

Electronic Supplementary Information

Mono- and ditopic hydroxamate ligands towards discrete and extended network architectures

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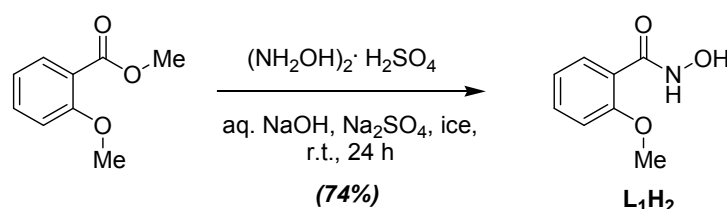
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Synthesis

Synthesis of 2-(acetoxymethyl)phenylhydroxamic acid (**L₁H₂**)



To a stirring solution of methyl 2-methoxybenzoate (6.14 g, 37 mmol), NaOH (7.41 g, 185 mmol, 30 cm³ water), Na₂SO₄ (0.58 g, 4.1 mmol), ice (30 g) and hydroxylamine sulphate (6.11 g, 37 mmol) was added and the solution left to stir for 24 hours. After this time the solution was left to cool and was subsequently pH adjusted to 6 using H₂SO₄, after which the product began to precipitate out. The precipitate was then collected and dried, before recrystallisation using hot water. The remaining solution was left overnight to allow more product to precipitate out which was then recrystallised with hot water. The remaining solution was then evaporated to dryness under reduced pressure to give a mixture of white and yellow solid, this solid was then dissolved in hot methanol and any remaining solid filtered off. The resultant filtrate was

evaporated to dryness under reduced pressure and the solid recrystallised from hot water to form a second batch of the ligand to give a final yield of 74% (4.58 g).

¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 3.83 (s, 3H, OCH₃), 7.01 (t, *J* = 7.5 Hz, 1H, CH-Ar) 7.10 (d, *J* = 8.3 Hz, 1H, CH-Ar) 7.44 (t, *J* = 8.9 Hz, 1H, CH-Ar), 7.56 (d, *J* = 7.5 Hz, 1H, CH-Ar), 9.07 (s, 1H, NH-OH), 10.61 (s, 1H, NH-OH).

¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) 56.06 (OCH₃), 112.18 (CH-Ar), 120.78 (CH-Ar), 122.95 (C-Ar) 130.19 (CH-Ar), 132.20 (CH-Ar), 157.03 (OC-Ar), 163.58 (C=O).

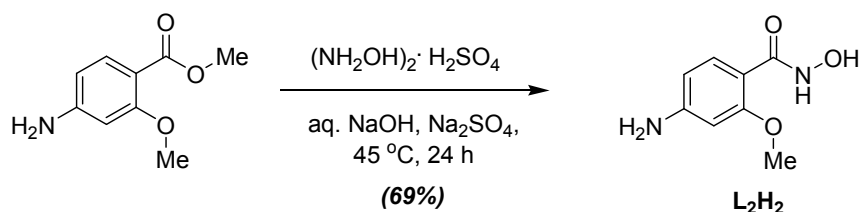
MS (EI⁺): *m/z* 167 (26%, {M⁺}), 153 (16%, {M-CH₃}⁺), 149 (9%, {M-OH}⁺), 135 (73%, {M-OCH₃}⁺ and/or {M-NHOH}⁺).

FT-IR: ν (cm⁻¹) 3351 (w), 3324 (s), 3119 (m/b), 3012 (w), 2979 (w), 2940 (w), 2842 (w), 2035 (m), 1967 (w), 1935 (w), 1903 (w), 1845 (w), 1812 (w), 1638 (s), 1598 (m), 1571 (w), 1507 (w), 1477 (s), 1434 (m), 1297 (s), 1243 (s), 1183 (s), 1156 (s), 1107 (s), 1056 (m), 1020 (s), 952 (w), 898 (m), 858 (w), 780 (w), 757 (s), 659 (w), 620 (m), 519 (m), 437 (w), 404 (w).

