Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Microporous Metal-Organic Frameworks built from Rigid Tetrahedral Tetrakis(4-tetrazolylphenyl)silane Connectors

Ivan Timokhin,[a,b] Andrew J. P. White,[a] Paul D. Lickiss,[a]
Claudio Pettinari,[b] Robert P. Davies*[a]

[a] *Department of Chemistry*
Imperial College London
South Kensington
London
UK SW7 2AZ

[b] *Scuola del Farmaco e dei Prodotti della Salute*
Università degli Studi di Camerino
via S. Agostino 1
I-62032 Camerino, MC
Italy

** Corresponding Author*
E-mail: r.davies@imperial.ac.uk
Fax: +44 870 1300438
Tel: +44 207 5945754

Experimental Procedures

General Methods

All reactions involving *n*BuLi were carried out in oven-dried glassware and were performed under an atmosphere of nitrogen. Diethyl ether and THF were dried by distillation over sodium metal prior to use. All other chemicals and solvents used in the syntheses were commercial reagent grade and were used without further purification. Tetrakis(4-cyanophenyl)silane was prepared according to literature procedures.[1] NMR spectra were recorded on a Bruker AV-400 spectrometer and Infrared spectra on a Perkin Elmer spectrum 100 series spectrometer with a universal ATR sampling accessory. Microanalytical data were obtained from the Science Technical Support Unit, London Metropolitan University. *Metal tetrazolates are potentially explosive, particularly when dry, and should be handled with appropriate care and respect.*

Synthesis of H_4ttps, tetrakis(4-2H-tetrazol-5-yl-phenyl)silane[2]

A mixture of tetrakis(4-cyanophenyl)silane (1.00 g, 2.29 mmol), sodium azide (1.72 g, 26.4 mmol) and triethylamine hydrochloride (3.63 g, 26.4 mmol) in 25 mL toluene and 10 mL methanol was heated at reflux for 4 days. After this period the mixture was cooled to room temperature and an aqueous solution of NaOH (25 mL, 1 M) was added. The solution was then stirred for 30 mins. The resultant aqueous layer was treated with dilute HCl (1 M) until no further precipitate formed. The precipitate was collected by filtration and dissolved in a solution of NaOH (1 M). The resulting solution was treated with portions of dilute HCl (1 M) until the approximate pH of the solution reached 4. The ensuing precipitate was filtered, washed three times with distilled water and dried under vacuum at 50 °C for 2 days to give

1.03g (73 %) of H_4ttps.4H_2O. M.p. > 300 °C. ^{1}H NMR (D_6-DMSO): 11.8 (br, 4H, NH), 8.17 (d, J = 8.0 Hz, 8 H, Ar-H), 7.80 (d, J = 8.0 Hz, 8 H, Ar-H) ppm. IR (ATR): ν(cm^{-1}) = 3405 (br), 1653, 1569, 1407, 1282, 1107, 1068, 929, 835, 741, 701. Anal. Calcd. (%) for $C_{28}H_{20}N_{16}Si.4H_2O$: C, 55.15; H, 3.64; N, 36.75.Found: C, 55.15; H, 3.66 ; N 36.44

Synthesis of IMP-16Mn, [H(Mn_4Cl)(ttps)$_2$(DMF)$_4$].18DMF

H_4ttps (50 mg, 0.08 mmol) and $MnCl_2.4H_2O$ (32 mg, 0.16 mmol) were dissolved in a mixture of 4.5 mL DMF, 1.5 ml MeOH and 0.1 mL of dilute HCl (1 M) to give a clear solution. This solution was subsequently heated in a sealed screw-top glass vial at 80 °C for 3 days. The mixture was allowed to cool to room temperature and the resultant pale purple crystals filtered and washed with anhydrous DMF. Yield = 105 mg (81%). IR (ATR): ν(cm^{-1}) = 2973 (br), 1653, 1527, 1448, 1406, 1099, 1008, 833, 745. Anal. Calcd. (%) for $C_{56}H_{33}ClMn_4N_{32}Si_2\cdot(C_3H_7NO)_4(CH_3OH)_{18}$; C, 44.24; H, 5.74; N, 21.60, Found; C, 44.07; H, 5.74; N, 21.49. Note that washing and drying procedures for elemental analysis and single crystal X-ray diffraction differed so that there are minor differences in solvation.

Synthesis of IMP-17Mn/Cd/Cu, [H(M_4Cl)(ttps)$_2$(DMF)$_4$] (M = Mn, Cd, Cu)

All **IMP-17** MOFs were prepared via the same synthetic protocol, starting from the appropriate metal nitrate salt. The synthesis of **IMP-17Mn** below is illustrative of the general protocol employed.

H_4ttps (50 mg, 0.08 mmol) and $Mn(NO_3)_2.4H_2O$ (41 mg, 0.16 mmol) were dissolved in a mixture of 4.5 mL DMF, 1.5 ml MeOH and 0.1 mL of dilute HNO_3 (1 M) to give a clear solution. This solution was subsequently heated in a sealed screw-top glass vial at 80 °C for 3 days. The mixture was allowed to cool to room temperature and the resultant colourless block crystals filtered and washed with anhydrous DMF to give [H(Mn_4Cl)(ttps)$_2$(DMF)$_4$]·20DMF,

IMP-17Mn. Yield = 190 mg (79%). IR (ATR): ν(cm^{-1}) = 2971 (br), 1652, 1525, 1448, 1404, 1096, 1040, 1009, 832, 743. Anal. Calcd. (%) for $C_{40}H_{44}Mn_2N_{20}O_4Si\cdot(C_3H_7NO)_4(CH_3OH)_3$; C, 47.34; H, 6.07; N, 24.09, Found; C, 46.60; H, 6.20; N, 24.17. Note that washing and drying procedures for elemental analysis and single crystal X-ray diffraction differed so that there are minor differences in solvation.

IMP-17Cd: Yield = 200 mg (83%). IR (ATR): ν(cm^{-1}) = 2931 (br), 1639, 1495, 1443, 1383, 1095, 1005, 837, 743. Due to the poor stability of the MOF (see main text) it was not possible to obtain satisfactory elemental analysis or powder X-ray diffraction data for this compound.

IMP-17Cu: Yield = 20 mg (31%). IR (ATR): ν(cm^{-1}) = 2973 (br), 1619 (br), 1529, 1446, 1407, 1304, 1101, 1006, 959, 823, 748. Due to poor stability of the MOF (see main text) it was not possible to obtain satisfactory elemental analysis or powder X-ray diffraction data for this compound.

Gas absorption measurements

Supercritical CO_2 activation was performed using a Polaron Critical Point Dryer. Approximately 100 mg of the MOF sample were soaked in anhydrous ethanol over a period of 3 days (refreshing the solution every day) in order to remove all residual DMF from the pores. The resultant material was then filtered on a glass frit and transferred to the Critical Point Dryer. After loading the sample the dryer was flushed with CO_2 for 1 minute before closing the venting valve and cooling the chamber to 7 °C. The chamber was then filled to approximately 60% capacity, and the MOF was left to soak for 10 hours with purging of the liquid CO_2 and refilling the chamber every 2 hours. The chamber was subsequently heated to 45°C for 2 hours and the supercritical fluid was slowly vented. After supercritical drying, samples were outgassed at 50 °C under 0.005 mbar vacuum for 10 hours. Gas adsorption isotherms for pressures in the range 0–1 bar were measured using a Beckman Coulter SA3100 instrument. N_2 isotherms at 77 K were measured in liquid nitrogen baths using Ultra high purity nitrogen (ALPHAGAZ™ 1 NITROGEN, 99.999%).

