Electronic Supplementary Information for Dalton Transactions

A tetrahedron in a cube: a dodecanuclear Zn^{II} benzoate cluster from the use of 2-pyridinealdoxime†

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Preparation of the complexes

$[Zn(O_2CPh)_2(paoH)_2]\cdot MeOH$ (1·MeOH). To a solution of paoH (122 mg, 1.0 mmol) in MeOH (10 mL) was added a solution of $Zn(O_2CPh)_2\cdot 2H_2O$ (173 mg, 0.5 mmol) in the same solvent (10 mL). The resulting colourless solution was stirred for 15 min and then allowed to slowly evaporate at room temperature. Prismatic colourless crystals of the product formed over 3 days. The crystals were collected by filtration, washed with cold MeOH (2x3 mL) and Et_2O (5 mL), and dried in *vacuo*. Yield, 55%. The dried solid analyzed as solvent free **1**. Anal. Calcd. for $C_{26}H_{22}ZnN_4O_6$: C, 56.58; H, 4.03; N, 10.15. Found: C, 56.31; H, 4.12; N, 10.07%. IR (KBr, cm^{-1}): 3596 wb, 3442w, 3062w, 3016w, 1858wb, 1654w, 1600m, 1544s, 1518sh, 1482m, 1436sh, 1398s, 1390sh, 1332m, 1306w, 1214w, 1154m, 1104w, 1058s, 1016m, 922m, 888m, 830m, 774m, 750w, 716s, 674s, 636m, 564wb, 520sh, 496m, 446m, 422m.

$[Zn_{12}(OH)_4(O_2CPh)_{16}(pao)_4]\cdot 2MeCN\cdot 2H_2O$ (2·2MeCN·2H₂O). To a solution of $Zn(O_2CPh)_2\cdot 2H_2O$ (334 mg, 1.0 mmol) in MeCN (10 mL) was added a solution of paoH (61 mg, 0.5 mmol) in the same solvent (20 mL). The resulting slurry was stirred for 30 min and then filtered to remove a small quantity of a white solid. The colourless filtrate was allowed to slowly evaporate at room temperature. Polyhedral colourless crystals of the product formed over a period of 1 week. The crystals were collected by filtration, washed with cold MeCN (2x5 mL) and Et_2O (5 mL), and dried in *vacuo*. Typical yields were in the 30-40% range (based on the metal available). The dried solid analyzed as **2**·H_2O. Anal. Calcd. for $C_{136}H_{106}Zn_{12}N_8O_{41}$: C, 49.60; H, 3.25; N, 3.40. Found: C, 49.26; H, 3.30; N, 3.46%. IR (KBr, cm^{-1}): 3424wb, 3066w, 1626s, 1606s, 1566s, 1494m, 1416vs, 1382s, 1328w, 1306w, 1176w, 1056m, 1024m, 932w, 888w, 846w, 776w, 718s, 678m, 646w, 456w.