UV-vis (MeOH): λ_{max} (nm) (ε_{max} 10³, dm³ mol⁻¹ cm⁻¹): 202 (31.9), 206 (33.2), 284 (5.80).

UV-vis (MeCN): λ_{max} (nm) (ε_{max} 10³, dm³ mol⁻¹ cm⁻¹): 204 (31.6), 228 (10.1), 288 (4.65).

Synthesis of 4-(amino)-2-(acetoxymethyl)phenyl hydroxamic acid (L₂H₂)



Hydroxylamine sulphate (6.10 g, 37mmol) and 30.03 g of ice were added to an aqueous solution of NaOH (7.41 g, 185 mmol, 30 cm³). Na₂SO₄ (0.58 g, 4.44 mmol) and methyl 4-amino-2-methoxybenzoate (6.70 g, 37 mmol) were then added to the solution. The mixture was subsequently stirred at 45 °C for 24 hours. The resultant solution was allowed to cool and the pH was adjusted to 6 using H₂SO₄ to initiate the precipitation of a pink solid. The solid was then collected via filtration and recrystallised from hot water and cooled with ice to give L₂H₂ in 69% yield (4.64 g).

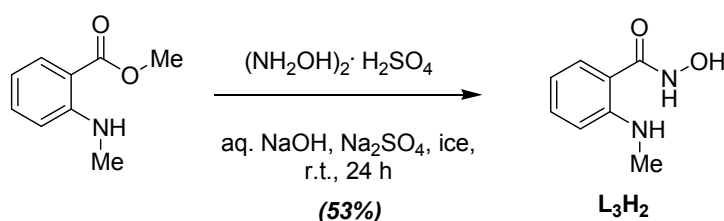
¹H NMR (DMSO-d₆, 400 MHz): δ (ppm) 3.78 (s, 3H, OMe), 5.69 (s, 2H, NH₂), 6.21 (m, 1H, Ar), 7.52 (d, *J* = 8.2 Hz, 1H, Ar-H), 8.78 (s, 1H, Ar-H), 10.11 (s, 1H, OH).

¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) 55.6 (OMe), 96.3 (C, Ar), 106.4 (CH, Ar), 108.3 (CH, Ar), 132.3 (CH, Ar), 153.3 (CH, Ar), 158.8 (C, Ar), 164.4 (C=O).

MS (EI⁺): *m/z* 182 (8%, {M⁺}), 166 (28%, {M-NH₂}⁺), 150 (100%, {M-OCH₃}⁺ and / or {M-NHOH}⁺).

FT-IR: ν (cm⁻¹) 3343 (s), 3316 (m), 3220 (m), 2831 (w), 1619 (s), 1594 (s), 1527 (s), 1497 (s), 1468 (s), 1459 (s), 1427 (s), 1335 (s), 1278 (s), 1260 (s), 1212 (s), 1192 (s), 1156 (s), 1118 (s), 1025 (s), 955 (s), 889 (s), 849 (s), 828 (m), 771 (s), 738 (s), 717 (w), 644 (s) 611 (s), 546 (s), 525 (s).

Synthesis of 2-(methylamino)phenylhydroxamic acid (L₃H₂)



To a stirring solution of dimethyl anthranilate (5.7 cm³, 35 mmol), NaOH (7.41 g, 185 mmol, 30 cm³ water), Na₂SO₄ (0.58 g, 4.1 mmol), ice (30 g) and hydroxylamine sulphate (6.11 g, 35mmol) was added and the solution left to stir for 24 hours. After this time the solution was left to cool and was subsequently pH adjusted to 6 using H₂SO₄, after which the product began to precipitate out. The resultant precipitate was collected and dried before recrystallisation using hot water, to give a final yield of 53% (3.25 g).

