Supporting information for:

# Coordination chemistry in the solid state: synthesis and interconversion of pyrazolium salts, pyrazole complexes, and pyrazolate MOFs

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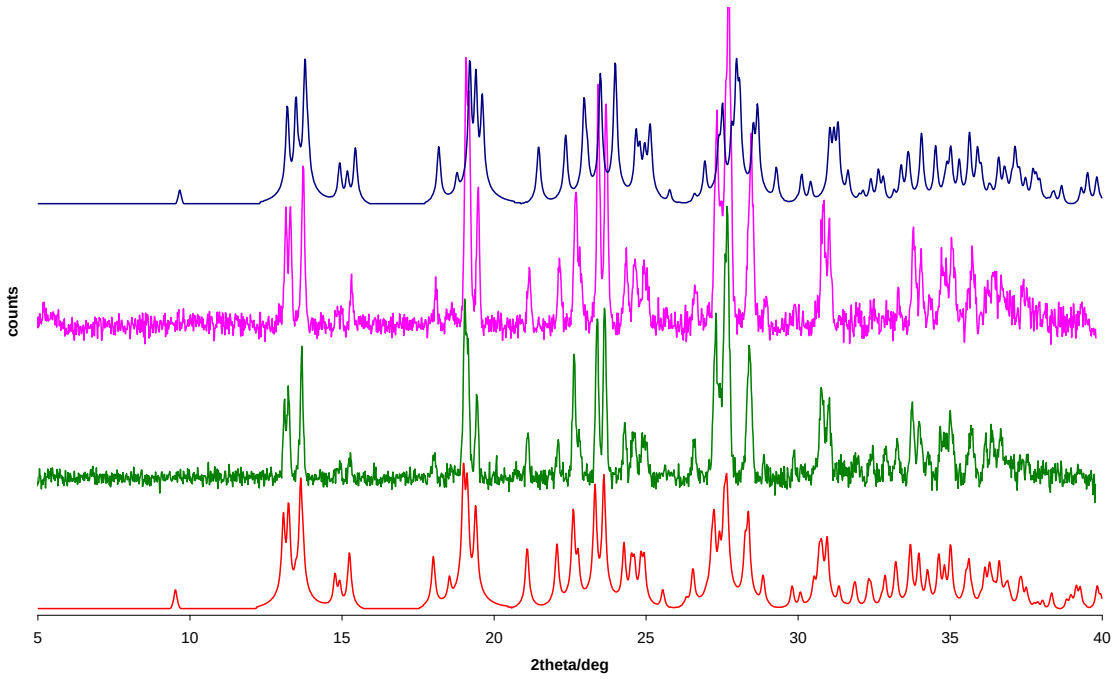
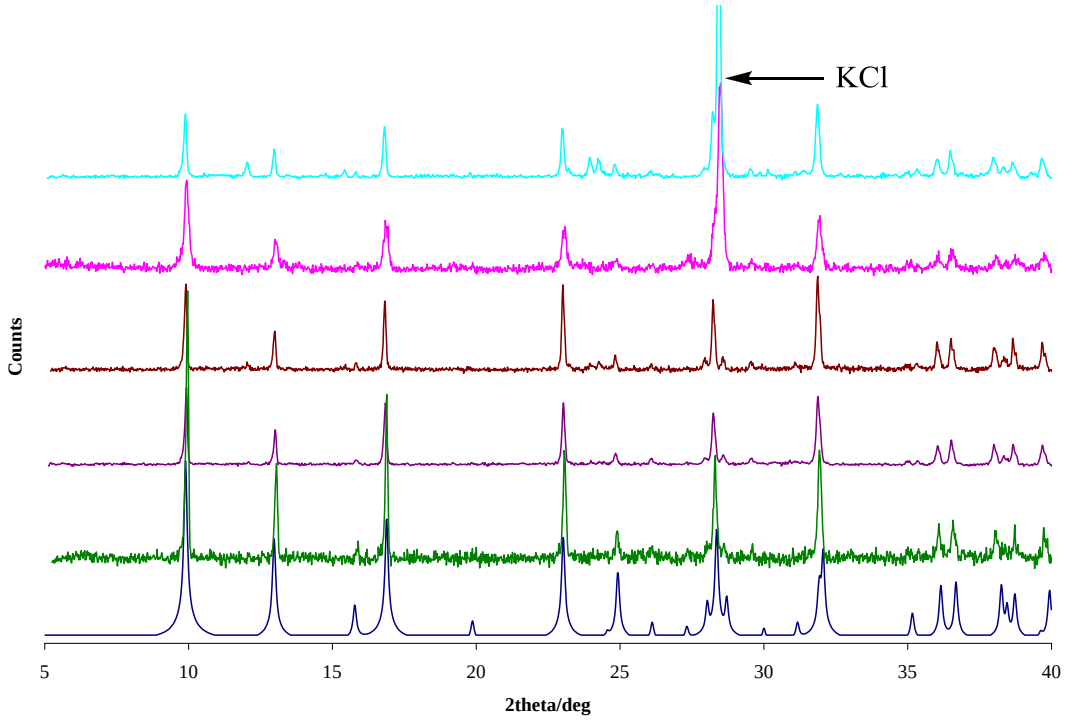
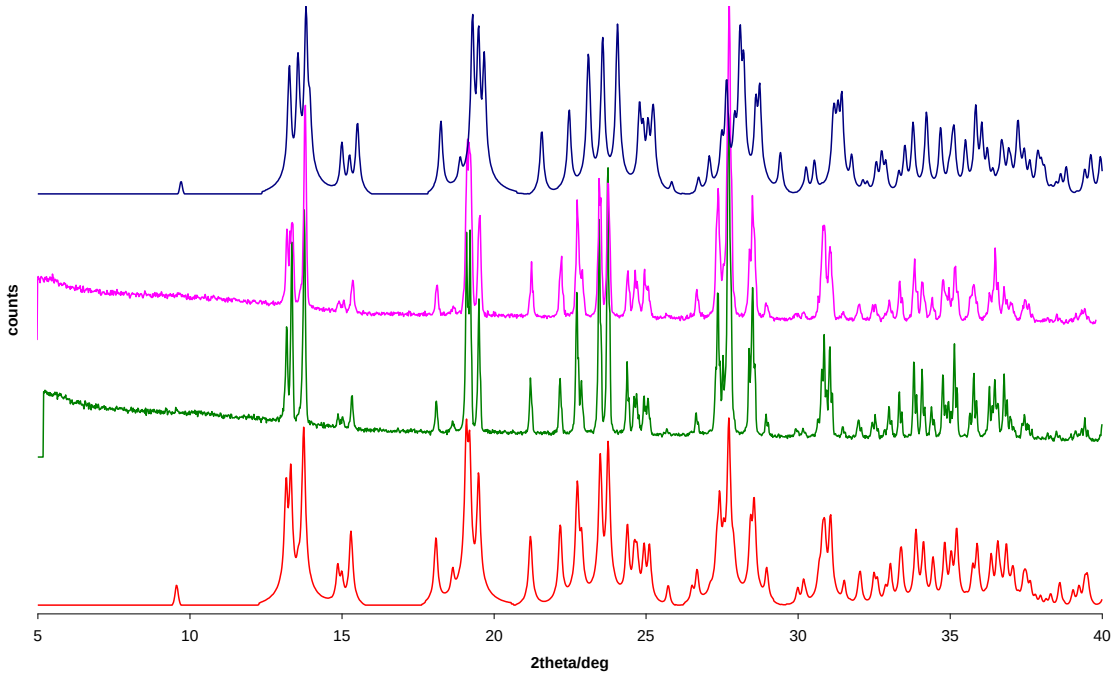