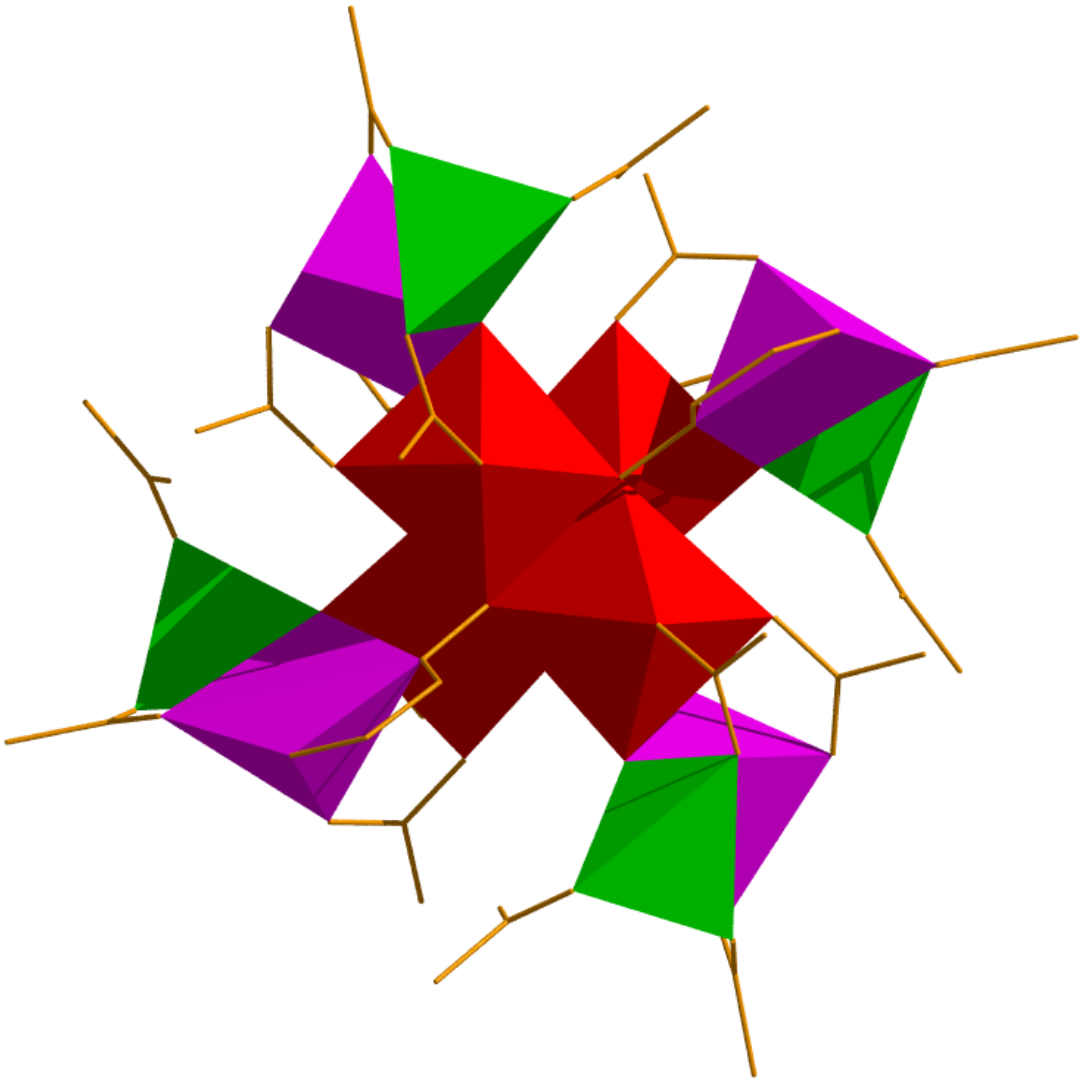

Fig. S1 Polyhedral representation of cluster **2**. Colour code: Zn1 red, Zn2 purple, Zn3 green.

