Experimental section

Materials and synthesis

3,5-Dibromopyridine, 4-bromotoluene, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and *N,N*-dimethylformamide (dmf) were purchased from Aldrich Chemical Co. and used as received without further purification.

Pyridine-3,5-bis(phenyl-4-carboxylic acid) (LH_2) was prepared by Suzuki coupling. 3,5-Dibromopyridine (0.948 g, 4 mmol), 4-ethoxycarbonylphenylboronic acid [1] (1.824 g, 9.6 mmol), $CsCO_3$ (5.53 g, 16.96 mmol) and $Pd(PPh_3)_4$ (0.1 g, 8 mmol) were added to EtOH (60 cm^3). This mixture was heated to 80°C and stirred under N_2 for 5 days, and extracted with $CHCl_3$ (3×100 cm^3). The $CHCl_3$ layer was separated and evaporated *in vacuo*. The white product was refluxed in 2M NaOH solution overnight and the resulting solution filtered. The filtrate was acidified to pH 2 with 38% HCl. The product was collected as a white powder. Yield: 56% (0.72 g). ^{1}H NMR (300MHz, DMSO): δ=9.05 (2H, d, *J*=3Hz), 8.70(1H, s), 8.32(2H, d, *J*=6Hz), 8.18(2H, d, *J*=6Hz), 7.50(2H, t, *J*=6Hz); ^{13}C NMR (300MHz, DMSO): δ=164.81, 163.08, 159.65, 143.63, 136.01, 135.29, 133.67, 132.05, 130.85, 120.32, 120.17, 117.97, 117.67.

Single crystals for compound **1** were grown by solvothermal reaction of equimolar amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and LH_2 in DMF at 130 °C for 3 days. Green columnar crystals were isolated, washed with DMF and air-dried to give the product (35 % yield based on ligand). Elemental analytical data corresponded to $\{[Ni_3(L)_3(OH)] \cdot 8(C_3H_7NO) \cdot 10(H_2O)\}_\infty$: calc: C, 50.94; H, 5.80; N, 8.07; found: C,50.81; H, 4.88; N, 8.05 %.

Single crystals for compound **2** were obtained by the same procedure but substituting $Fe(NO_3)_3 \cdot 9H_2O$ for $Ni(NO_3)_2 \cdot 6H_2O$. A brown solid was isolated from the reaction. Elemental analytical data corresponded to $\{[Fe_3(L)_3(O)] \cdot 3(C_3H_7NO) \cdot 17(H_2O)\}_\infty$: calc: C, 42.01; H, 5.77; N, 5.21; found: C,42.06; H, 4.36; N, 5.41 %.

Formulae were determined by single crystal structure analysis, TGA and elemental analyses. Bond valence sum (BVS) analysis was used to identify the central anion as hydroxo or oxo as well as the oxidation states of metal ions [2]. The volatility and variations of crystallization solvent in the samples contribute to the discrepancy in elemental analytical data.

Single Crystal X-ray Diffraction Studies

Single crystal X-ray diffraction data were collected at 150 K using Bruker SMART CCD area detector diffractometers equipped with Oxford Cryosystems open flow cryostats [3]. The radiation used was either graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) for **1** or synchrotron radiation (λ = 0.6906 Å) for **2** on Station 9.8 of the Daresbury Synchrotron Radiation Source. Absorption corrections based on symmetry equivalent reflections were applied to the data using SADABS [4]. The structures were solved by direct methods using SHELXS97 [5] and refined by full-matrix least squares on F^2 using SHELXL97 [6].

With the exception of the carbon atoms from disordered phenyl rings and the bridging hydroxo anion, all non-hydrogen atoms were treated with anisotropic displacement parameters. Aromatic hydrogen atoms were placed in calculated positions and refined using the riding model. The phenyl rings were each disordered over two partially occupied sites, and were refined with isotropic displacement parameters and suitable restraints. The large volume fractions of disordered solvent in the lattice pores could not be modelled in terms of atomic sites and were treated using the SQUEEZE routine in the PLATON software package [7]. The U_{iso} value proved to be unstable for refinements against single crystal data collected after heating the crystal to 423 K, 473 K and 500 K and it was therefore constrained to be comparable to the other oxygen atoms in the same refinement.

A total of six datasets were collected for compound **1**, as described above, with the aim of following the temperature dependence of the solvent loss from this framework. These all show the same crystal symmetry and conservation of the framework. However, inconsistencies in the electron density calculated using SQUEEZE make it impossible to discuss the solvent content or detailed changes in the structure with confidence. Any details given are for the initial structure determined for the fresh sample.

