Supplementary Material (ESI) for Chemical Communications

A route to large pore metal phosphonates – Supplementary Information

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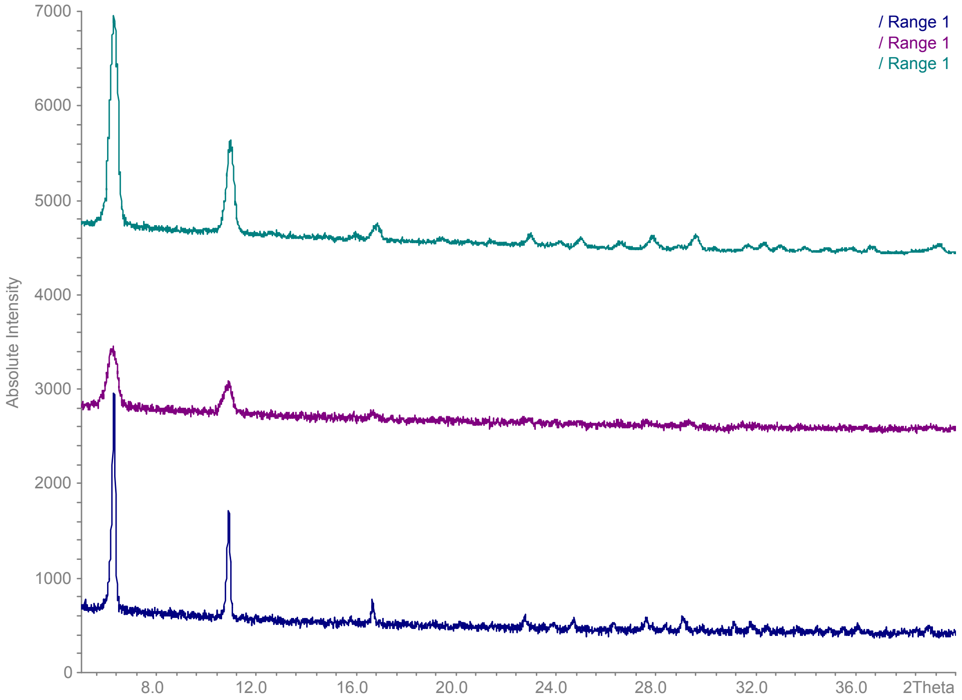
1. Table of synthesis conditions. Representative hydrothermal reactions[a] with divalent Fe, Co and Ni salts and phosphonic acids H_4L and H_4L'

Metal Source	Phosphonic acid	Temp./ °C	Time / h	Initial pH[c]	Product structure
$FeCl_2$	H_4L	160	120	5.0	$FeLH_2.H_2O$[b]
$Fe(OAc)_2$	H_4L	190	120	5.0	**1**
$CoCl_2$	H_4L	190	280	6.0	$CoLH_2.H_2O$[12]
$CoCl_2$	H_4L	190	120	8.0	**1**
$Co(OAc)_2$	H_4L	140	120	7.0	**1**
$NiCl_2$	H_4L	190	160	5.0	**1**
$Ni(OAc)_2$	H_4L	190	120	8.5	**1**
$CoCl_2$	H_4L'	160	120	6.0	**1**
$CoAc_2$	H_4L'	160	150	7.0	**2** + impurity
$NiCl_2$	H_4L'	160	120	5.5	**1**
$Ni(OAc)_2$	H_4L'	160	120	7.0	**1**

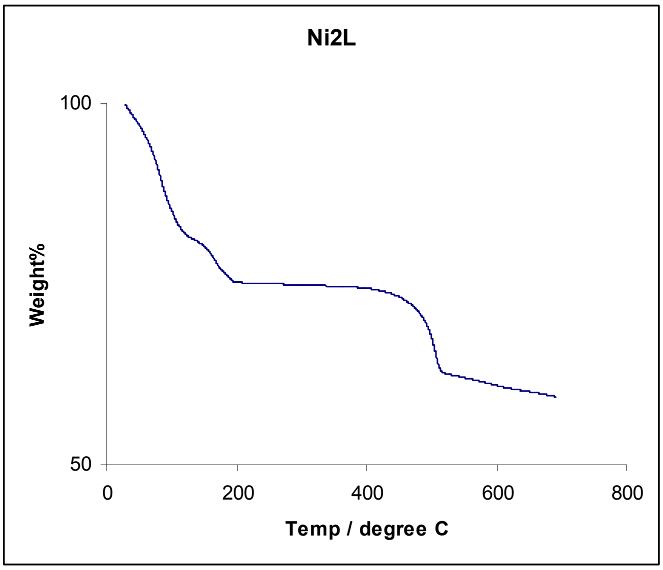
[a] In each reaction the molar ratio of M^{2+} : L : H_2O is 0.002:0.001:9
[b] isostructural with $CoLH_2.H_2O$[13]
[c] initial pH adjusted by addition of KOH(aq)