¹H NMR (DMSO-d₆ 400 MHz): δ (ppm) 2.76 ppm (s, 3H, CH₃), 6.46 (s, 1H, NH-CH₃) 6.50 (m, 2H, CH-Ar) 7.13 (t, *J* = 8.9 Hz, 1H, CH-Ar), 7.59 (dd, *J* = 7.7, 1.6 Hz, 1H, CH-Ar), 8.86 ppm (s, 1H, NH-OH) 10.96 ppm (s, 1H, NH-OH).

¹³C NMR (DMSO-d₆, 100 MHz): δ (ppm) 29.30 (CH₃), 110.90 (CH-Ar), 114.00 (C-Ar), 114.50 (CH-Ar), 128.00 (CH-Ar), 132.70 (CH-Ar), 150.20 (NH-C-Ar), 167.50 (C=O).

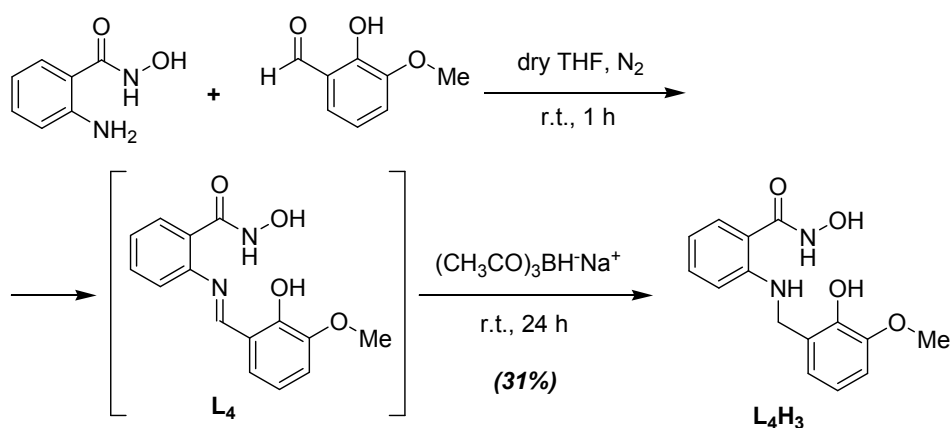
MS (EI⁺): *m/z* 166 (57%, {M⁺}), 134 (100%, {M-NHOH}⁺).

FT-IR: ν (cm⁻¹): 3409 (s), 3295 (m/b), 3076 (w), 3033 (w), 2911 (w), 2819 (m), 1937 (w), 1910 (w), 1815 (w), 1788 (w), 1622 (s), 1581 (s), 1511 (s), 1445 (m), 1417 (m), 1327 (m), 1282 (m), 1252 (w), 1173 (s), 1153 (s), 1102 (w), 1069 (m), 1028 (s), 969 (w), 942 (w), 897 (s), 846 (m), 803 (m), 782 (m), 748 (s), 706 (m), 668 (m), 599 (m), 565 (w), 552 (m), 515 (w), 474 (w), 409 (w).

UV-vis (MeOH): λ_{max} (nm) (ϵ_{max} 10³, dm³ mol⁻¹ cm⁻¹): 218 (sh), 255.5 (5.53), 341 (1.78).

UV-vis (MeCN): λ_{max} (nm) (ϵ_{max} 10³, dm³ mol⁻¹ cm⁻¹): 215 (26.93) 258 (14.01), 342 (7.73).

Synthesis of (*N*-hydroxy-2-((2-hydroxy-3-methoxybenzyl)amino)benzamide (**L₄H₃**))



Equimolar amounts of 2-aminophenylhydroxamic acid (2.00 g, 13.00 mmol) and *ortho*-vanillin (1.99 g, 13.00 mmol) were dissolved in dry tetrahydrofuran (30 cm³) under nitrogen atmosphere and the solution was stirred at room temperature for 1 hour. The reaction mixture was then left to cool before being treated with sodium triacetoxyborohydride (4.16 g, 19.50 mmol) under nitrogen conditions at room temperature for 24 h. The progress of the reaction was monitored by TLC. Upon completion the reaction was quenched with saturated sodium bicarbonate solution and the organic layer was subsequently extracted with ethyl acetate (30 cm³) before washing repeatedly with water until all traces of sodium triacetoxyborohydride were removed. The organic layer was then dried with anhydrous magnesium sulphate and the solvent evaporated to dryness to give **L₄H₃** in 31% yield (1.17 g).