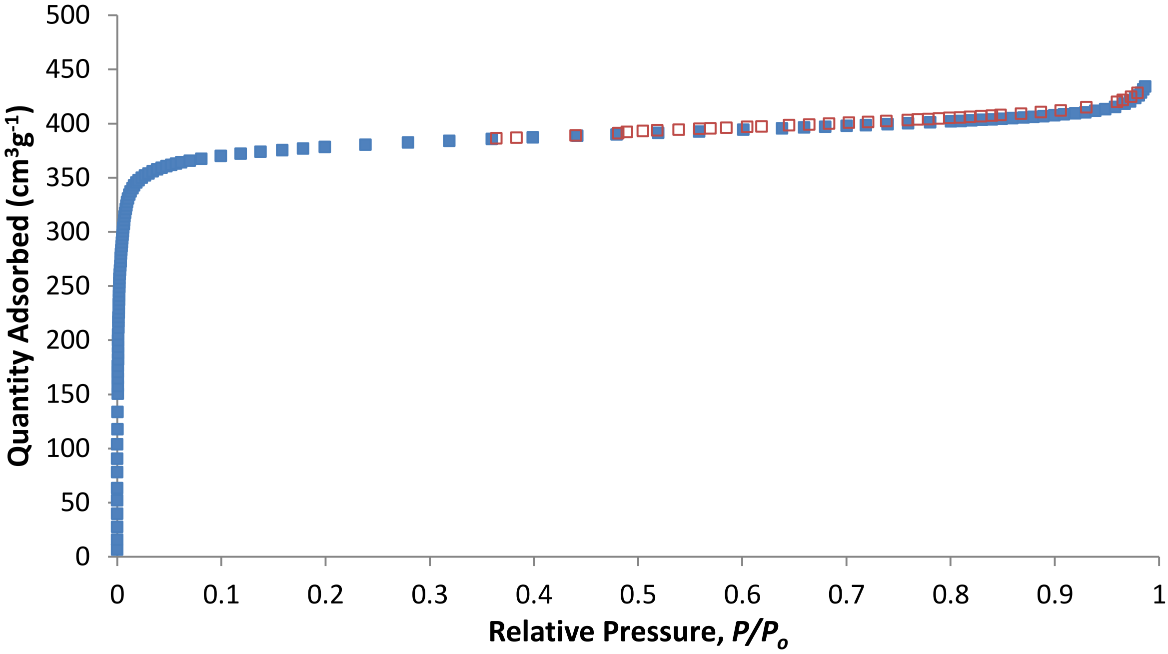

Fig. S1 Nitrogen gas sorption isotherm for the ‘cadmium MOF product / product-mix’ (see main text) formed from the treatment of $CdCl_2$ with H_4ttps. Filled and empty symbols represent adsorption and desorption data respectively.

X-Ray Crystallography Supporting Information

IMP-16Mn

The presumed “extra” hydrogen atom in the structure of $[H(Mn_4Cl)(ttps)_2(DMF)_4]\cdot 20DMF$ (**IMP-16Mn**) could not be located in the crystal structure (unsurprising given the high symmetry and the significant disorder in the coordinated and included solvent, see below), and so the atom list for the asymmetric unit is low by 0.125(H).

The chlorine atom at the centre of each Mn_4 node sits on an *mmm* position, the two unique manganese centres occupy sites with *mm* symmetry, and the silicon atom is on a -4 position. The contents of the asymmetric unit are shown in Figs. S1 and S2.

Both the coordinated and the included solvent molecules were found to be highly disordered. The two coordinated solvent molecules, based on O(20) and O(30), are both disordered across sites with *mm* symmetry, and in each case only the donor oxygen atom could be located with any reliability; from an inspection of the electron density maps, combined with a knowledge of the solvents used, the most likely identity of both the coordinated and included molecules was deemed to be dimethylformamide, $Me_2N–C(H)=O$, C_3H_7NO (40 electrons). The best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.[3] This suggested a total of 1830 electrons per unit cell, equivalent to approximately 114.4 electrons per asymmetric unit. Because SQUEEZE does not remove electron density that is within bonding distance of defined atoms, that for the carbonyl carbon atom of each coordinated solvent molecule would not be removed, meaning that only C_2H_7N for each coordinated solvent molecule would contribute to the total electron density removed by SQUEEZE. Due to the symmetry, this would amount to $0.5(C_2H_7N)$ per asymmetric unit, accounting for 13 electrons, leaving 101.4 electrons for the included solvent. 2.5 Dimethylformamide molecules corresponds to 100 electrons, so this was used as the solvent present; this amounts to 20 dimethylformamide molecules per Mn_4 unit.

As a result of the missing NH hydrogen atom, the only partial located coordinated solvent molecules, and the absent included solvent molecules, the atom list for the asymmetric unit is low by $0.125(H) + 0.5(C_3H_7N) + 2.5(C_3H_7NO) = C_9H_{21.125}N_3O_{2.5}$ (and that for the unit cell low by $C_{144}H_{338}N_{48}O_{40}$) compared to what is actually presumed to be present.

IMP-17Cd

The silicon and both cadmium centres in the structure of $[Cd_2(ttps)(DMF)_4]\cdot 16DMF$ (**IMP-17Cd**) occupy special positions; the Si(1) site has -4 symmetry, the Cd(1) site has -3 symmetry, and the Cd(2) site has 3-fold symmetry. The contents of the asymmetric unit are shown in Figs. S3 and S4.

The coordinated DMF solvent molecule was found to be disordered. Two orientations sharing a common oxygen site were identified, of *ca*. 63 and 37% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The included solvent molecules were found to be highly disordered, and the best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.[3] This suggested a total of 15066 electrons per unit cell, equivalent to approximately 156.9 electrons per asymmetric unit. From an inspection of the electron density maps, combined with a knowledge of the solvents used, the most likely identity for the included solvent was deemed to be dimethylformamide, $Me_2N–C(H)=O$, C_3H_7NO (40 electrons). 4 Dimethylformamide molecules corresponds to 160 electrons, so this was used as the solvent present (equivalent to 16 per Cd_2 unit).

As a result, the atom list for the asymmetric unit is low by 4(C_3H_7NO) = $C_{12}H_{28}N_4O_4$ (and that for the unit cell low by $C_{1152}H_{2688}N_{384}O_{384}$) compared to what is actually presumed to be present.

IMP-17Mn

The crystals of [Mn_2(ttps)(DMF)$_4$]·28DMF (**IMP-17Mn**) were found to be very poor scatters at high angle; despite an 88 hour data collection designed to capture just unique cubic data to a resolution of 0.84 Å, the mean I/σ for the data set was still only 1.03 with a very poor R_{int} of *ca*. 22%. In spite of this, however, it was still perfectly possible to identify the metal-ligand superstructure of the MOF, and to show that it is indeed isomorphous with the cadmium and copper analogues **IMP-17Cd** and **IMP-17Cu**. Being isomorphous with **IMP-17Cd**, the silicon and both metal centres again occupy special positions; the Si(1) site has -4 symmetry, the Mn(1) site has -3 symmetry, and the Mn(2) site has 3-fold symmetry. The contents of the asymmetric unit are shown in Figs. S5 and S6.