The solvent for both **1** and **2** was accounted for using SQUEEZE [8], implemented in PLATON [7], which calculates the electron density in the unit cell and accounts for it in the refinement. This electron density was assigned as some specific solvent content. In the case of the two compounds reported here it does not match the elemental analysis due to changes in solvent composition during recrystallisation and loss of solvent due to evaporation. The solvent was assigned as 4.8 molecules of dmf per 3Ni atoms and 4 molecules of dmf per 3Fe atoms. There are inconsistencies in the electron density calculated using SQUEEZE for the heat treated samples. There are clearly molecules of dmf visible in the difference maps for these materials, but they could not be refined satisfactorily and there was further solvent content which was much less well defined.

Crystal data for **1**. $C_{71.4}H_{67.6}N_{7.8}Ni_3O_{17.8}$, $M = 1495.86$, trigonal, $a = b = 18.9996(16)$, $c = 45.997(8)$ Å, $U = 14380(7)$ Å^3, $T = 150(2)$ K, space group R-3c (No. 167), $Z = 6$, μ(Mo-$K\alpha$) = 0.639 mm^{-1}, 2812 unique reflections measured, corrected for absorption (R_{int} 0.049) and used in all calculations. Electron density in poorly defined solvent regions was accounted for using SQUEEZE [8] which estimated a void volume of 7626 Å^3 and a total of 1145 electrons per unit cell, assigned as 4.8 molecules of DMF per Ni_3 unit. The phenyl ring C1–C6 showed disorder and was modelled over two partially occupied sites, with occupancies of 0.60 and 0.40. Final R_1 [2342 $F > 4\sigma(F)$] = 0.0423 and wR(all F^2) was 0.129.

Crystal data for **2**. $C_{69}H_{61}Fe_3N_7O_{17}$, $M = 1427.8$, trigonal, $a = b = 19.2442(14)$, $c = 45.613(7)$ Å, $U = 14629(2)$ Å^3, $T = 150(2)$ K, space group R-3c (No. 167), $Z = 6$, $\mu = 0.493$ mm^{-1}, 3333 unique reflections measured, corrected for absorption (R_{int} 0.110) and used in all calculations. Diffraction data for **2** were collected using synchrotron radiation ($\lambda = 0.6906$ Å) on Station 9.8 on the Daresbury SRS. The 1005 electrons occupying 7829 Å^3/cell found by SQUEEZE [8] correspond to four molecules of DMF per Fe_3 unit. Phenyl rings disorder was modelled over two partially occupied sites, C4–C9 with occupancy 0.70 and C4'–C9' with occupancy 0.30. Final R_1 [2246 $F > 4\sigma(F)$] = 0.0623 and wR(all F^2) was 0.177. The transformation from the non-disordered coordinates for **1** to those for **2** is (x, x-y, z).

Characterization of compounds

Elemental microanalyses of all products were performed at the University of Nottingham, School of Chemistry. Powder X-ray diffraction (PXRD) data were recorded either under ambient conditions or *in situ* under vacuum on a Bruker AXS D8 Advance diffractometer operated at 1600 W (40 kV, 40 mA) for Cu $K\alpha_1$ ($\lambda = 1.5406$ Å), with a temperature ramp rate of 2°/min and a step size of 0.04° in 2θ. An MRI TCP-20 with PtRh strip heater was used for the *in situ* variable temperature powder X-ray diffraction experiments. Simulated PXRD patterns were calculated using Powder Cell Version 2.4 from corresponding single-crystal structural models. Thermal gravimetric analyses (TGA) were performed under N_2 at a scan rate of 2°C/min using a TA Universal Analysis 2000 system.

Sorption isotherm measurement

The out-gassing and isotherm measurements were carried out using a Hiden Isochema (Warrington, U.K.) Intelligent Gravimetric Analyzer (IGA), equipped with a micro-gram balance, 2 mbar, 100 mbar and 20 bar pressure transducers and a Hüber ministat circulating water bath. For measurements at liquid nitrogen temperature, a standard low-temperature liquid Dewar vessel was employed. All isotherm data points were fitted by the IGASwin systems software v.1.03.143 (Hiden Isochema, 2004) using a linear driving force model when > 98% equilibration had been reached. All changes in sample weight were corrected for buoyancy effects.