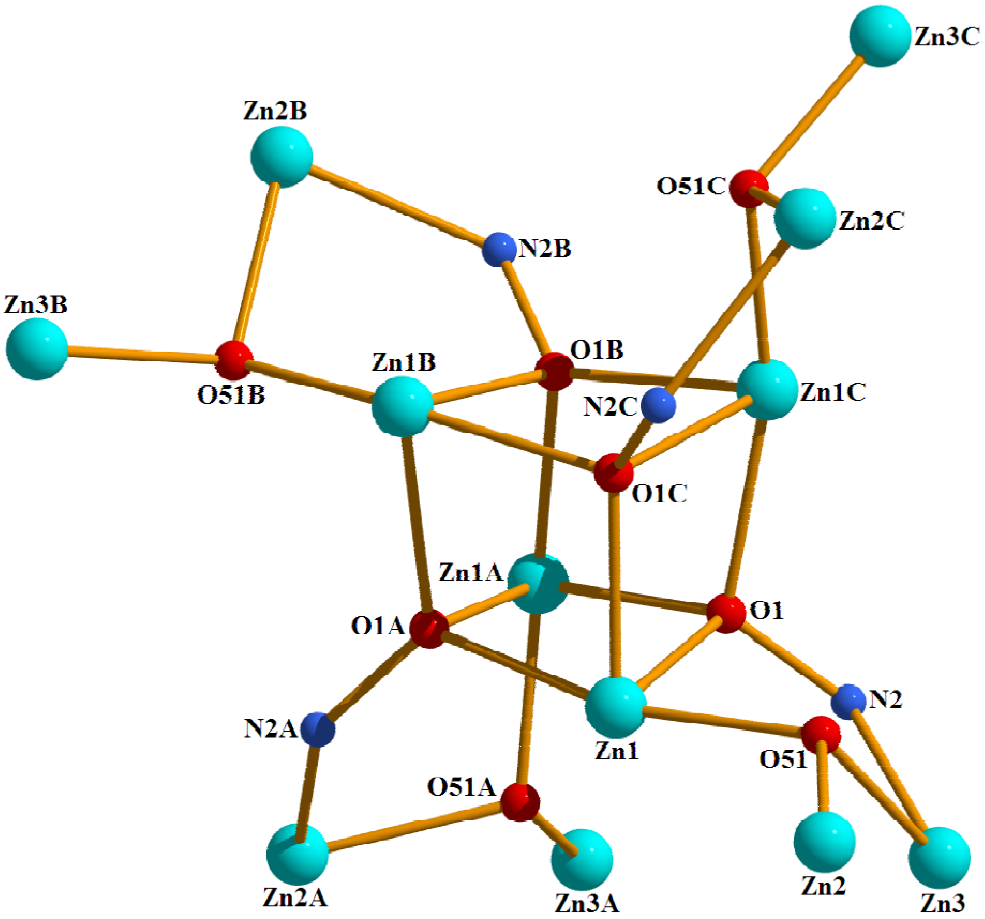

Fig. S2 The $[Zn_{12}(\mu_3\text{-}OH)_4(\mu_4\text{-}ONR')_4]^{16+}$ core of complex **2** ($R'NO^-$ = pao^-). Colour code: Zn turquoise, O red, N blue.