The coordinated solvent molecule was found to be highly disordered, and only the donor oxygen atom could be located with any reliability; from an inspection of the electron density maps, combined with a knowledge of the solvents used, the most likely identity of both the coordinated and included molecules was deemed to be dimethylformamide, $Me_2N–C(H)=O$, C_3H_7NO (40 electrons). The best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.[3] This suggested a total of 29377 electrons per unit cell, equivalent to approximately 306 electrons per asymmetric unit. Because SQUEEZE does not remove electron density that is within bonding distance of defined atoms, that for the carbonyl carbon atom of the coordinated solvent molecule would not be removed, meaning that only C_2H_7N would contribute to the total electron density removed by SQUEEZE. This amounts to 26 electrons, leaving 280 electrons for the included solvent.7

Dimethylformamide molecules corresponds to 280 electrons, so this was used as the solvent present (equivalent to 28 per Mn_2 unit).

As a result, the atom list for the asymmetric unit is low by (C_3H_7N) +7(C_3H_7NO) = $C_{24}H_{56}N_8O_7$ (and that for the unit cell low by $C_{2304}H_{5376}N_{768}O_{672}$) compared to what is actually presumed to be present.

IMP-17Cu

The coordinated solvent molecule was found to be highly disordered, and only the donor oxygen atom could be located with any reliability; however the most likely identity of both the coordinated and included molecules was deemed to be dimethylformamide, Me_2N–C(H)=O, C_3H_7NO (40 electrons). The best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.[3] This suggested a total of 3910 electrons per unit cell, equivalent to approximately 47 electrons per asymmetric unit. Because SQUEEZE does not remove electron density that is within bonding distance of defined atoms, that for the carbonyl carbon atom of the coordinated solvent molecule would not be removed, meaning that only C_2H_7N would contribute to the total electron density removed by SQUEEZE. This amounts to 26 electrons, leaving 21 electrons for the included solvent.0.5 dimethylformamide molecules corresponds to 20 electrons, so this was assumed to be the amount of solvent present (equivalent to 2 per Cu_2 unit). As a result, the atom list for the asymmetric unit is low by (C_3H_7N) + 0.5(C_3H_7NO) = $C_{4.5}H_{10.5}N_{1.5}O_{0.5}$ (and that for the unit cell low by $C_{432}H_{1008}N_{138}O_{48}$) compared to what is actually presumed to be present.

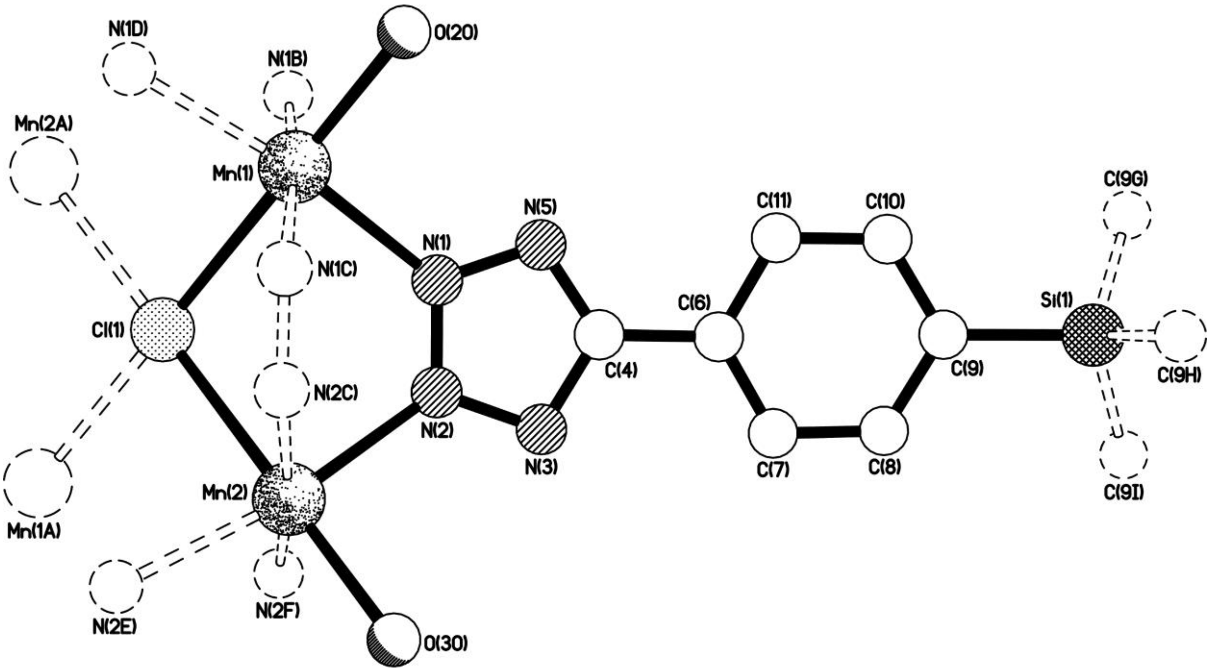

Fig. S2 The crystal structure of **IMP-16Mn** showing the contents of the asymmetric unit. Symmetry transformations used to generate equivalent atoms - A: -y+1,-x+1,z. B: x,y,-z+1. C: -y+1,-x+1,-z+1. D: y,x,z. E; -x+1,-y+1,z. F; -x+1,-y+1,-z+1. G; y+1/2,-x+1/2,-z+3/2. H; -x+1,-y,z. I; -y+1/2,x-1/2,-z+3/2.