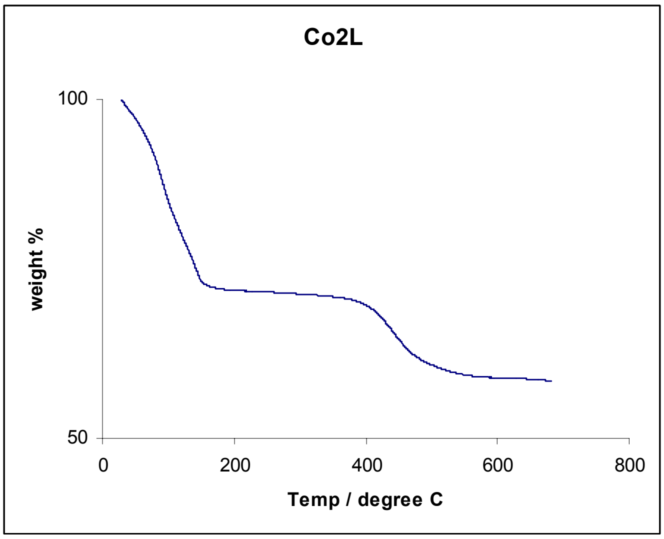
2. Powder XRD patterns of Iron, Cobalt and Nickel versions of Structure Type 1

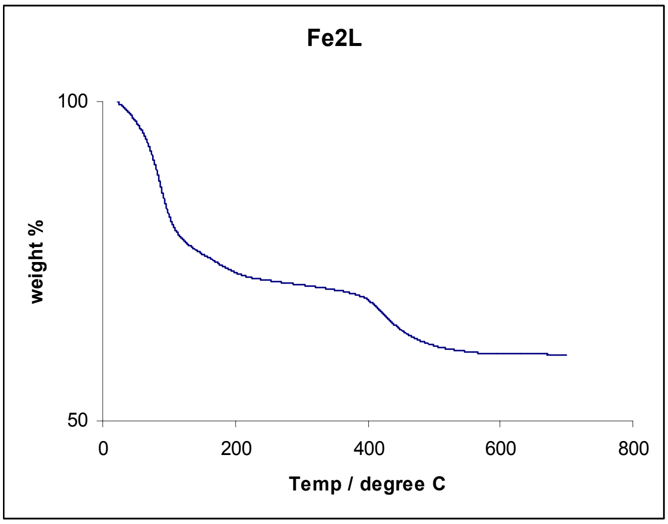


Lab XRD patterns of (bottom) Fe(II), (middle) Co(II) and (top) Ni(II) versions of $M_2(H_2O)_2L.xH_2O$

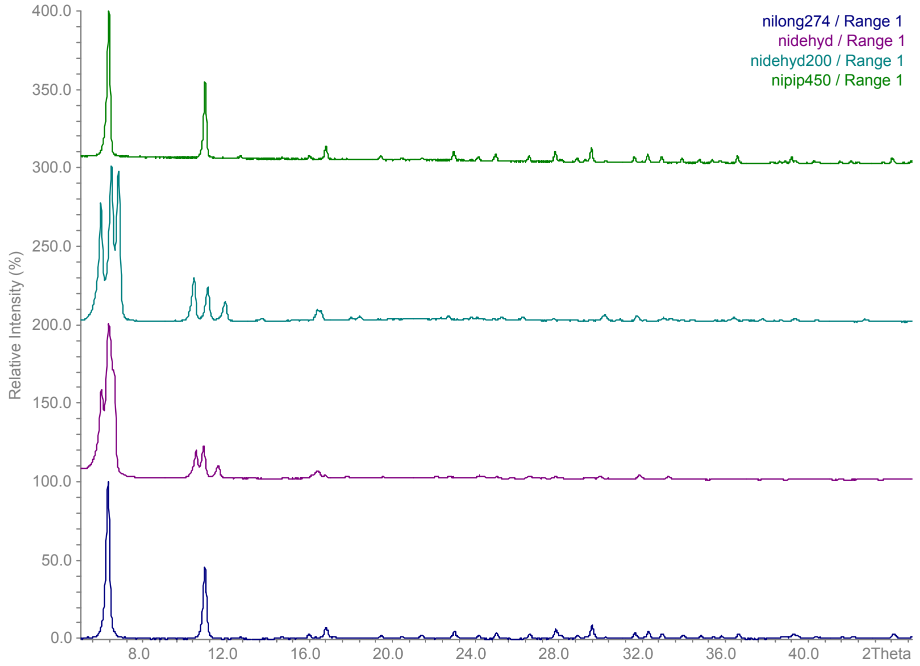
3. TGAs of Iron, Cobalt and Nickel versions of Structure Type 1