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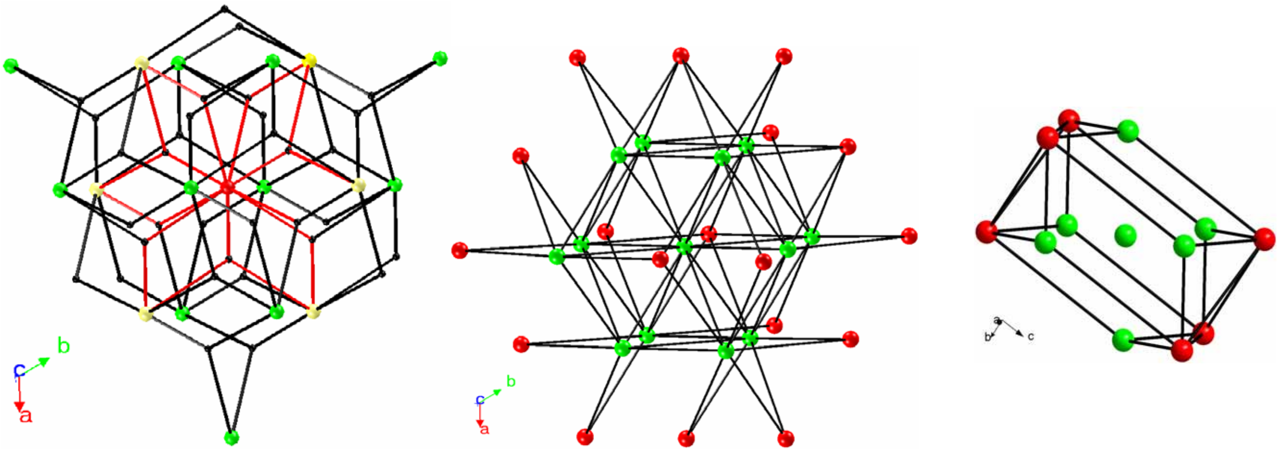
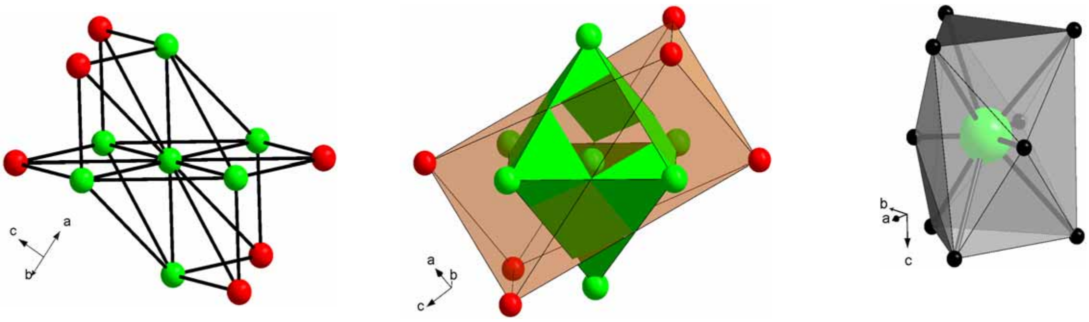


(a) (b) (c)

Fig. SI-1 (a) View of connectivity in **1** (a) $(4^2 6)\cdot(4^6 6^{21} 8^9)$ topology defined by lattice built by 3-connected ligand nodes and 9-connected cluster nodes, respectively; (b) $3^{18}4^{42}5^6$ topology defined by lattice built up of 12-connected cluster nodes only; (c) distorted cube-octahedral polyhedron in **1**.



(a) (b) (c)

Figure SI-2: (a) Schematic of 12-connected polyhedron between cluster nodes in **1** (b) view of octahedron capped by two triangular units in **1**, (d) view of 9-connectivity between metal cluster and ligand nodes in **1.**