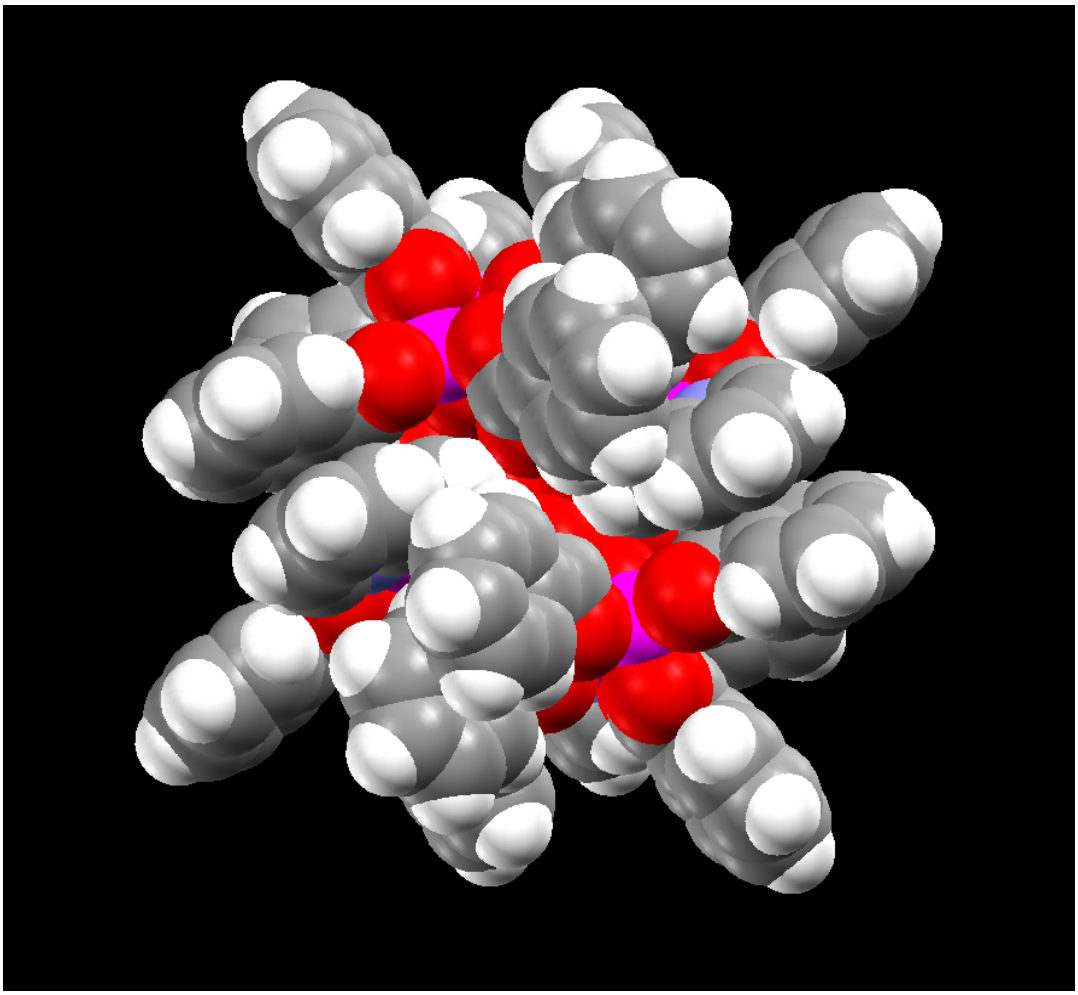

Fig. S3 A space-filling diagram of **2**. Colour code: Zn magenta, O red, N blue, C grey.

