Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Assembly of a trinuclear metallo-capsule from a tripodal tris(β-diketone) derivative and copper(II)

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Synthesis of 1,3,5-tris(3-methyl-2,4-pentanedione)benzene (2)

2,4-Pentanedione (4.0 g, 40 mmol) was added to a refluxing solution of potassium *tert*-butoxide (3.4 g, 30 mmol) in *tert*-butanol (500 mL). 1,3,5-Tris(bromomethyl)benzene[1] (4.0 g, 11 mmol) was then added in small portions along with a catalytic amount of potassium iodide. The reaction mixture was heated at the reflux for 20 h, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane (2 x 125 mL). The organic phase was washed with water (3 x 200 mL) then dried over anhydrous Na_2SO_4. The dichloromethane was removed under vacuum to yield a pale yellow oil which was purified by preparative tlc (2% MeOH in DCM). (3.8 g, 82 %). Found HRMS-ESI $(M + Na)^+$, *m*/z = 437.1935. $C_{24}H_{30}O_6Na$ requires 437.1935. ^1H NMR (200 MHz, $CDCl_3$, 300 K): δ (keto): 2.04 (s), 3.06 (d), 3.94 (t), 6.79 (s); δ (enol): 2.14 (s), 3.58 (s), 6.79 (s), 16.79 (s).This data was consistent with the literature values.[2]

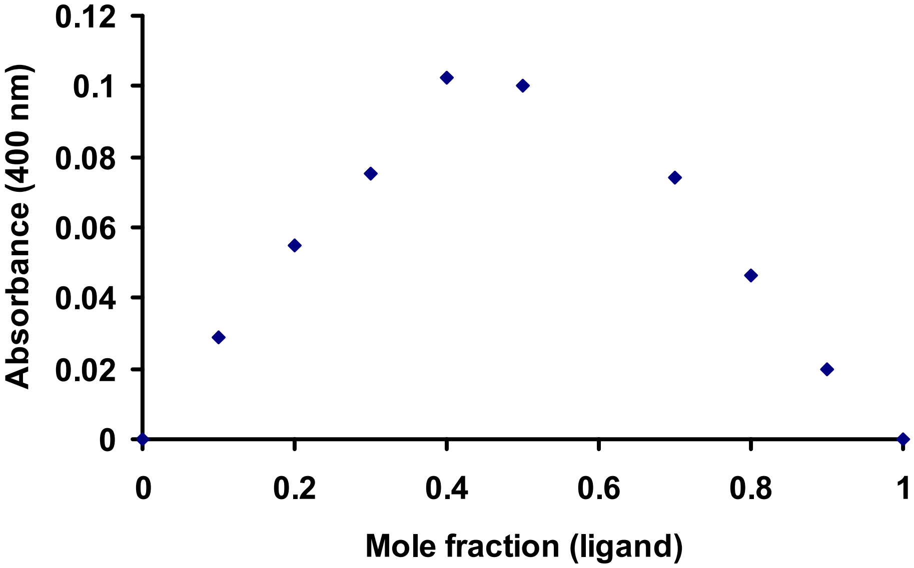

Fig. S1 Job plot derived from the change in absorbance at 400 nm of pyridine solutions of **2** and copper(II) acetate monohydrate incorporating varying mole fractions of each reagent.

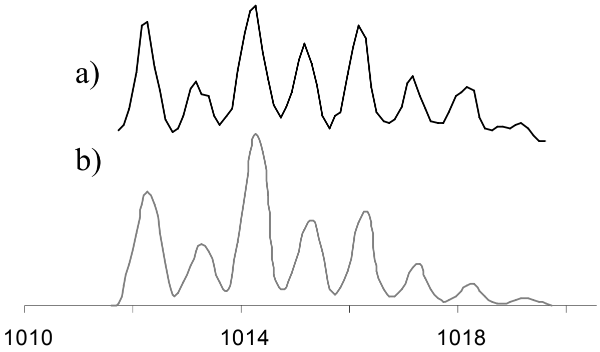

Fig. S2 (a) Observed isotopic distribution for the $[M + H]^+$ ion in the MALDI mass spectrum of the pyridine reaction solution (b) predicted mass spectral distribution for the copper(II) complex of **2**; $[C_{48}H_{54}O_{12}Cu_3 + H]^+$.

Additional X-ray data

Structure of 3 : Throughout the lattice, each of the *β*-diketone rings are involved in a variety of inter- and intramolecular interactions. The O(1)- and O(3)-containing rings are involved in weak intra-molecular face-to-face π-interactions, (O(1)-O(3) separation of 3.50 Å). The O(3)-containing ring is involved in further intermolecular interactions. There are strong offset face-to-face interactions between the O(3)-

containing ring and the equivalent ring in an adjacent molecule (O(3) – C(10) separation of 3.12 Å). There is also an intermolecular hydrogen bonding interaction present between O(3) and O(1) in adjacent molecules and, although not ideal in terms of geometry (D-H-A 109.2 º), a D-A separation of 3.11 Å is in keeping with the presence of an interaction. The remaining 2,4-pentanedione group (containing O(5)) is also involved in offset face-to-face π-π stacking, reflected by a C(16) - C(16) separation of 3.35 Å. Overall, these interactions result in the generation of an infinite three-dimensional network.

Crystallographic details : Structural data were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans.[3] Data were collected to approximately 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP[3] and subsequent computations were carried out using the WinGX-32 graphical user interface.[4] Structures were solved by direct methods using SIR97.[5] Multi-scan empirical absorption corrections were applied to data sets using the program SADABS.[6] Data were refined and extended with SHELXL-97.[7] Non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen-bound hydrogen atoms were first located in the difference Fourier map, before refinement with bond length restraints.

Formula $C_{18}H_{21}N_3O_6S_3$, M 471.56, triclinic, space group $P\,\overline{1}$(#2), a 7.0789(4), b 9.7470(7), c 16.2360(11) Å, α 101.357(3), β 99.921(3), γ 94.398(3)º, V 1074.77(12) Å^3, D_c 1.457 g cm^{-3}, Z 2, crystal size 0.300 by 0.070 by 0.050 mm, colour colourless, habit needle, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.385 mm^{-1}, T(SADABS)$_{\mathrm{min,max}}$ 0.853, 0.981, 2θ_{max} 56.68, hkl range -8 9, -12 13, -21 21, N 20872, N_{ind} 5224(R_{merge} 0.0473), N_{obs} 3847(I > 2σ(I)), N_{var} 292, residuals* $R1(F)$ 0.0382, $wR2(F^2)$ 0.0970, GoF(all) 1.019, $\Delta\rho_{\mathrm{min,max}}$ -0.358, 0.338 e$^-$ Å^{-3}.

*$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections
$w=1/[\sigma^2(F_o^2)+(0.0390P)^2+0.5838P]$ where $P=(F_o^2+2F_c^2)/3$

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