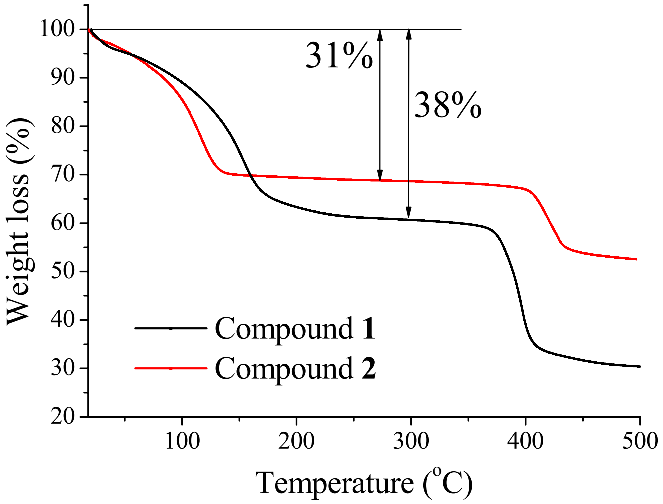


Fig. SI-3: TGA analysis for compound **1** and **2**

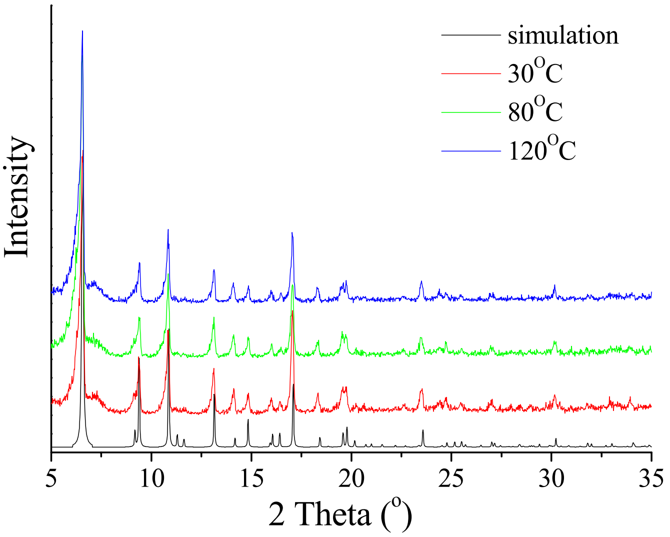


Fig. SI-4: *In situ* PXRD patterns for compound **2**

Table SI-1: Single crystal X-ray diffraction data for $\{[Ni_3(OH)(L)_3]\cdot n\ (solv)\}_\infty$ at varied temperatures. The temperature was controlled by N_2 flow, and was set via a gradient of 2°C/min and then held for 1 h at the set temperature and cooled down to 150 K at a rate of 2°C/min

Heat and hold temperature (data collection temperature) Data	original sample (150 K)	323 K (150 K)	373 K (150 K)	423 K (150 K)	473 K (150 K)	500 K (150 K)
Space group	*R*-3c	*R*-3c	*R*-3c	*R*-3c	*R*-3c	*R*-3c
Unit cell parameters	18.994(2) 18.994 45.983(6) 90, 90, 120	18.890(3) 18.890 46.326(6) 90, 90, 120	19.046(3) 19.046 45.767(6) 90, 90, 120	19.084(3) 19.084 45.113(7) 90,90,120	19.126(4) 19.126 44.782(10) 90,90, 120	19.160(5) 19.160 44.584(13) 90, 90, 120
Unit cell volume/$Å^3$	14367(5)	14316(6)	14378(6)	14229(6)	14187(10)	14175(13)
Ni-O bond length in $Ni_3O(CO_2)_6$ cluster/Å	1.9823(4)	1.9980(4)	1.9853(4)	2.0342(7)	2.0465(8)	2.0502(10)
Ni-Ni distance in $Ni_3OH\ (CO_2)_6$ cluster/Å	3.430(1)	3.461(0)	3.439(1)	3.523(1)	3.545(1)	3.550(1)
$R1(wR2)$	0.0423 (0.1086)	0.0450 (0.1128)	0.0415 (0.0893)	0.0688 (0.1458)	0.0681 (0.1638)	0.0861 (0.2073)
GOOF value	1.089	0.994	0.926	0.916	0.888	0.808

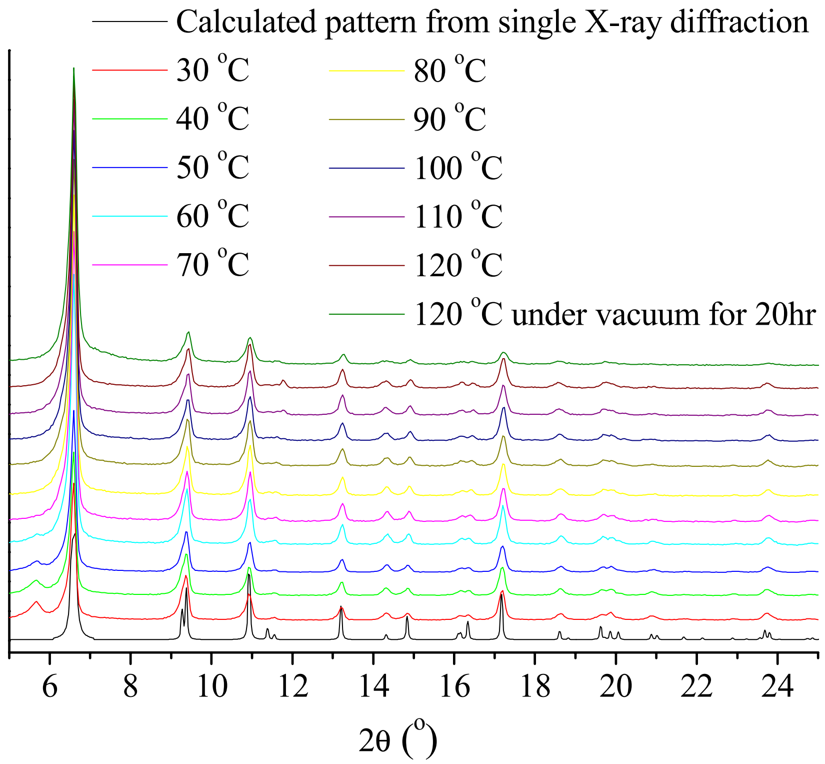


Fig. SI-5: Powder XRD diffraction patterns for **1**. *In situ* PXRD patterns (30 to 120 °C under vacuum) and pattern for sample heated at 100 °C under vacuum for 20 h. All scans were recorded over the 2θ range 5–25°, with an acquisition time of 16 minutes for each scan.