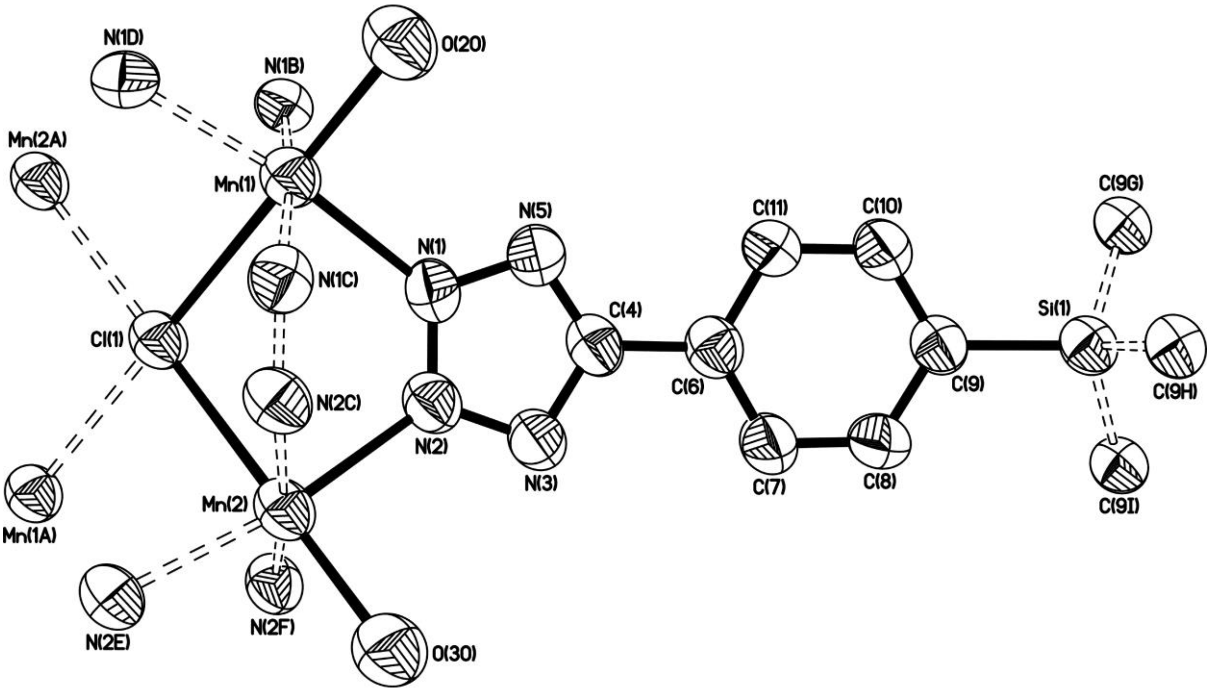

Fig. S3 The crystal structure of **IMP-16Mn** showing the contents of the asymmetric unit (30% probability ellipsoids). Symmetry transformations used to generate equivalent atoms - A: -y+1,-x+1,z. B: x,y,-z+1. C: -y+1,-x+1,-z+1. D: y,x,z. E; -x+1,-y+1,z. F; -x+1,-y+1,-z+1. G; y+1/2,-x+1/2,-z+3/2. H; -x+1,-y,z. I; -y+1/2,x-1/2,-z+3/2.

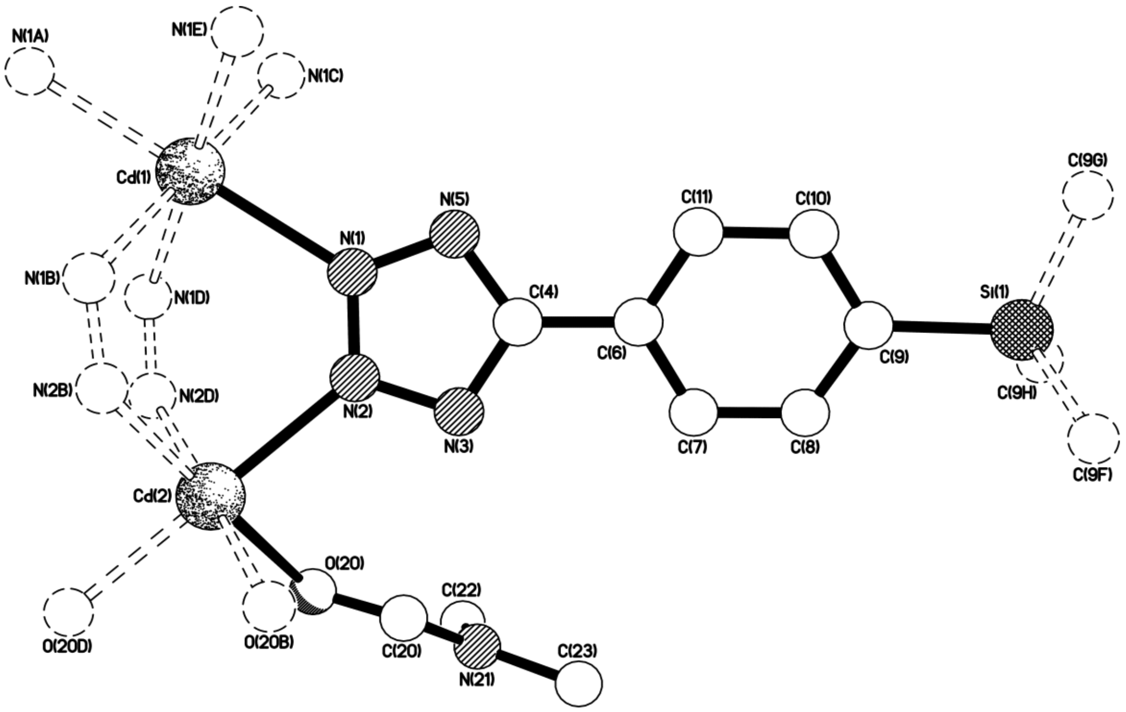

Fig. S4 The crystal structure of **IMP-17Cd** showing the contents of the asymmetric unit. Symmetry transformations used to generate equivalent atoms - A; y,z,x. B; -z+1,-x+1,-y+1. C; -x+1,-y+1,-z+1. D; z,x,y. E; -y+1,-z+1,-x+1. F; -x+3/2,y+0,-z+1. G; z+1/4,-y+3/4,-x+5/4. H;-z+5/4,-y+3/4,x-1/4.

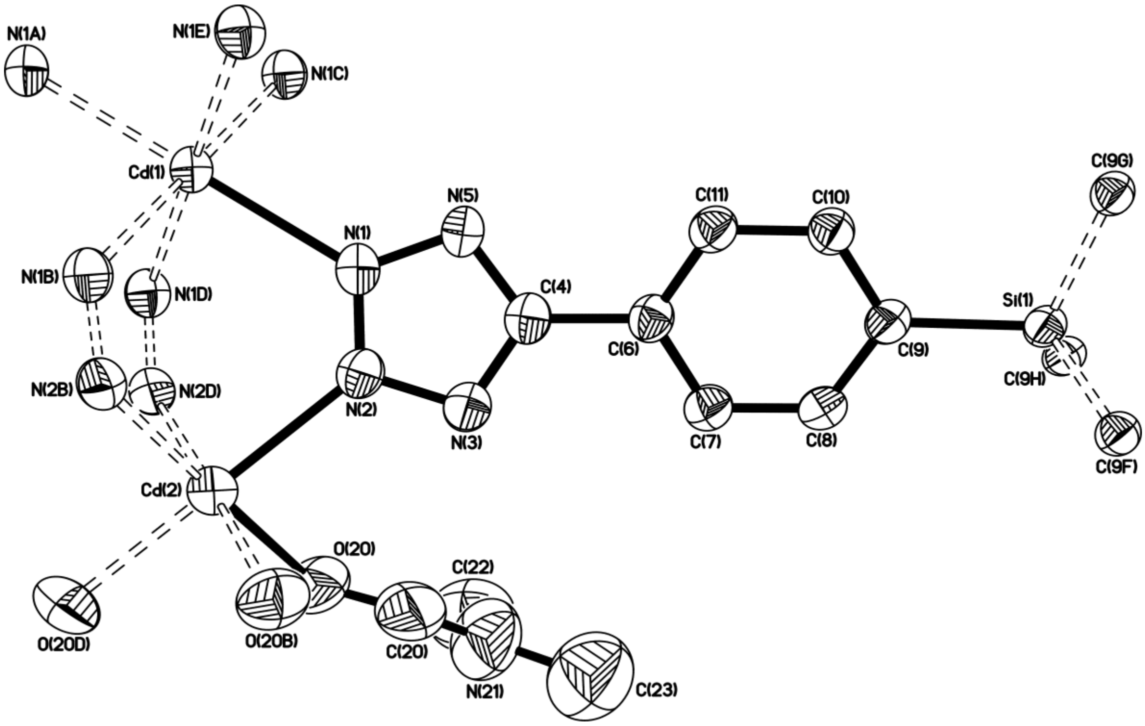

Fig. S5 The crystal structure of **IMP-17Cd** showing the contents of the asymmetric unit (30% probability ellipsoids). Symmetry transformations used to generate equivalent atoms - A; y,z,x. B; -z+1,-x+1,-y+1. C; -x+1,-y+1,-z+1. D; z,x,y. E; -y+1,-z+1,-x+1. F; -x+3/2,y+0,-z+1. G; z+1/4,-y+3/4,-x+5/4. H;-z+5/4,-y+3/4,x-1/4.