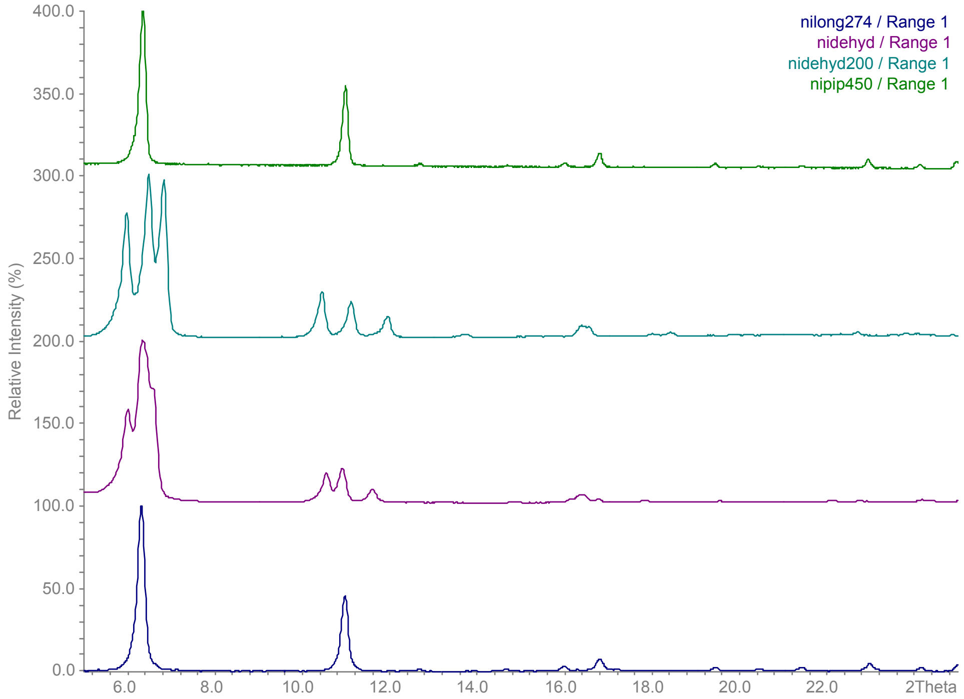






4. Powder XRD patterns of dehydration/rehydration of Nickel-Structure Type 1





From bottom to top, and expanded in the lower plot, XRD patterns of $Ni_2L.xH_2O$ as-prepared, heated at 100 ºC in vacuum, heated at 200 ºC in vacuum and heated at 450 ºC and rehydrated.

The pattern of the sample heated at 200 ºC can be indexed in P-1, *a* = 16.48Å, *b*= 16.28Å, *c*=6.21Å, α=65.8º, β=102.4º, γ=116.4º, V=1360Å, M(20)=13, F(20)= 27.

5. Chemical Analysis, Structure solution and Rietveld refinement of Ni-1

Compounds of type **1**, $M_2L.xH_2O$, M = Fe, Co, Ni, were obtained as microcrystalline powders with closely similar X-ray powder diffraction patterns. The nickel compound gave the best resolved diffraction pattern, and so this was used for structure solution. Chemical analysis of Ni-**1** by EDX gave Ni/P ratio of 1.0(1) and indicated that no chloride or alkali metals were present. Elemental (C, H and N) analysis is then consistent with a formula of $Ni_2L.7.4H_2O$. Examination of the TGA indicated a two step water loss below 220 ºC, and the second weight loss event was attributed to loss of one coordinated water molecule from each nickel cation. The formula was therefore $[Ni_2(H_2O)_2L].5.4H_2O$. (Calculated composition: C, 13.87%; H, 5.16%; N, 5.39%; Measured: C, 13.77%; H, 4.87%; N, 5.23%)

The laboratory X-ray diffraction pattern was indexed using the DICVOL91 program on a rhombohedral cell, a = 27.9343 Å, c = 6.2372 Å (hexagonal setting) with absences indicating the space group to be R-3, R-3m, R3 or R3m. Attempts were made to solve the structure in these space groups using the direct methods package adapted for use with powder data within the EXPO2004 suite of programs, using the non-hydrogen unit cell contents determined from chemical analysis and density measurements, based on $Ni_{18}L_9$. A partial solution was achieved in the space group R-3 in which the nickel atom and coordinating atoms were located. Further analysis located the phosphorus atom and oxygen atoms of water molecules coordinated to the nickel cations and coordinated within the pores, but it was not possible to locate the atomic positions of the ligand unambiguously at this stage.