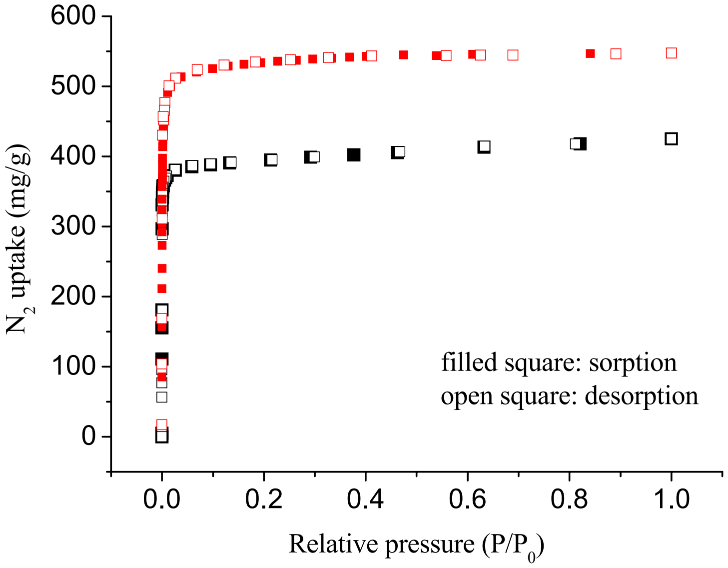


Fig. SI-6: N_2 isotherms for compound **1** (in red) and **2** (in black) at 77 K.

Bond valence sum (BVS) analysis

$$V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r_o - r_{ij}}{B}\right)$$

The valence of a bond between two atoms, *i* and *j* is given by S_{ij}. Bond valences are defined so that the sum of all bond valences of the bonds formed by a given atom, *i*, is the atom valency, V_i; r_0 is the length of a single bond; values of r_0 can be determined for pairs of atoms, using a variety of co-ordination modes from parameters in experimental crystal structures. Here it is obtained from SI-Reference [2]; r_{ij} is the bond length between atoms *i* and *j*. Thus, in this work, *i* and *j* are either Ni, O or Ni, N for compound **1** or Fe, O or Fe, N for compound **2**. B is a constant, the "universal parameter" ~0.37 Å. Each metal ion centre in the framework is six co-ordinate and bound to one central bridging oxygen (O_{1H}), one N, and four other O-centres from carboxylate groups. The value for r_0 for M-O and M-N bonds is based upon previous work (SI-Reference [2]). The charge V_i on one Fe or Ni in the trinuclear M_3 unit is the sum of S_{ij} calculated from all six bonds connected to it *(i.e.,* one M-O_{1H}, two M-O_1 and two M-O_2 and one M-N bonds). The total charge on the M_3 core within the trinuclear unit is three times the charge on a single M. The charge V_i on the central bridging O or OH is the sum of S_{ij} calculated from all equal three O-M bonds because the central O or OH is bonded to the same three metals.