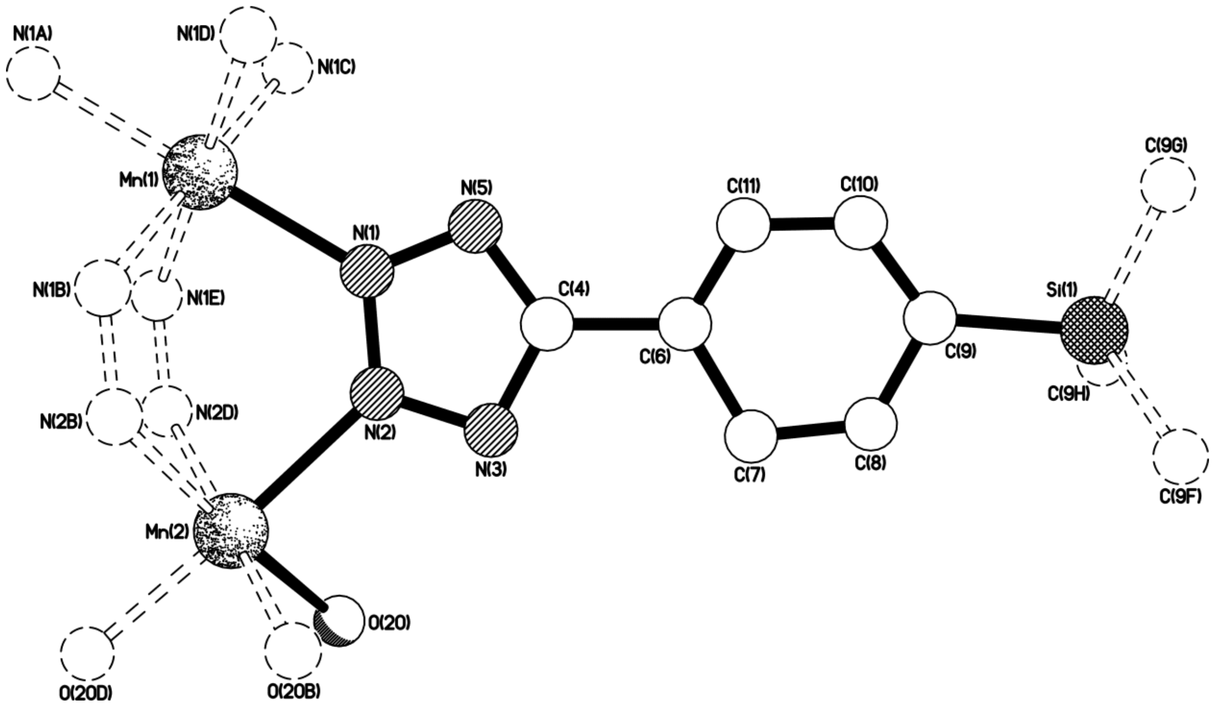

Fig. S6 The crystal structure of **IMP-17Mn** showing the contents of the asymmetric unit. Symmetry transformations used to generate equivalent atoms – A; y,z,x. B; -z+1,-x+1,-y+1. C; -x+1,-y+1,-z+1. D; z,x,y. E; -y+1,-z+1,-x+1. F; -z+5/4,-y+3/4,x-1/4. G; -x+3/2,y+0,-z+1. H; z+1/4,-y+3/4,-x+5/4.

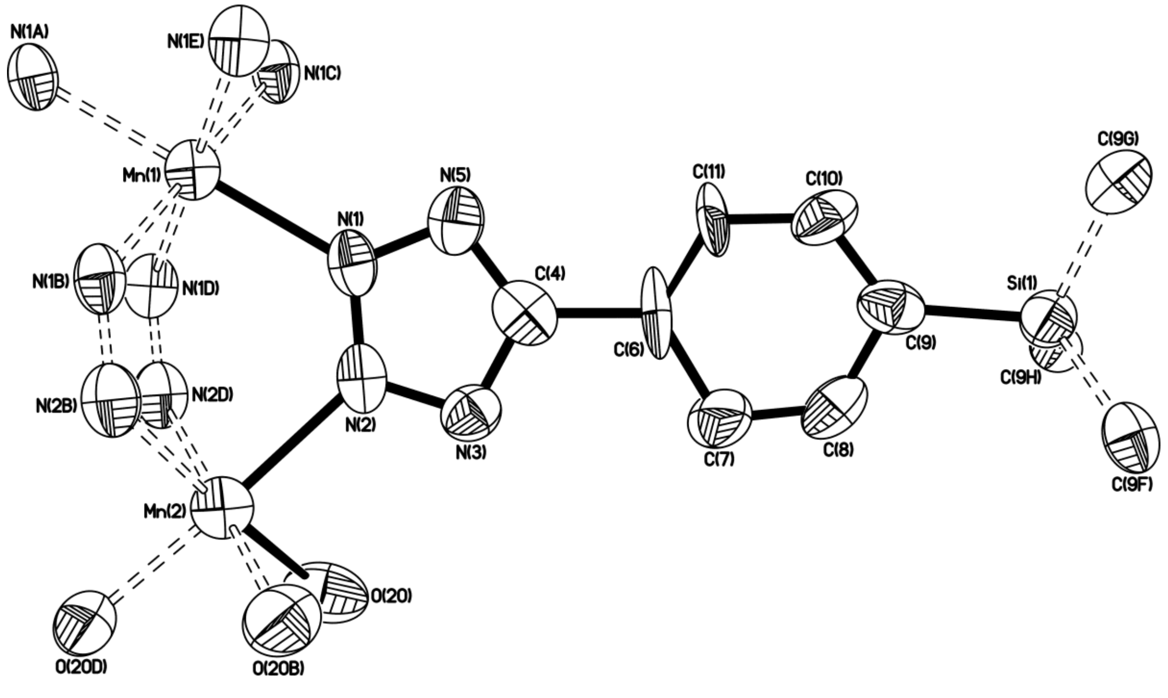

Fig. S7 The crystal structure of **IMP-17Mn** showing the contents of the asymmetric unit (15% probability ellipsoids). Symmetry transformations used to generate equivalent atoms – A; y,z,x. B; -z+1,-x+1,-y+1. C; -x+1,-y+1,-z+1. D; z,x,y. E; -y+1,-z+1,-x+1. F; -z+5/4,-y+3/4,x-1/4. G; -x+3/2,y+0,-z+1. H; z+1/4,-y+3/4,-x+5/4.