¹H NMR (DMSO-*d*₆ 400 MHz): δ (ppm) 3.79 (s, 3H, OCH₃), 4.51 (s, 2H, CH₂), 6.93 (dt, *J* = 7.6, 1.9 Hz, 1H, Ar-H), 6.84 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar-H), 6.76 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar-H), 8.32 (s, 1H, NH), 8.50 (s, 1H, NH), 10.2 (s, 1H, OH), 11.2 (s, 1H, OH).

¹³C NMR (DMSO-*d*₆, 100 MHz): δ (ppm) 163.1 (CO), 148.0 (C, Ar), 146.5 (C, Ar), 144.3 (C, Ar), 133.5 (CH, Ar), 127.4 (C, Ar), 126.8 (CH, Ar), 118.9 (CH, Ar), 118.8 (CH, Ar), 117.5 (CH, Ar), 114.8 (C, Ar), 112.1 (CH, Ar), 69.7 (CH₃, OMe), 56.4 (CH₂, CHO).

MS (EI⁺): *m/z* 286.04 (100%; {M⁺}), 269.22 (30%, {M-OH}⁺), 255.24 (18%, {M-OCH₃}⁺).

FT-IR: ν (cm⁻¹) 3379 (br), 3069 (w), 2938 (w), 2839 (w), 2341 (w), 1905 (w), 1722 (w), 1611 (s, sh), 1592 (w), 1515 (m), 1484 (m), 1462 (w), 1442 (w), 1371 (m), 1328 (w), 1272 (m), 1163 (w), 1083 (m), 1056 (w), 988 (m), 988 (m), 912 (w), 829 (w), 747 (s, sh), 686 (m), 539 (w), 411 (w).

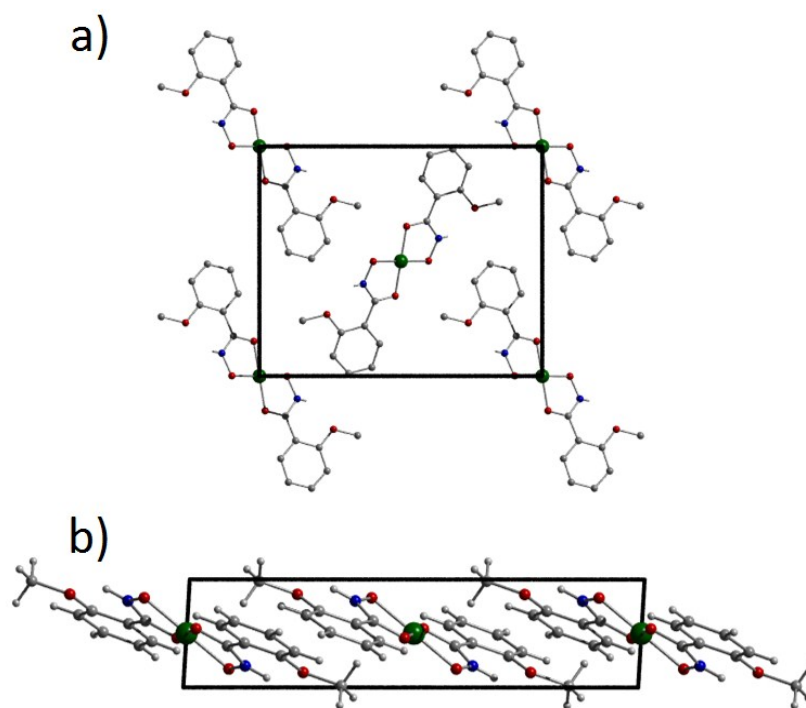


Figure S1 Crystal packing representations of $[\text{Cu}(\text{II})(\text{L}_1\text{H})_2]$ (**1**) as viewed along the a -(**a**) and the b -axis (**b**) of the unit cell.