Given the location of the inorganic part of the structure, which consist of a chain of edge-sharing octahedra, and the position of the phosphorus atoms, which are linked between chains by the $–CH_2-NC_4H_8N-CH_2-$ part of the ligand, the organic part of the structure was modelled using the CVFF forcefield within the CERIUS program. Two types of linkage were attempted, one in which the chains were linked by bidentate phosphonate groups only (leaving two coordinating atoms from an additional ligand) or another in which the phosphonate ligand also coordinated the nickel via the nitrogen of the piperazine ring. Energy minimisation of these starting models suggested that the second mode of coordination was strongly favoured, and the resulting structure gave a simulated diffraction pattern very close to that measured experimentally. After this, the position of the organic group was fixed and the inorganic framework was minimised using a universal force field type. All minimisations were carried out in P1 and with no electron density in the pore, although the unit cell was fixed. After the minimisations were performed, the symmetry was found to be R-3.

The modelled structure, including all non-hydrogen atoms and oxygen atoms of water molecules within the pores, was refined against the X-ray powder diffraction profile, collected in Debye-Scherrer geometry to avoid preferred orientation, by the Rietveld method using the GSAS suite of programs. Peakshape was modelled by a Pseudovoigtian function. The background, which includes a broad hump of scattering from the 0.7 mm o.d. quartz glass capillary, was fitted using a cosine Fourier series with 28 terms. A single thermal displacement parameter was refined for all atoms. Bond distances were initially constrained to be chemically reasonable (Ni-O, 2.04Å; Ni-N, 2.10Å; P-O, 1.53Å; P-C, 1.80Å;C-C, 1.54Å; C-N, 1.47Å) and then the constraints were removed. The final Rietveld plot is given in supplementary figure 4 (Rwp = 6.1%, Rp = 4.6%) and structural data is given in Tables S2-4.

Finally, hydrogen atoms were placed on the organic groups geometrically and not refined.

Atom	x	y	z	frac.	Uiso (x100)
Ni	0.63786(19)	0.02840(21)	0.0517(7)	1	0.53(4)
P	0.61355(32)	0.03959(32)	-0.4271(13)	1	0.53(4)
N	0.5567(9)	0.0062(8)	-0.0294(31)	1	0.53(4)
C(1)	0.5468(11)	-0.0115(8)	-0.2700(32)	1	0.53(4)
C(2)	0.5180(10)	-0.0387(9)	0.084(4)	1	0.53(4)
C(3)	0.5437(9)	0.0568(9)	-0.014(4)	1	0.53(4)
O(1)	0.6141(6)	0.0947(5)	-0.4815(23)	1	0.53(4)
O(2)	0.6306(7)	0.0104(6)	-0.6308(26)	1	0.53(4)
O(3)	0.6611(6)	0.0472(7)	-0.2712(25)	1	0.53(4)
O(4)	0.6566(5)	0.1098(6)	0.1253(24)	1	0.53(4)
O(5)	0.1950(6)	0.0835(6)	0.1743(27)	0.9	0.53(4)
O(6)	0.0375(6)	0.0745(6)	0.1830(26)	0.9	0.53(4)
O(7)	0.1422(7)	0.1488(6)	0.4453(25)	0.9	0.53(4)
H(1A)	0.515234	-0.009787	-0.325145	1	(fixed)
H(1B)	0.539643	-0.049054	-0.285413	1	(fixed)
H(2A)	0.524336	-0.069448	0.061971	1	(fixed)
H(2B)	0.522429	-0.029880	0.235876	1	(fixed)
H(3A)	0.569326	0.086805	-0.105549	1	(fixed)
H(3B)	0.549636	0.070409	0.132390	1	(fixed)

$Ni_2(H_2O)_2L].5.4H_2O$ R-3, *a* = 27.9486(4)Å, *c* = 6.2302(1)Å, V = 4214.6(1)Å^3