Powder X-ray Diffraction Studies

Phase purity was confirmed using a Philips PW1700 series automated powder X-ray diffractometer with Cu-K$_\alpha$ radiation and a graphite secondary crystal monochromator.

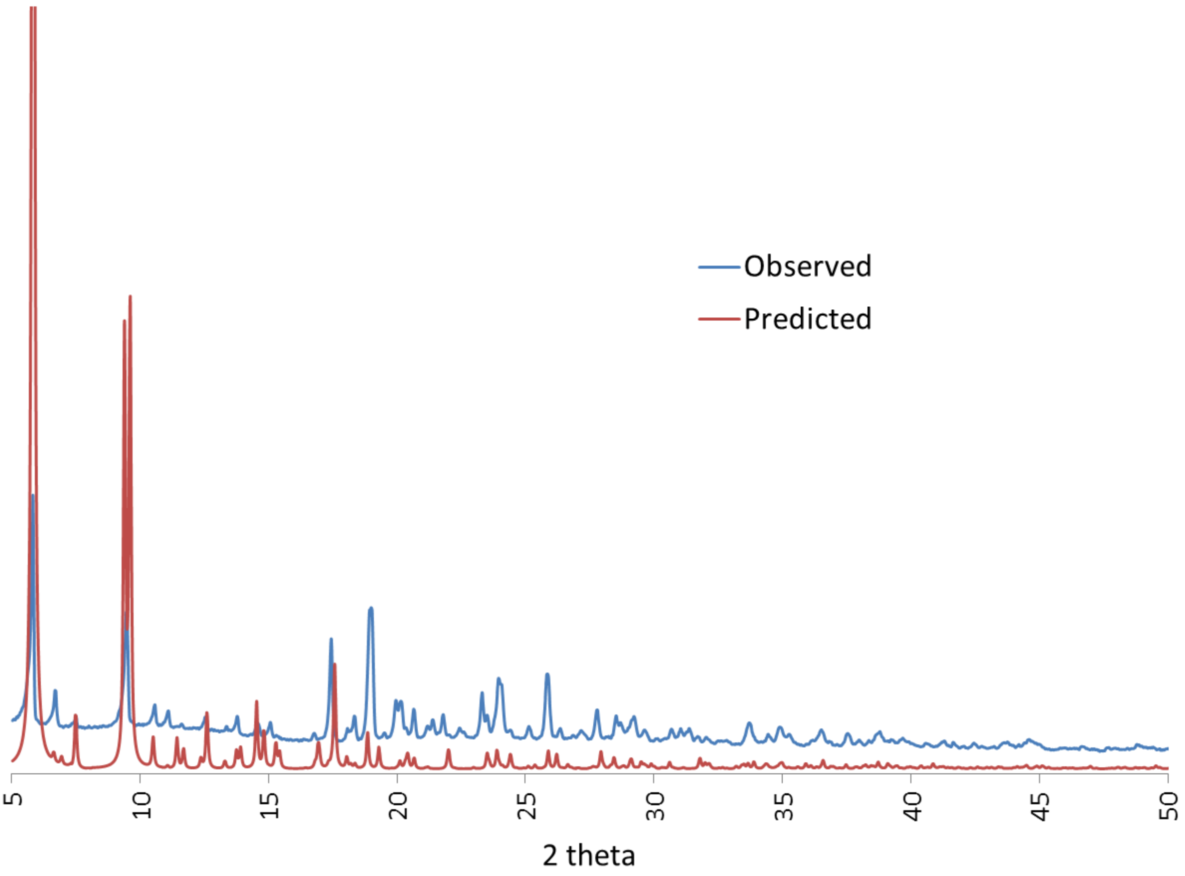

Fig. S8 Powder X-ray diffraction (PXRD) patterns for **IMP-16Mn** both calculated from the single-crystal data (Predicted) and measured experimentally on a fresh bulk sample of **IMP-16Mn** (Observed).

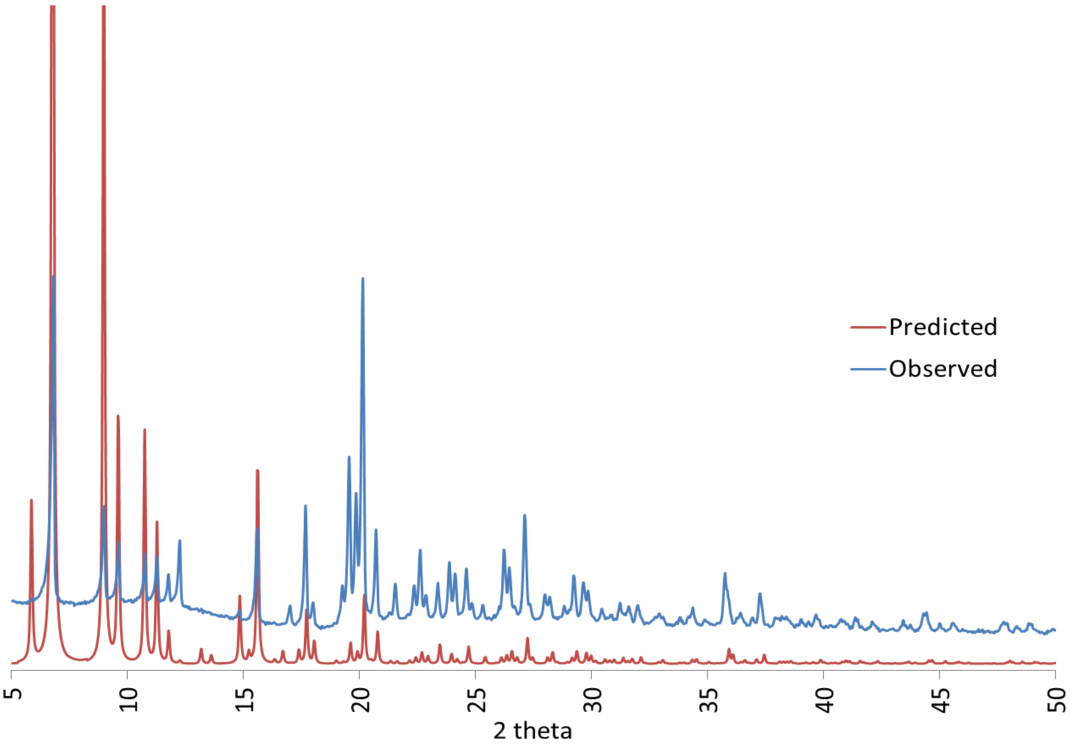

Fig. S9 Powder X-ray diffraction (PXRD) patterns for **IMP-17Mn** both calculated from the single-crystal data (Predicted) and measured experimentally on a fresh bulk sample of **IMP-17Mn** (Observed).

Themogravimetric Analysis

Thermal Gravimetric Analysis (TGA) was carried out using a Perkin Elmer Pyris 1 machine, under a constant stream of dry nitrogen gas (flow rate 20 mL min^{-1}) over the temperature range of 30 to 650 °C and at a heating rate of 5 °C min^{-1}.

