) to produce a clear orange solution. Et_3N (0.035 mL, 0.25 mmol) was then added and the solution turned dark orange. X-ray quality purple crystals of **1** were formed over a period of a week with Et_2O (40 mL) diffusion. The crystals were collected by vacuum filtration, washed with acetonitrile (3 mL) and Et_2O (5 mL) and dried in air. Yield: 0.061 g, 75%. Elemental analysis (%) calcd for $C_{44}H_{38}N_{12}O_{21}Co_4$: C 40.45, H 2.93, N 12.86, found: C 40.50, H 3.00, N 12.90.

Synthesis of $[Co_4\{(py)_2C(OMe)O\}_4(4,4'bpy)_2(MeOH)_4](NO_3)_4{\cdot}2MeOH$ (**2**·2MeOH)

$[Co_4\{(py)_2C(OH)O\}_4(NO_3)_3(H_2O)]NO_3$ (**1**) (0.086 g, 0.066 mmol) were dissolved in MeOH (10 mL) with stirring over a period of three hours to produce a clear pink solution. Solid 4,4'-bipyridine (0.02 g, 0.012 mmol) was added and the solution turned orange. X-ray quality orange crystals of **2**·2MeOH were formed in two days

with Et_2O (30 mL) diffusion. The crystals were collected by vacuum filtration, washed with MeOH (5 mL) and Et_2O (5 mL) and dried in air. The crystals loose immediately two molecules of MeOH per formula unit. Yield: 0.076 g, 65% for **2**. Elemental analysis (%) calcd for $C_{72}H_{76}N_{16}O_{24}Co_4$ (**2**): C 48.44, H 4.29, N 12.55, found: C 48.52, H 4.33, N 12.61.

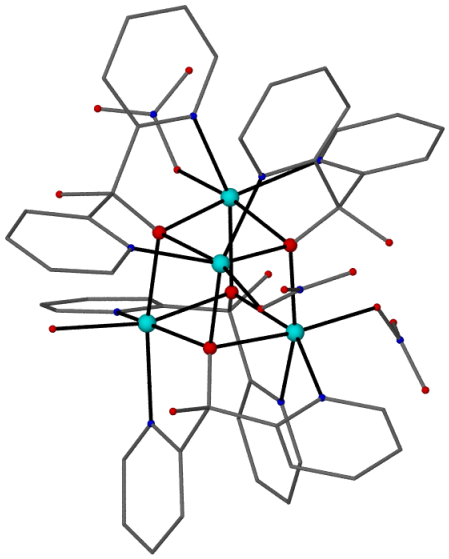

Fig. S1. The molecular structure of $[Co_4\{(py)_2C(OH)O\}_4(NO_3)_3(H_2O)]^+$. Colour code: Co = cyan, O = red, N = blue, C = grey. All H atoms have been omitted for clarity.

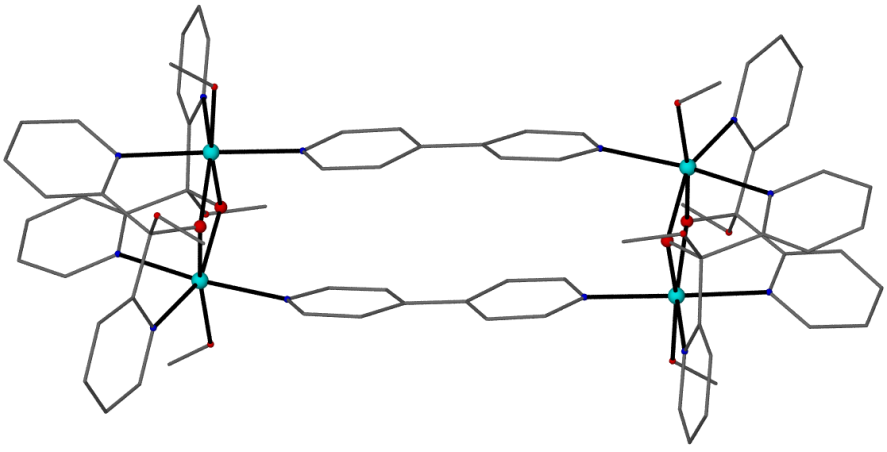

Fig. S2. The molecular structure of $[Co_4\{(py)_2C(OMe)O\}_4(4,4'bpy)_2(MeOH)_4]^{4+}$. Colour code: Co = cyan, O = red, N = blue, C = grey. All H atoms have been omitted for clarity.