Table S2. Fractional Atomic Coordinates

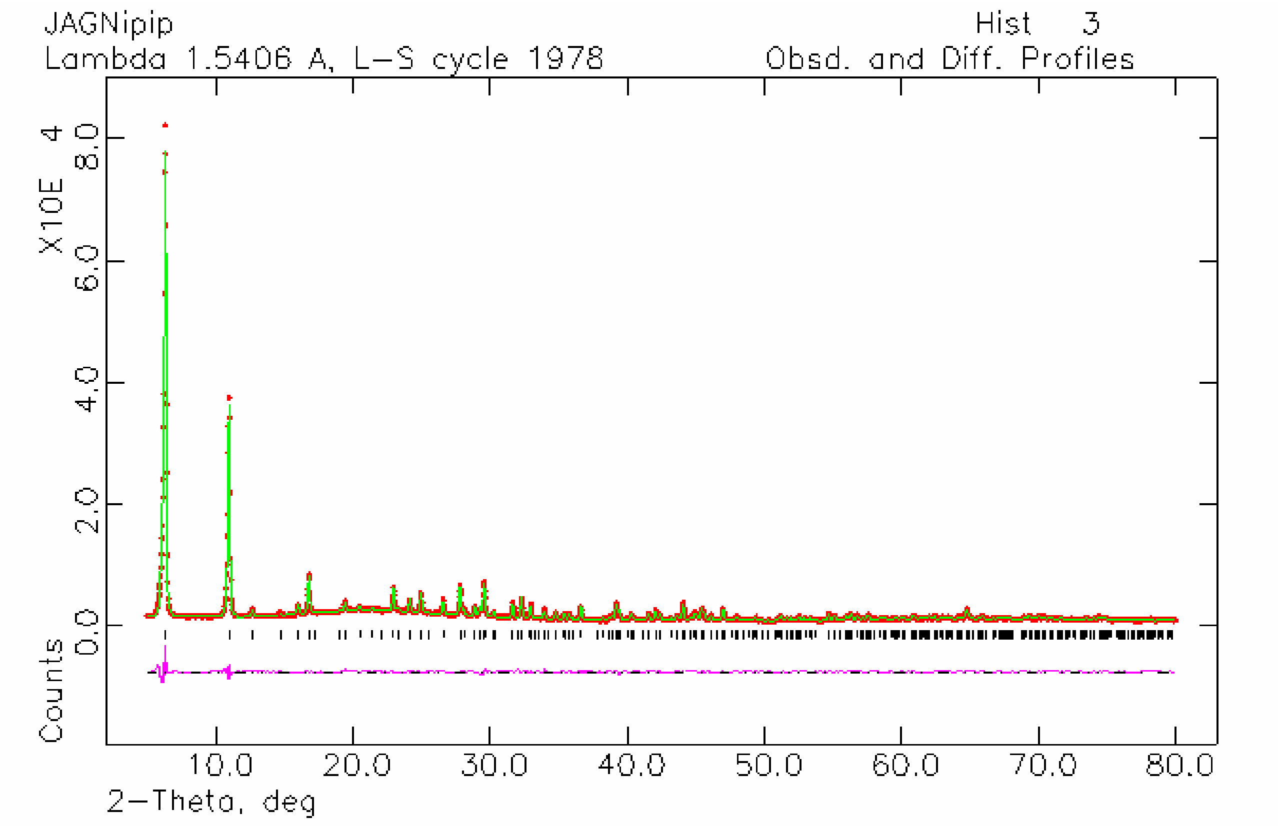
Table S3 Selected bond lengths

Ni-O2	2.026(17)
Ni-O2	2.008(15)
Ni-O3	2.098(17)
Ni-O3	2.061(15)
Ni-O4	2.114(16)
Ni-N	2.093(20)
P-O1	1.568(13)
P-O2	1.701(16)
P-O3	1.573(14)
P-C1	1.952(25)
N-C1	1.628(22)
N-C2	1.373(25)
N-C3	1.559(22)
C2-C3	1.596(26)

Table S4 Selected bond angles

O1-P-O2	116.2(9)
O1-P-O3	114.0(10)
O1-P-C1	111.3(10)
O2-P-O3	96.0(8)
O2-P-C1	114.7(10)
O3-P-C1	102.7(24)
O2-Ni-O2	92.5(7)
O2-Ni-O3	168.0(7)
O2-Ni-O4	89.7(6)
O2-Ni-N	101.7(7)
O2-Ni-O3	75.9(7)
O2-Ni-O3	75.5(6)
O2-Ni-O4	102.3(7)
O3-Ni-O3	100.5(7)
O3-Ni-O4	93.4(6)
O3-Ni-N	89.8(6)
O3-Ni-N	92.5(7)
O4-Ni-N	91.2(6)
C2-N-C3	110.4(19)
C3-N-C1	104.5(18)
C2-N-C1	105.7(21)
N-C3-C2	112.6(16)
N-C2-C3	112.4(22)
P-C1-N	107.4(16)