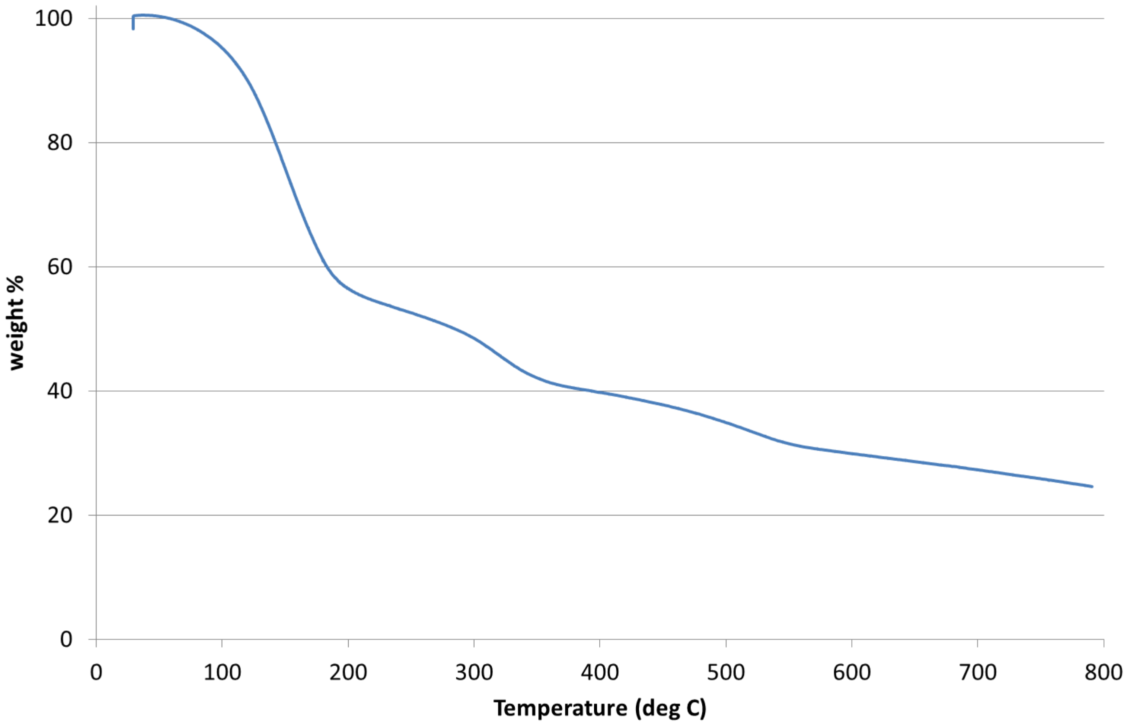

Fig. S10 TGA trace for **IMP-16Mn** (freshly prepared)

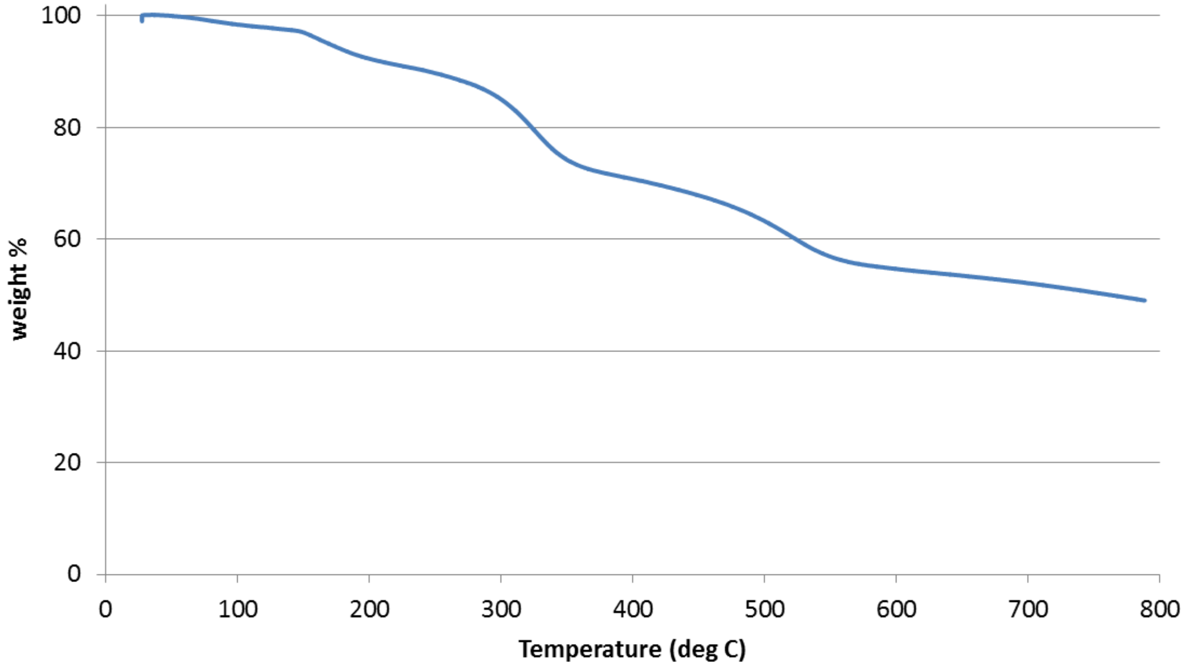

Fig. S11 TGA trace for **IMP-16Mn** (after drying with supercritical CO_2)