For compound **1**

i=Ni, j=O

Ni-O_{1H} bond distance is 1.9847

	r_0	S_{ij}
Ni^{2+}-O	1.670	0.427

Ni-O_1 bond distance is 2.052

	r_0	S_{ij}
Ni^{2+}-O	1.670	0.356

Ni-O_2 bond distance is 2.088

	r_0	S_{ij}
Ni^{2+}-O	1.670	0.323

i=Ni, j=N

Ni-N bond distance is 2.099

	r_0	S_{ij}
Ni^{2+}-N	1.647	0.295

$$V_{O_{1H}} = 3 \times r_{NiO} = 3 \times 0.427 = 1.281$$

$$\overline{V}_{Ni} = S_{NiN} + S_{NiO_1} + 2S_{NiO_1} + 2S_{NiO_2} = 2.08$$

i=Ni, j=O

Ni-O_{1H} bond distance is 1.9847

	r_0	S_{ij}
Ni^{3+}-O	1.750	0.530

Ni-O_1 bond distance is 2.052

	r_0	S_{ij}
Ni^{3+}-O	1.750	0.475

$Ni-O_2$ bond distance is 2.088

	r_0	S_{ij}
Ni^{3+}-O	1.750	0.401

i=Ni, j=N

Ni-N bond distance is 2.099

	r_0	S_{ij}
Ni^{3+}-N	1.731	0.370

$$V_{O_{1H}} = 3 \times r_{NiO} = 3 \times 0.530 = 1.590$$

$$\overline{V}_{Ni} = S_{NiN} + S_{NiO_1} + 2S_{NiO_1} + 2S_{NiO_2} = 2.652$$

For compound **2**