Figure S4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Hist 3
Obsd. and Diff. Profiles
Counts
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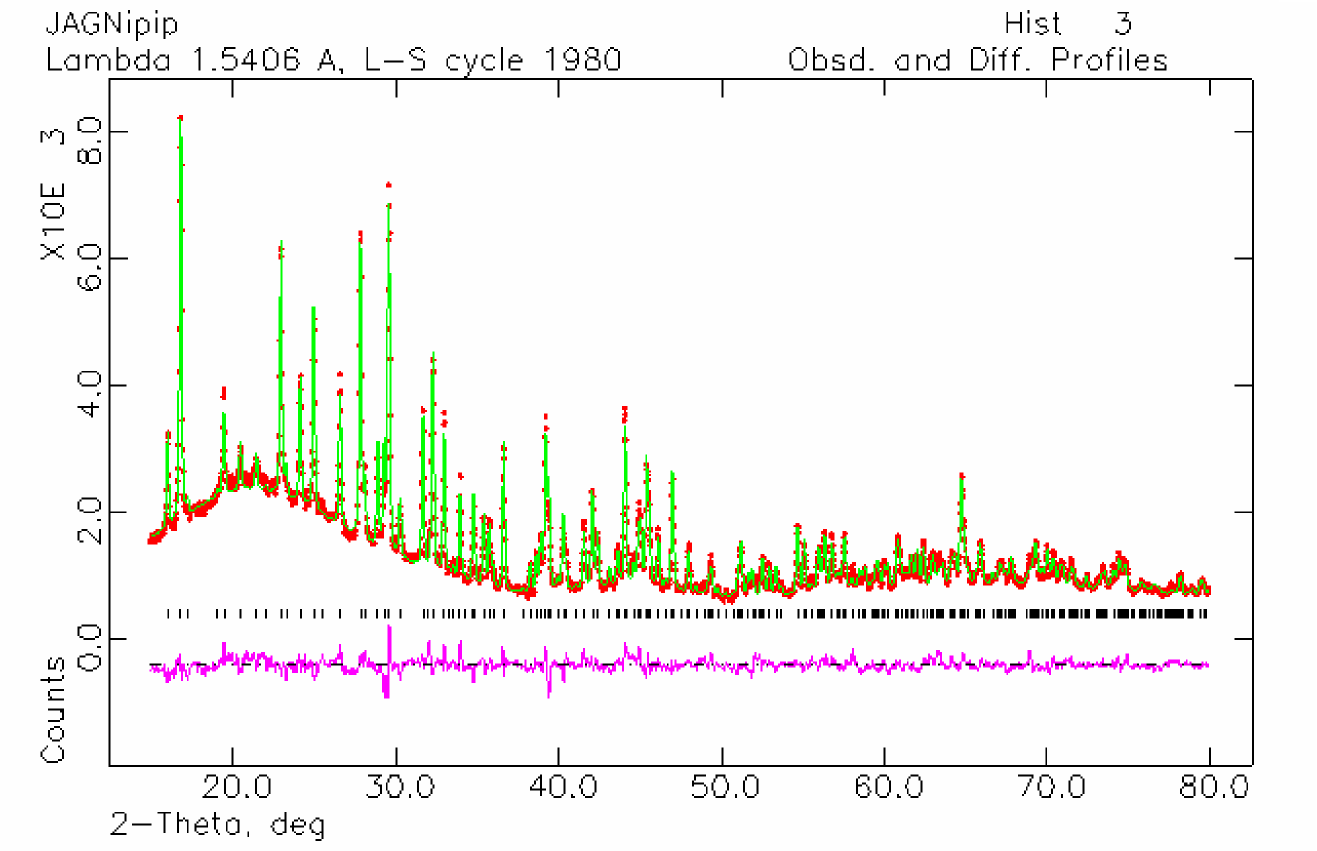
6.0
8.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
2-Theta, deg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Obsd. and Diff. Profiles