Table S1 Selected crystal data obtained from **1–3**.

	1	2·2MeCN	3·3.5H₂O·0.14MeOH
Formula ^a	C ₁₆ H ₁₆ N ₂ O ₆ Cu ₁	C ₃₆ H ₃₈ N ₆ O ₁₂ Cl ₂ Fe ₂	C ₉₈ H ₁₅₇ N ₁₃ O _{60.5} Co ₇
M _w	395.85	929.32	2897.88
Crystal System	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /c	P-1	P-1
a/Å	3.69870(10)	10.0272(3)	17.7308(7)
b/Å	12.6213(4)	10.6948(3)	19.4055(4)
c/Å	15.7971(5)	10.8905(4)	19.8470(4)
α/°	90	76.760(3)	103.669(2)
β/°	93.451(3)	65.622(3)	101.741(3)
γ/°	90	69.977(3)	96.955(3)
V/Å ³	736.11(4)	994.20(6)	6393.1(3)
Z	2	1	2
T/K	100.0(2)	100.0(2)	100(2)
λ ^b /Å	0.71073	0.71073	1.54178
D _c /g cm ⁻³	1.786	1.552	1.207
μ(Mo-Kα)/ mm ⁻¹	1.524	0.934	7.560
Meas./indep. (R _{int}) refl.	9835/ 1343 (0.0322)	12861 / 3554 (0.0516)	18366 / 12485 (0.1040)
Restraints, Parameters	0, 120	0, 265	0, 1302
wR2 (all data)	0.2177	0.1719	0.1871
R1 ^{d,e}	0.0616	0.0613	0.0621
Goodness of fit on F ²	1.563	1.170	1.093

^a Includes guest molecules. ^bMo-Kα radiation, graphite monochromator.

^cwR2 = [Σw(IF_o²I - IF_c²I)² / ΣwIF_o²I]^{1/2}. ^dFor observed data. ^eR1 = Σ|F_oI - IF_cII / ΣIF_oI

Table S2 Selected crystal data obtained from **4 - 7**.

	4·H₂O	5·2MeOH	6·3H₂O	7·3H₂O·4MeOH
Formula ^a	C ₈ H ₁₃ N ₃ O ₈ Cu ₁	C ₁₈ H ₂₆ N ₄ O ₆ Zn ₁	C ₃₂ H ₃₈ N ₁₀ O ₁₇ Cu ₅	C ₆₆ H ₈₆ N ₁₀ O ₃₁ Cu ₅
M _w	342.75	459.80	1152.37	1833.17
Crystal System	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	P2 ₁ /c	Pcc2	P-1	P-1
a/Å	12.2451(4)	14.3459(4)	11.3704(6)	11.464(2)
b/Å	10.0658(2)	10.8600(3)	13.3009(7)	12.740(3)
c/Å	10.9339(3)	6.3652(2)	14.8558(8)	14.419(3)
α/°	90	90	91.179(4)	109.97(3)
β/°	114.906(4)	90	106.814(5)	97.74(3)
γ/°	90	90	108.726(5)	106.55(3)
V/Å ³	1222.34(6)	991.68(5)	2020.8(2)	1833.3(8)
Z	4	2	2	1
T/K	100(2)	100(2)	100.0(2)	100.0(2)
λ ^b /Å	0.71073	0.71073	0.71073	0.71073
D _c /g cm ⁻³	1.852	1.540	1.884	1.494
μ(Mo-Kα)/mm ⁻¹	1.832	1.282	2.676	1.507
Meas./indep. (R _{int}) refl.	13558 / 2233 (0.0232)	17587 / 1787 (0.0335)	33372 / 7391 (0.0770)	16866 / 6705 (0.0248)
Restraints, Parameters	4, 193	1, 135	0, 569	9, 449
wR2 (all data)	0.0675	0.1165	0.1287	0.2305
R1 ^{d,e}	0.0249	0.0457	0.0494	0.0776
Goodness of fit on F ²	1.071	1.044	1.076	1.14

^a Includes guest molecules. ^bMo-Kα radiation, graphite monochromator.