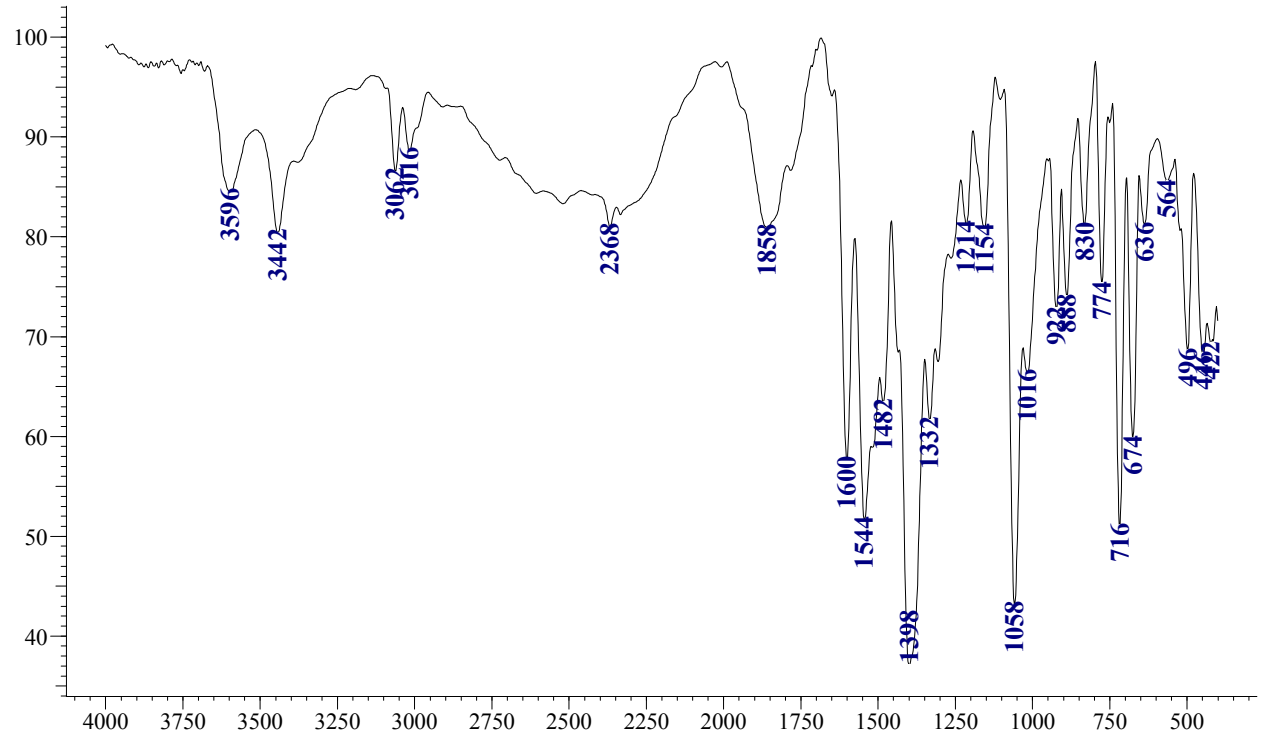

Fig. S4 The IR spectrum (KBr, cm^{-1}) of complex **1**.

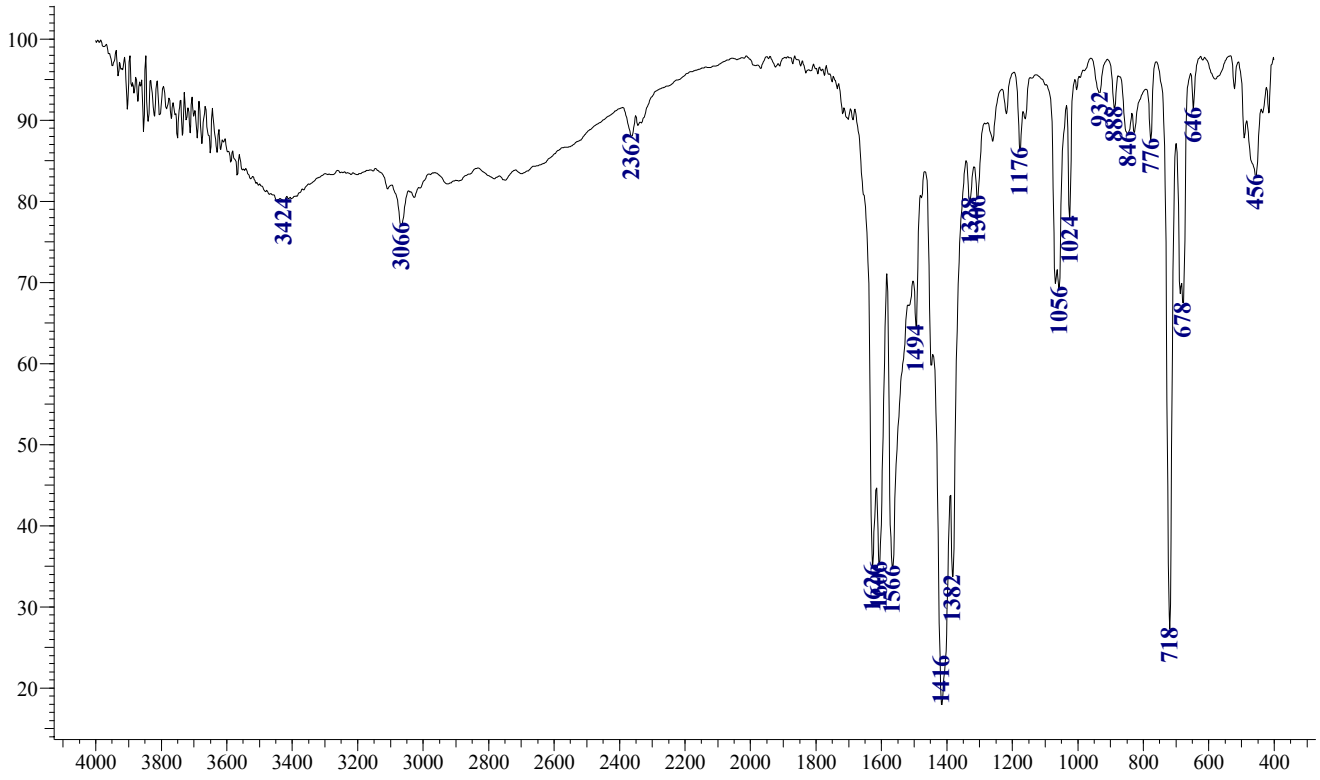

Fig. S5 The IR spectrum (KBr, cm^{-1}) of cluster **2**.