i=Fe, j=O

$Fe-O_{1H}$ bond distance is 1.902

	r_0	S_{ij}
Fe^{2+}-O	1.700	0.579

$Fe-O_1$ bond distance is 2.047

	r_0	S_{ij}
Fe^{2+}-O	1.700	0.391

$Fe-O_2$ bond distance is 2.054

	r_0	S_{ij}
Fe^{2+}-O	1.700	0.384

i=Fe, j=N

Fe-N bond distance is 2.121

	r_0	S_{ij}
Fe^{2+}-N	1.769	0.386

$$V_{O_{1H}} = 3 \times r_{FeO} = 3 \times 0.579 = 1.737$$

$$\overline{V}_{Fe} = S_{FeN} + S_{FeO_1} + 2S_{FeO_1} + 2S_{FeO_2} = 2.515$$

$Fe-O_{1H}$ bond distance is 1.902

	r_0	S_{ij}
Fe^{3+}-O	1.765	0.690

$Fe-O_1$ bond distance is 2.047

	r_0	S_{ij}
Fe^{3+}-O	1.765	0.467

$Fe-O_2$ bond distance is 2.054

	r_0	S_{ij}
Fe^{3+}-O	1.765	0.458

i=Fe, j=N

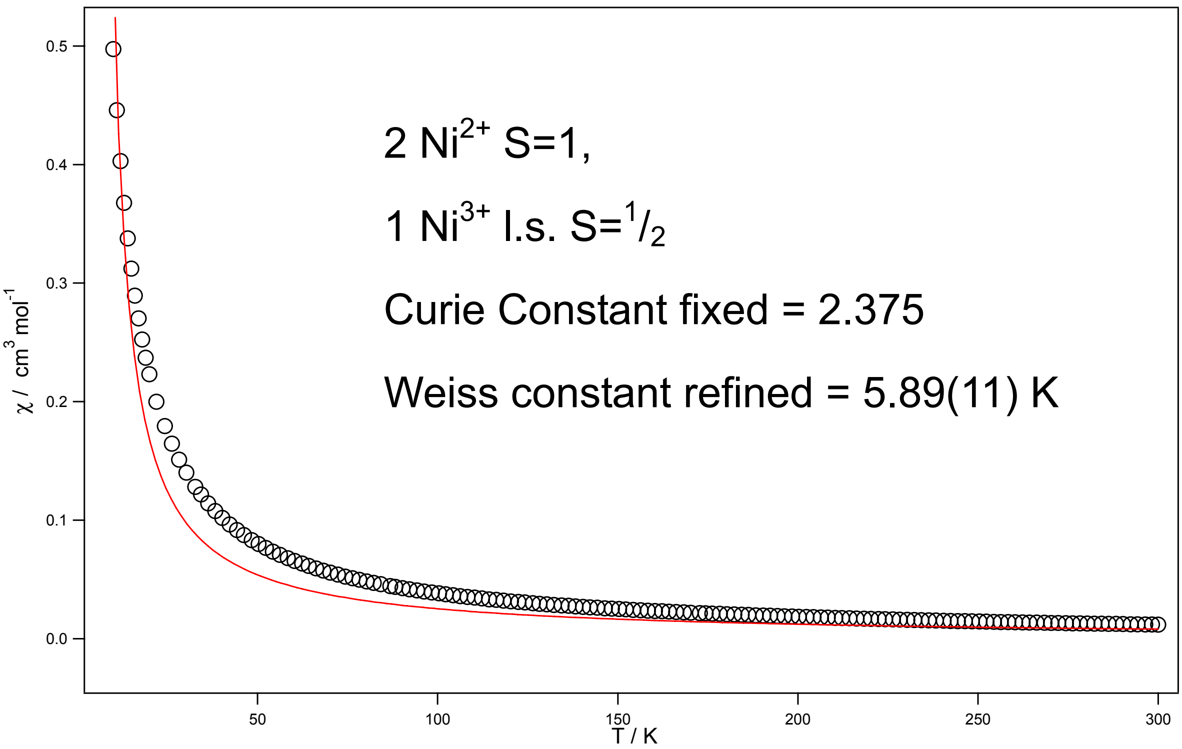
Fe-N bond distance is 2.121

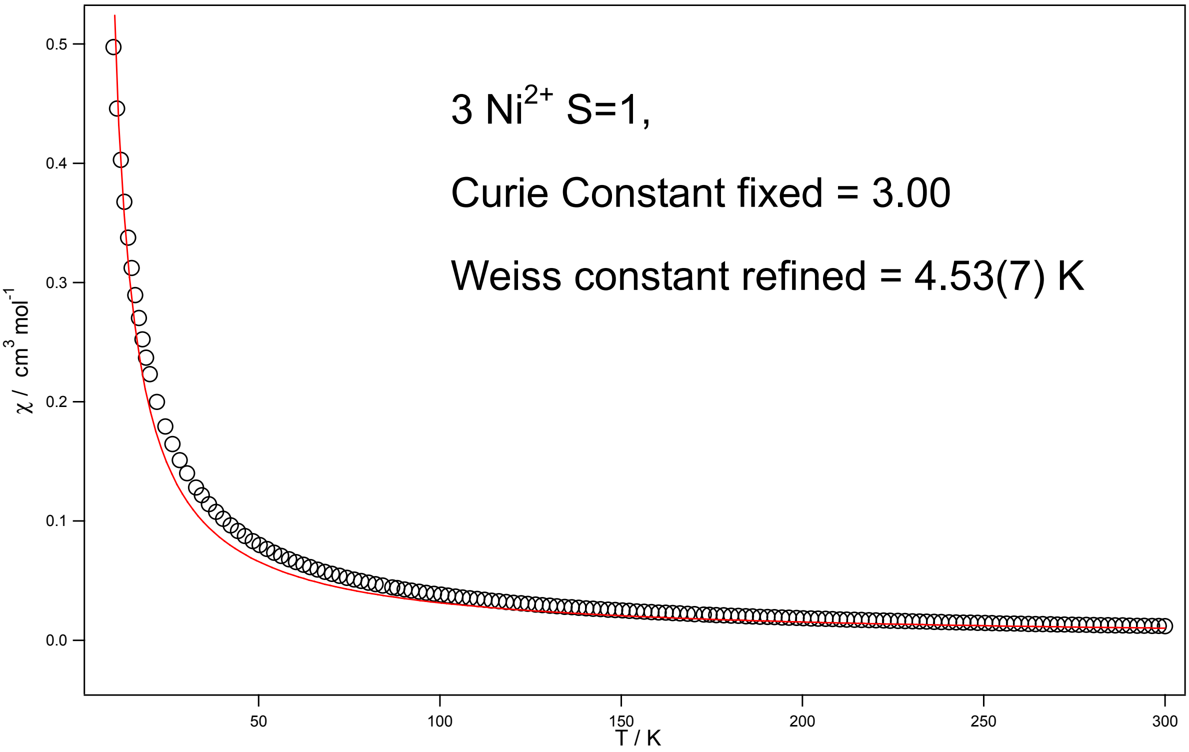
	r_0	S_{ij}
Fe^{3+}-N	1.815	0.437

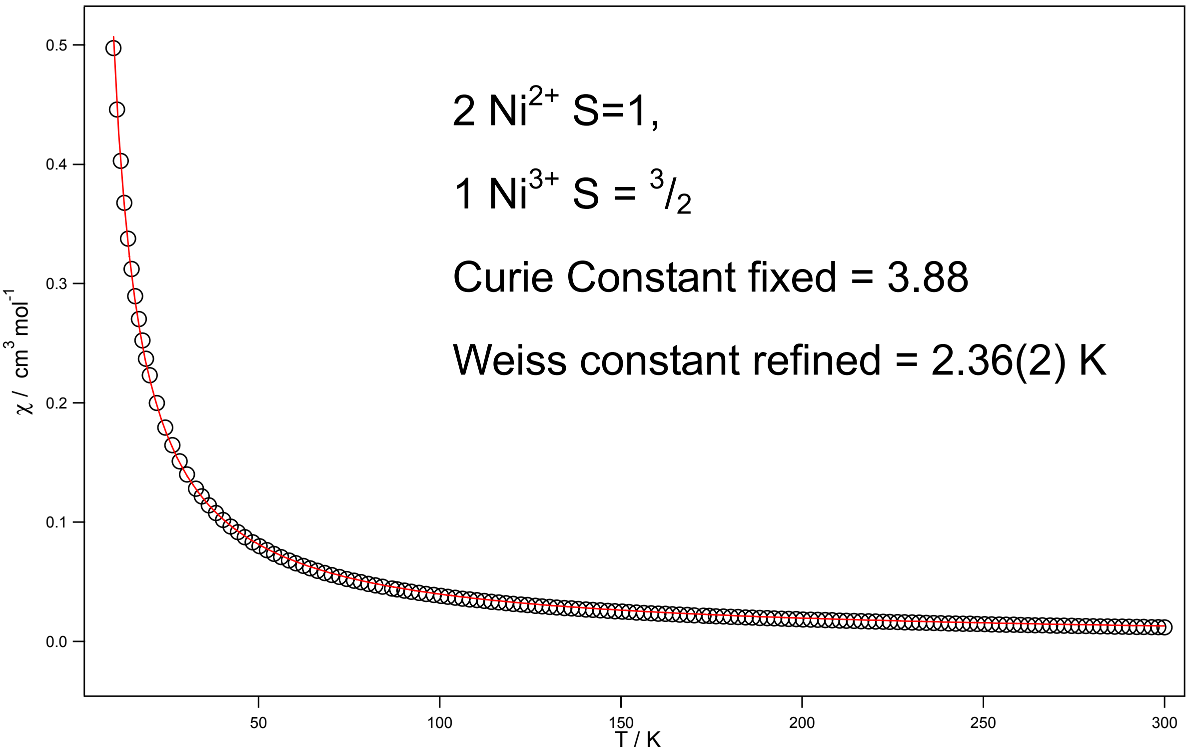
$$V_{O_{1H}} = 3 \times r_{FeO} = 3 \times 0.690 = 2.07$$