^cwR2 = [Σw(IF_o²I - IF_c²I)² / ΣwIF_o²I²]^{1/2}. ^dFor observed data. ^eR1 = Σ|F_oI - IF_cI| / ΣIF_oI

Table S3 Magnetic moment data obtained from a polycrystalline sample of complex **1**.

Sample	[Cu(II)(L ₁ H) ₂] (1)
C (calibration constant) [‡]	1.18
T (K)	302
L (sample length; cm)	2.6
MW (g mol ⁻¹)	395.88
M ₀ (g)	0.6990
M ₁ (g)	0.8643
M (M ₁ -M ₀) (g)	0.1653
R ₀	-0.27
R	145
R-R ₀	145.27
μ _{eff}	1.61

[‡] Johnson Matthey balance was calibrated using Hg[Co(II)(NCS)₄] prior to use.¹
Magnetic moments calculated using the equations below.

$$\chi_g = c \cdot L \cdot (R - R_0) / 10^9 \cdot m$$

$$\chi_m = \chi_g \cdot Mw$$

$$\mu = 2.828 \cdot (\chi_m \cdot T)^{1/2}$$

Table S4 BVS data on [Fe(III)₂(L₁H)₄Cl₂]₂MeCN (**2**)

Atom label	BVS result
Fe1	2.62

Table S5 BVS data on [Co(III)Co(II)₆(L₁H)₈(L₁)₂(MeOH)₄(NO₃)₂]NO₃·3.5H₂O·14MeOH (**3**).

Atom label	BVS result
Co1	1.98
Co2	2.05
Co3	3.29
Co4	2.06
Co5	2.07
Co6	2.10
Co7	2.11

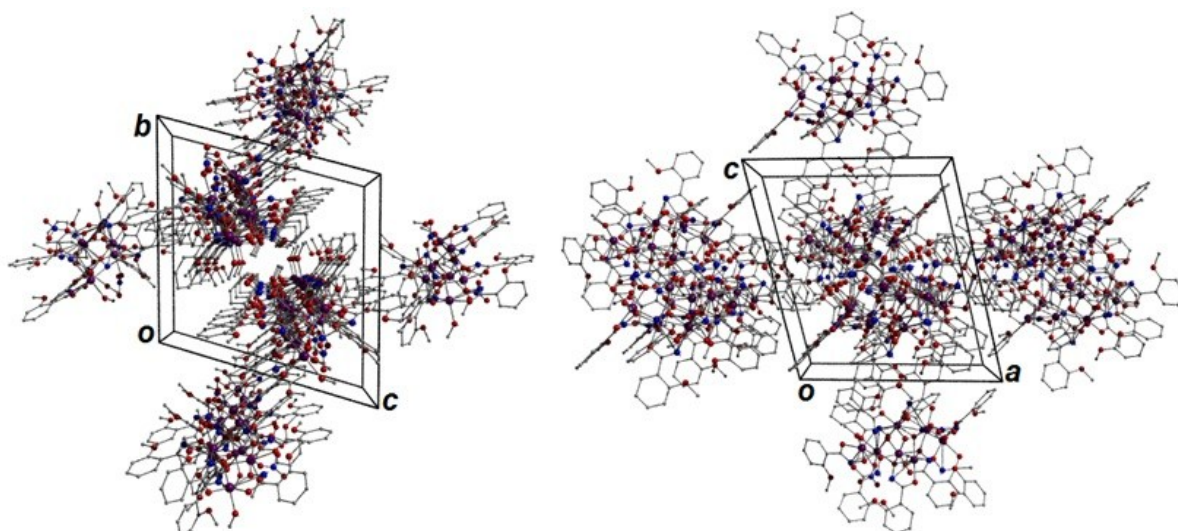


Figure S2 The crystal packing of $[\text{Co(III)Co(II)}_6(\text{L}_1\text{H})_8(\text{L}_1)_2(\text{MeOH})_4(\text{NO}_3)_2]\text{NO}_3 \cdot 3.5\text{H}_2\text{O} \cdot 14\text{MeOH}$ (**3**) as viewed along the *a* (left) and *b* (right) unit cell directions.