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40.0
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60.0
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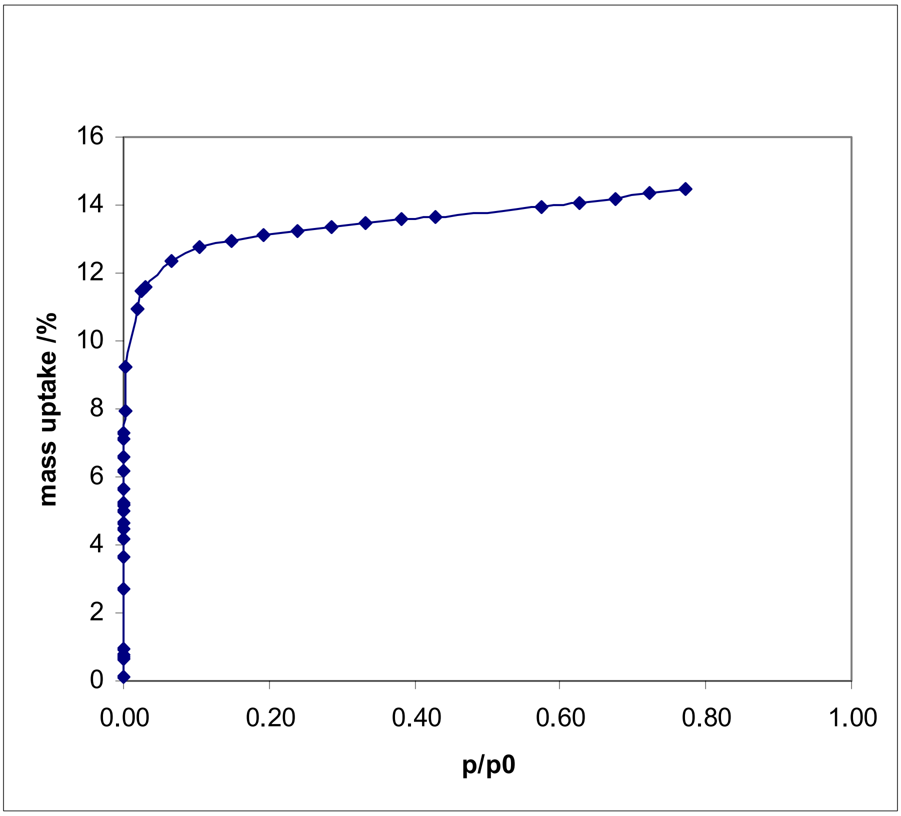
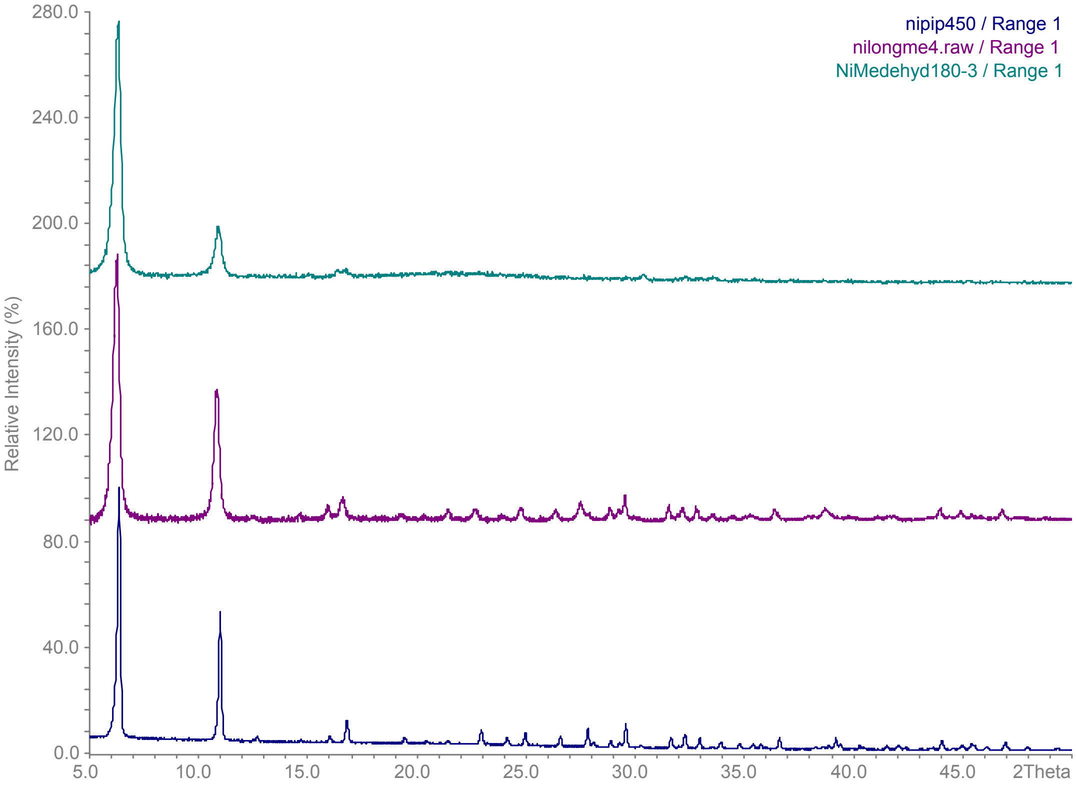
80.0
2-Theta, deg