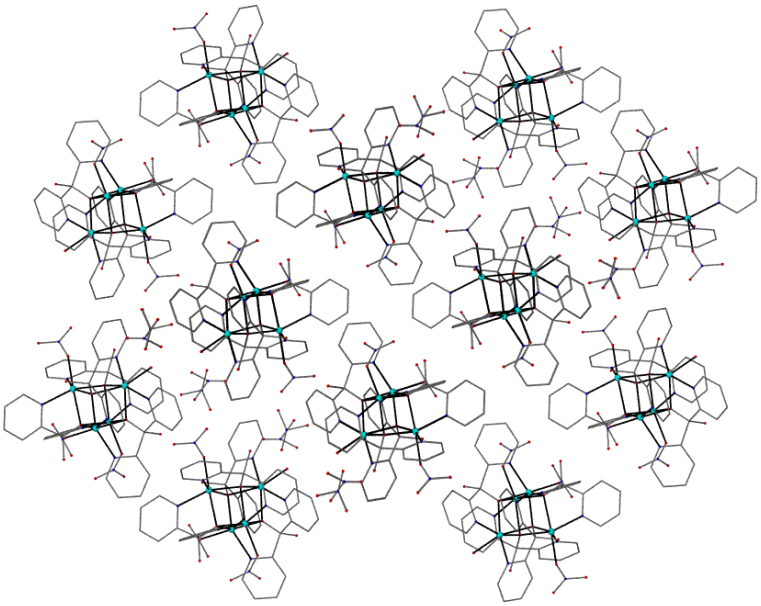

Fig. S3. The packing diagram of **1** along the *b* axis. Colour code: Co = cyan, O = red, N = blue, C = grey. All H atoms have been omitted for clarity.

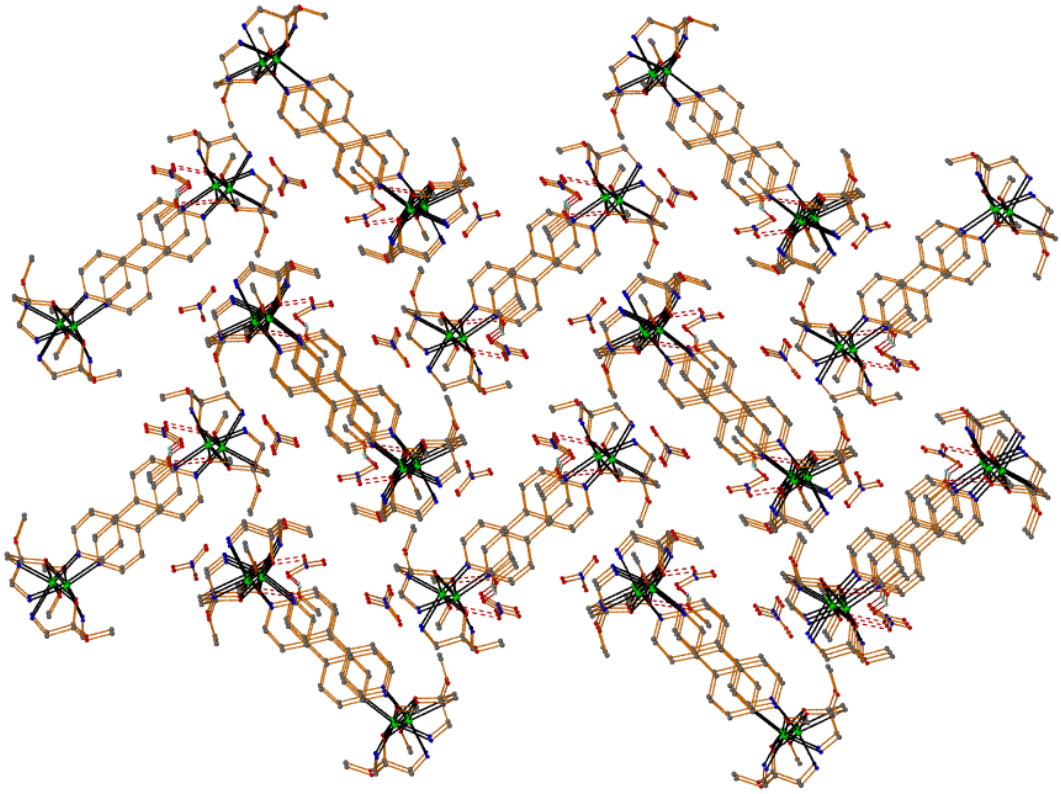

Fig. S4. The packing diagram of **2**·2MeOH along the *a* axis showing the herringbone arrangement of the hydrogen-bonded ladders. Colour code: Co = green, O = red, N = blue, C = grey. Most H and C atoms have been omitted for clarity.

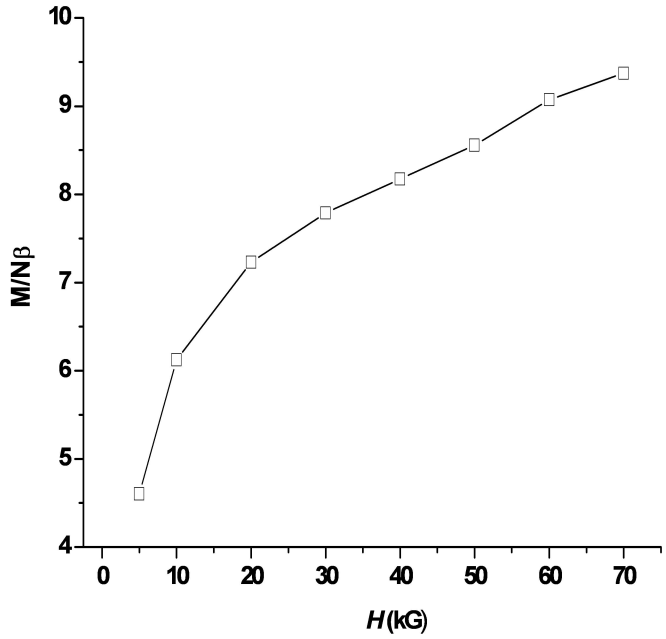

Fig. S5 A plot of magnetization versus field for **1** measured at 2 K and 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 T.