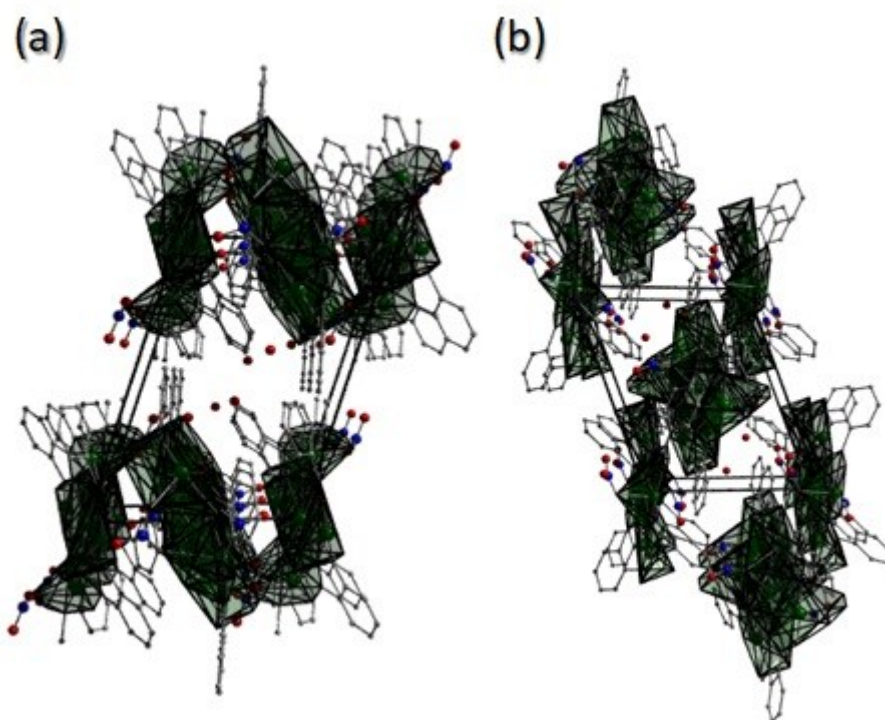


Figure S3 Packing arrangement in **6** as viewed down the *b*-axis (a) and *c*-axis (b) of the unit cell. All hydrogen atoms were omitted for clarity.

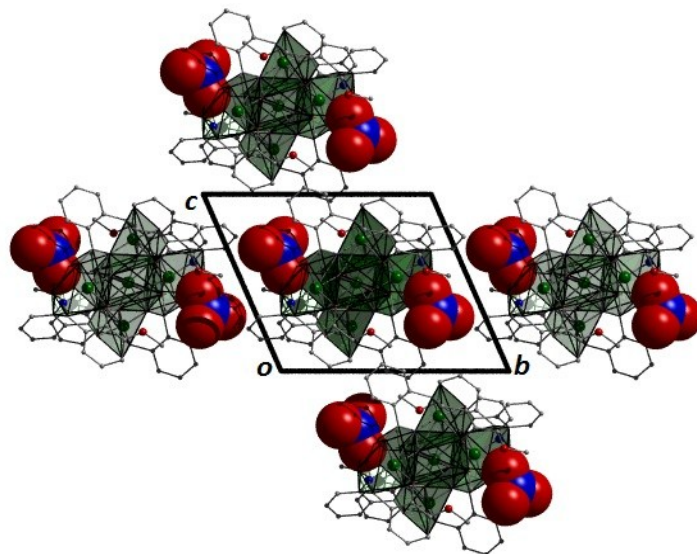


Figure S4 Packing arrangement in complex 7 as viewed down the a -axis of the unit cell. The NO_3^- counter anions are space-fill represented.