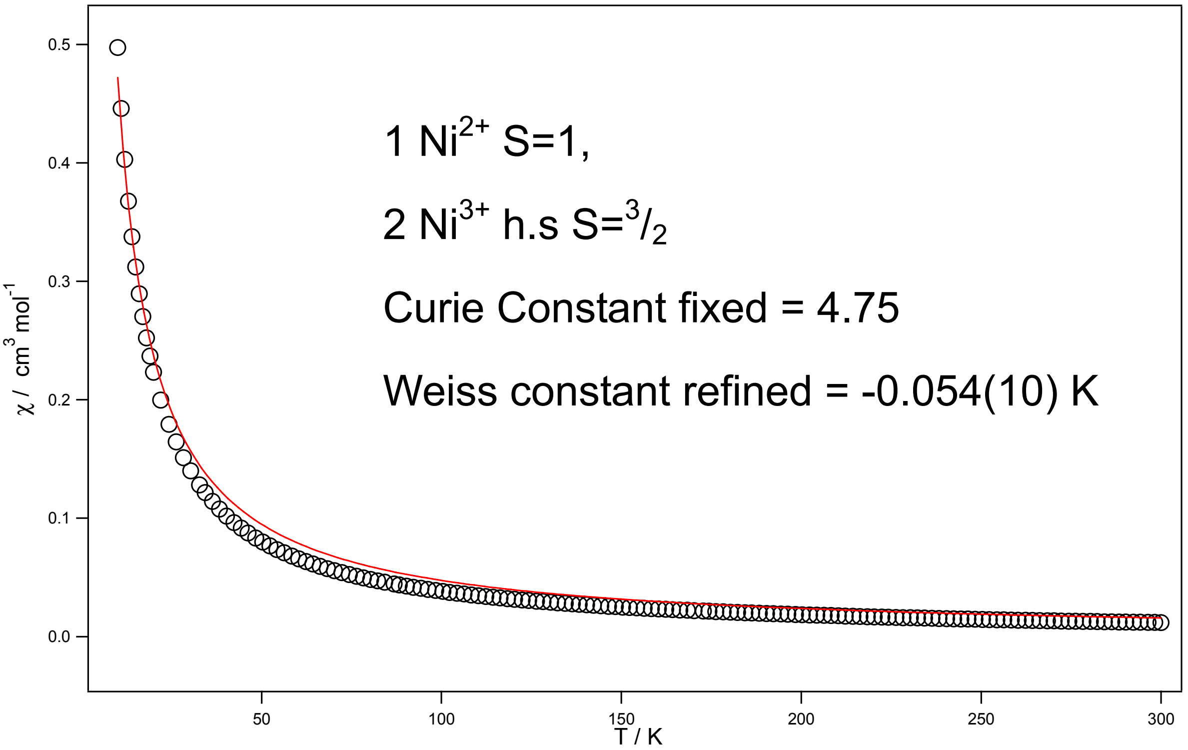
$$\overline{V}_{Fe} = S_{FeN} + S_{FeO_1} + 2S_{FeO_1} + 2S_{FeO_2} = 2.977$$

Fig. SI-7: Plots of χ versus T for **1**: experimental data (open circle) and fitted line (red)









Magnetic measurements were carried out using a Quantum Design SQUID magnetometer. The samples were contained in gelatine capsules which were mounted in straws to provide an invariant diamagnetic background that did not influence the SQUID detection coils. DC susceptibility measurements were carried out in applied fields of 1000 G after cooling the sample in zero applied field. The data were not corrected for diamagnetism. Data were fitted to the Curie Weiss law in the temperature range $10 < T/K < 300$. The Curie constants were fixed at possible values based on complete orbital quenching and the Weiss constant was refined to give the best possible fit. These clearly show a uniquely satisfactory match to a Curie constant of 3.88 corresponding to the presence of 2 Ni^{2+} (S=1) and 1 high spin Ni^{3+} (S=3/2) per formula unit, consistent with a μ_3-OH moiety in the complex **1**.