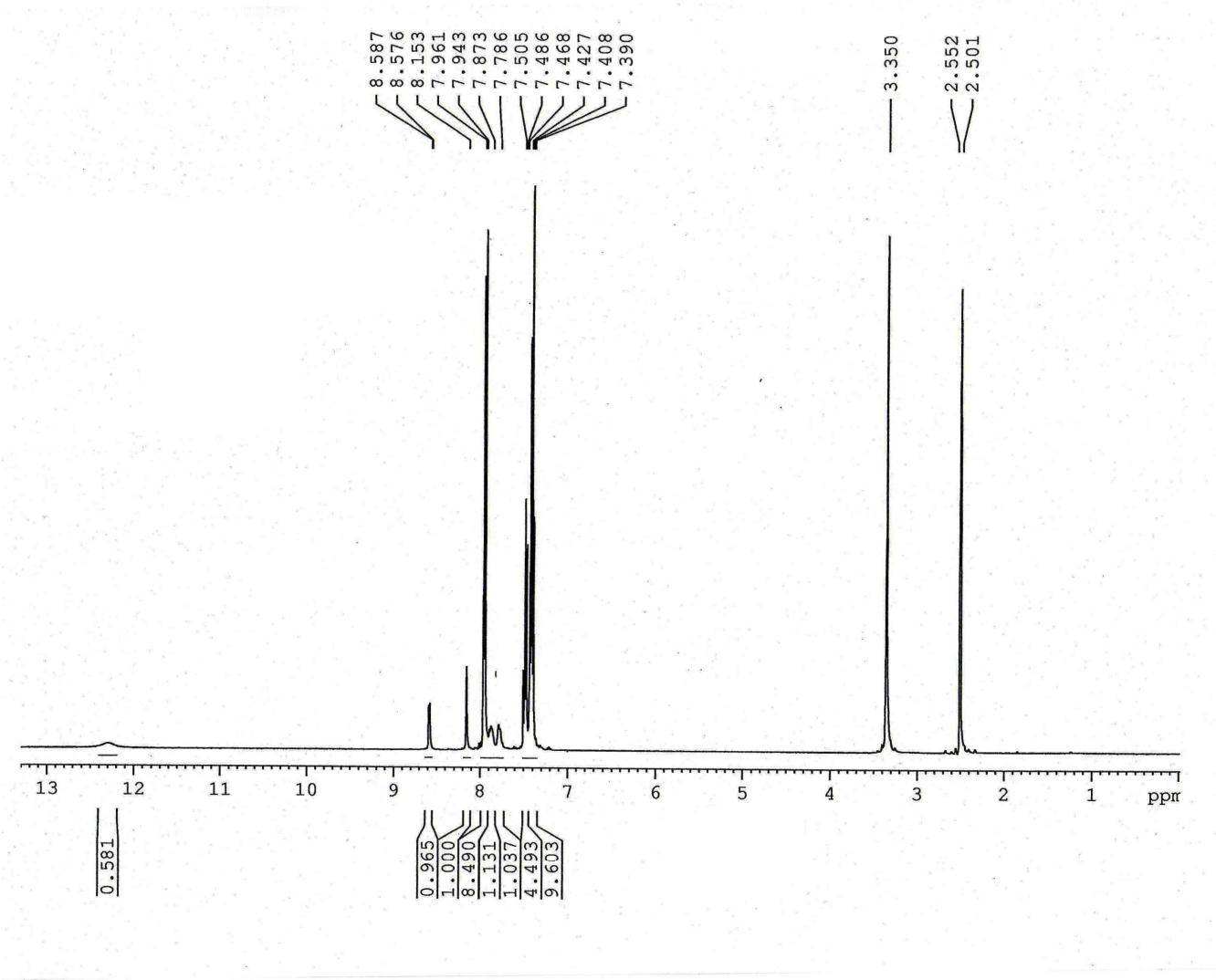

Fig. S6 ^{1}H NMR spectrum of cluster **2** in DMSO-d_6.