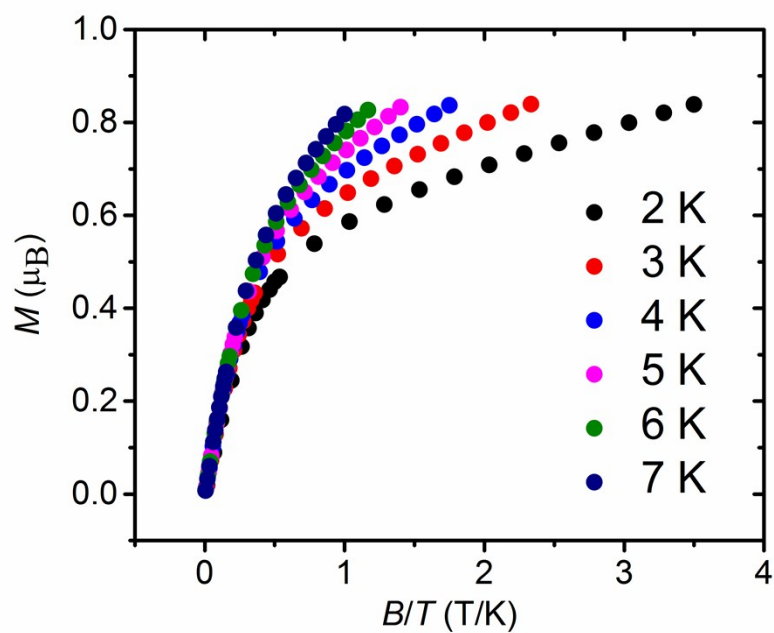


Figure S5 Reduced magnetisation (M/μ_B) vs. B/T (T/K) data obtained from a polycrystalline sample of complex 3 measured within the 2–7 K temperature range and 0–7 T magnetic field range.

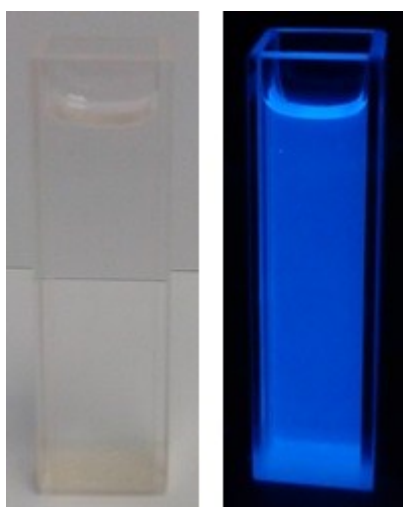


Figure S6 Solution of complex **5** in dichloromethane under ambient light (left) and under hand-held UV lamp irradiation, $\lambda = 365$ nm (right).

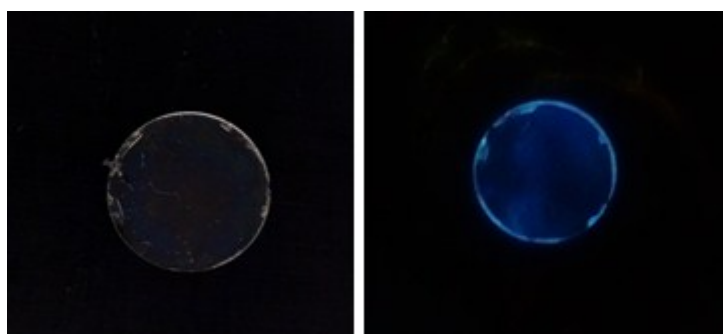


Figure S7 Thin films of complex **5** drop-casted on quartz disks from chloroform solution, under ambient light (left) and under hand-held UV lamp irradiation, $\lambda = 365$ nm (right).

References

- [1] B. N. Figgis and R. S. Nyholm, A convenient solid for calibration of the Gouy magnetic susceptibility apparatus. *J. Chem. Soc.*, 1958, 4190.