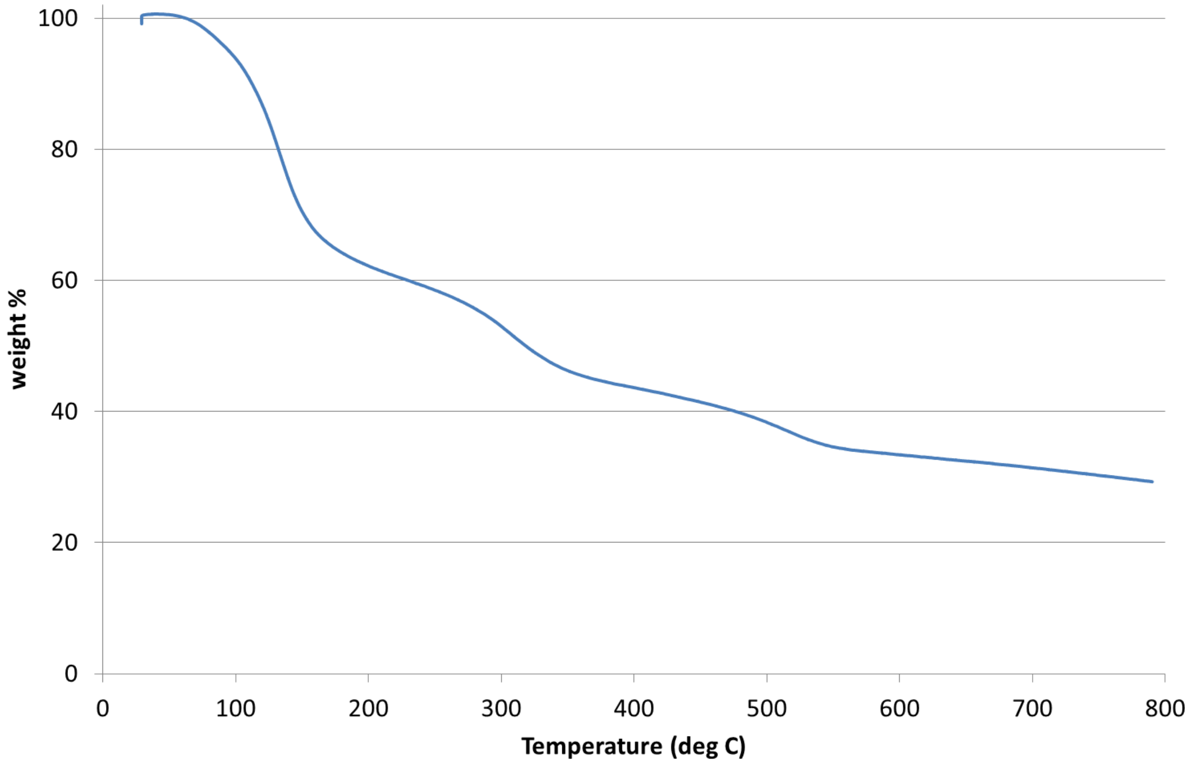

Fig. S12 TGA trace for **IMP-17Mn**

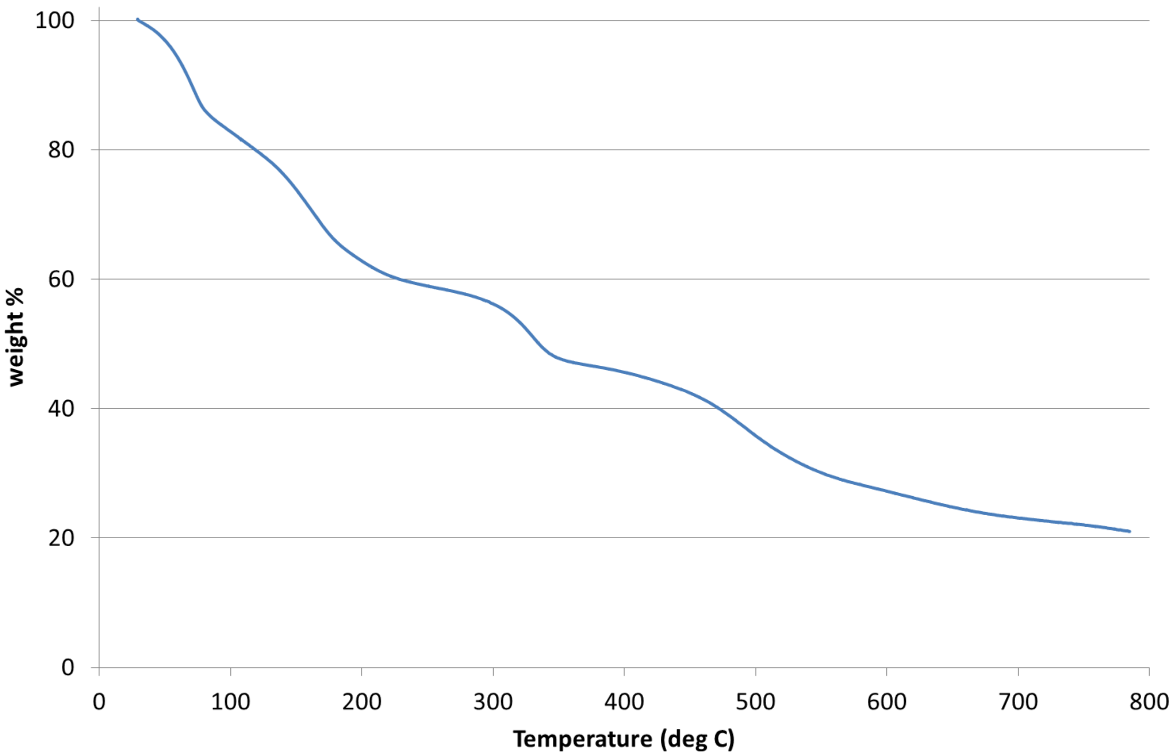

Fig. S13 TGA trace for **IMP-17Cd**

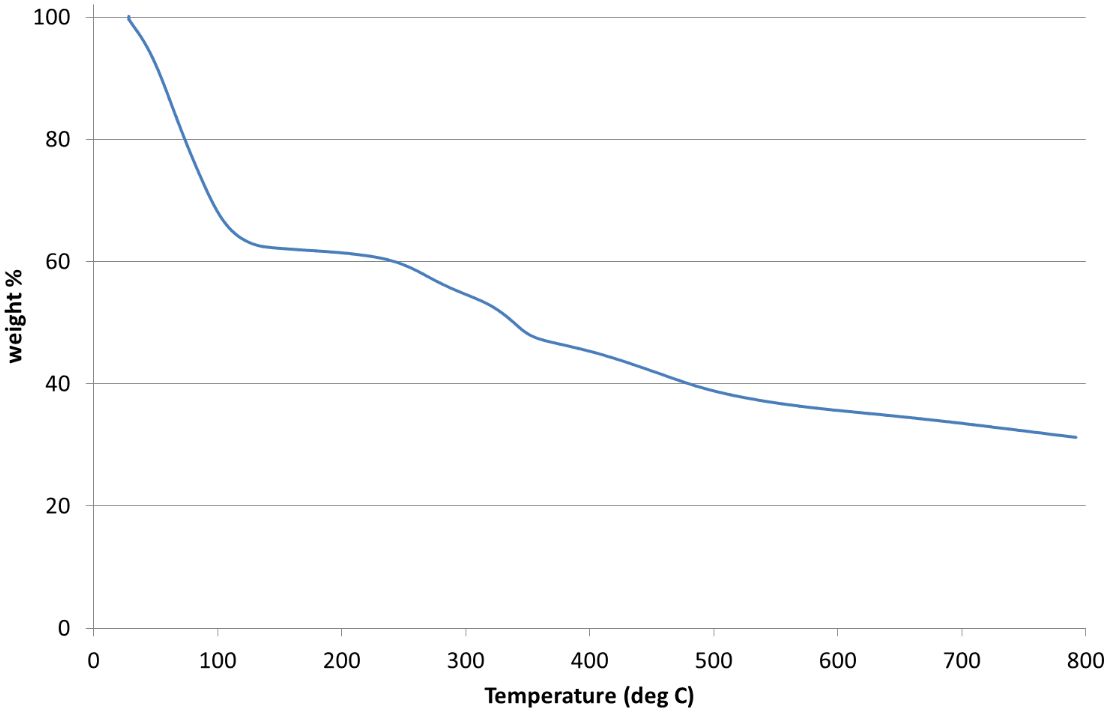

Fig. S14 TGA trace for **IMP-17Cu**

References

1. F. Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36**, 5090-5096.
2. I. Timokhin, J. Baguña Torres, A. J. P. White, P. D. Lickiss, C. Pettinari and R. P. Davies, *Dalton Trans.***,** **2013**, *42,* 13806-13808.
3. A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.