6. Nitrogen adsorption at 77K on Ni_2L



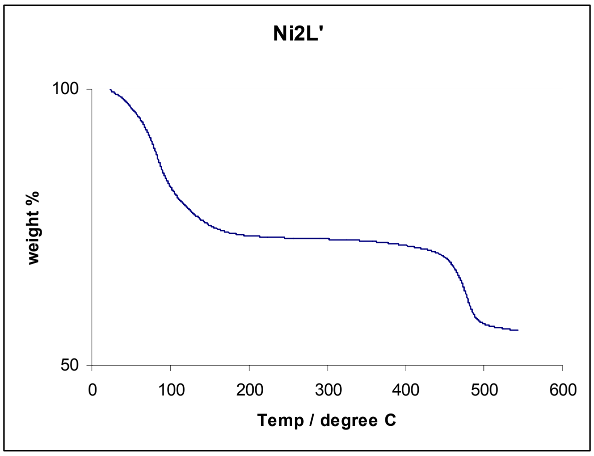
7. XRD of as-prepared (middle) and dehydrated (top) Ni-N,N'-2-methylpiperazine-bismethylene-phosphonate, compared with (bottom) Ni-N,N'-piperazine-bismethylenephosphonate



R -3 *a* = 28.229(4) Å, *c* = 6.232(1) Å, V = 4301(1) Å^3

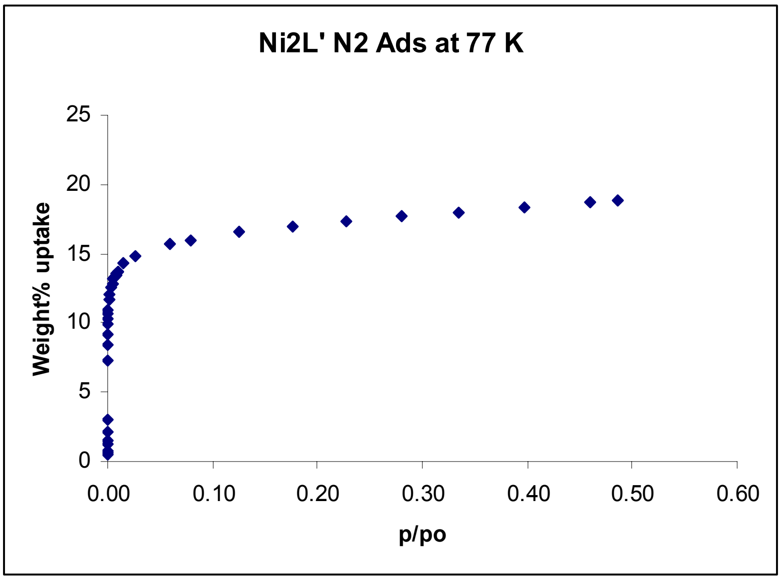
8. TGA and Analysis of Nickel-N,N'-2-methylpiperazinebismethylenephosphonate

Assuming all water lost by 200 ºC, 26 wt%, the hydrated formula weight is 542 amu

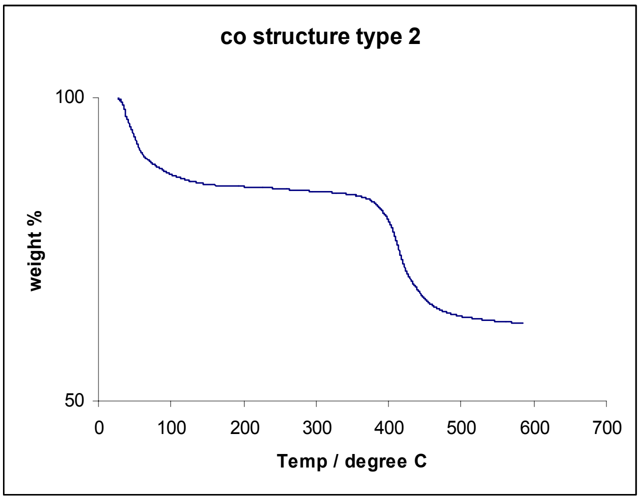


$[Ni_2(H_2O)_2L']\cdot5.8H_2O$:
Calculated
C, 15.5%; H, 5.4%; N, 5.2%,
Measured:
C, 15.9%; H, 5.3%; N, 5.2%.

9. Nitrogen adsorption isotherm of Ni_2L' at 77K



10. TGA and chemical analysis of $Co_4L'_{1.5}(CH_3CO_2)_{1.5}(H_2O,OH)_3(NH_4)_z.aH_2O$



Weight loss below 250 °C attributed to H_2O only (15%). SXRD indicates acetate is only partly occupied (occ. 0.5)

Hydroxyl ions are required for charge balance, and extra nitrogen is required to give measured N content. Assuming some ligand has decomposed to give ammonium ions, estimated composition :

$[Co_4L'_{1.5}(CH_3CO_2)_{1.5}(OH(H_2O)_2)](NH_4)_{0.5}(H_2O)_{5.5}$

Calculated

C, 17.9%; H, 5.0%; N, 5.5%,

Measured:

C, 17.43%; H, 5.75%; N, 5.72%.

Some electron density in the pores is attributed to nitrogen of ammonium ions in the single crystal diffraction.