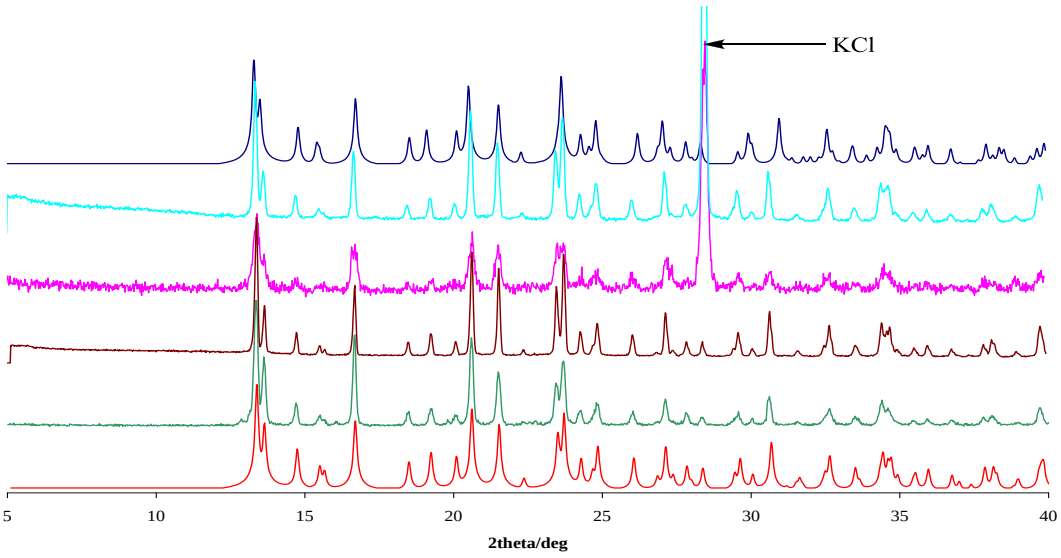

XRPD for $[H_2Pz]_2[CoCl_4]$ **1**. Red = calculated from **1** (RT); green = mechanochemical; pink = vapour absorption; blue = calculated from **1** (LT).



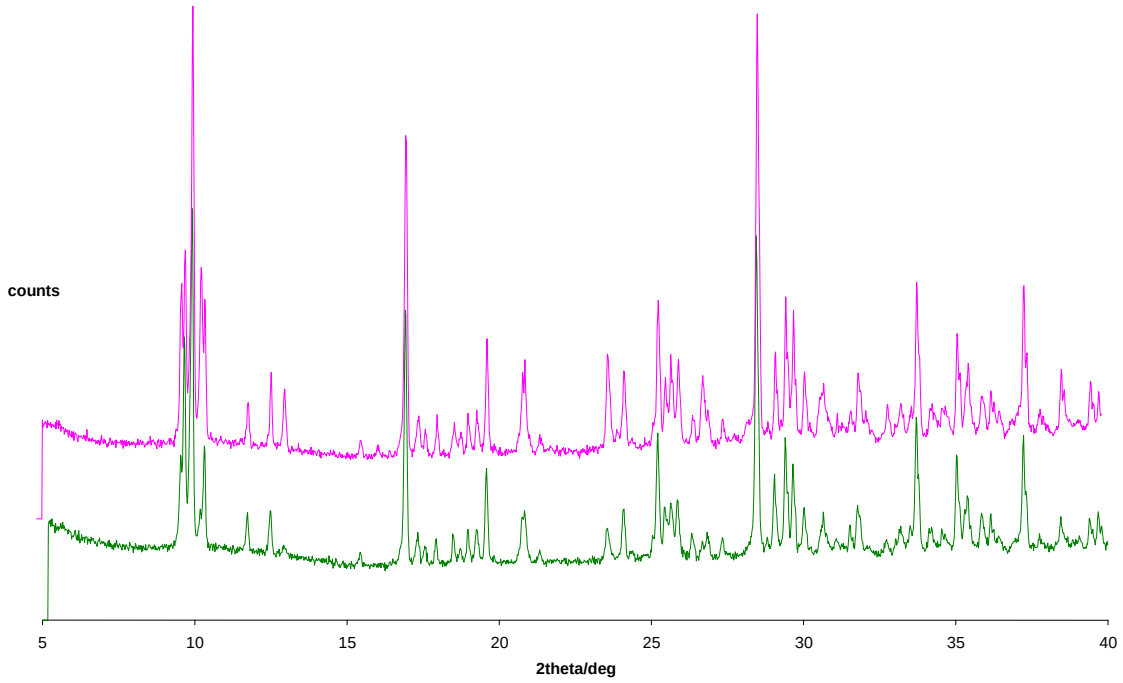

XRPD for $[CoCl_2(Hpz)_2]$ **2** Blue = calculated from the crystal structure; green = mechanochemical; purple = $2[H_2pz]Cl + Co(OH)_2$; brown = $2[H_2pz]Cl + CoCO_3$; pink = **1** + 2KOH; turquoise = **1** + $K_2CO_3$.



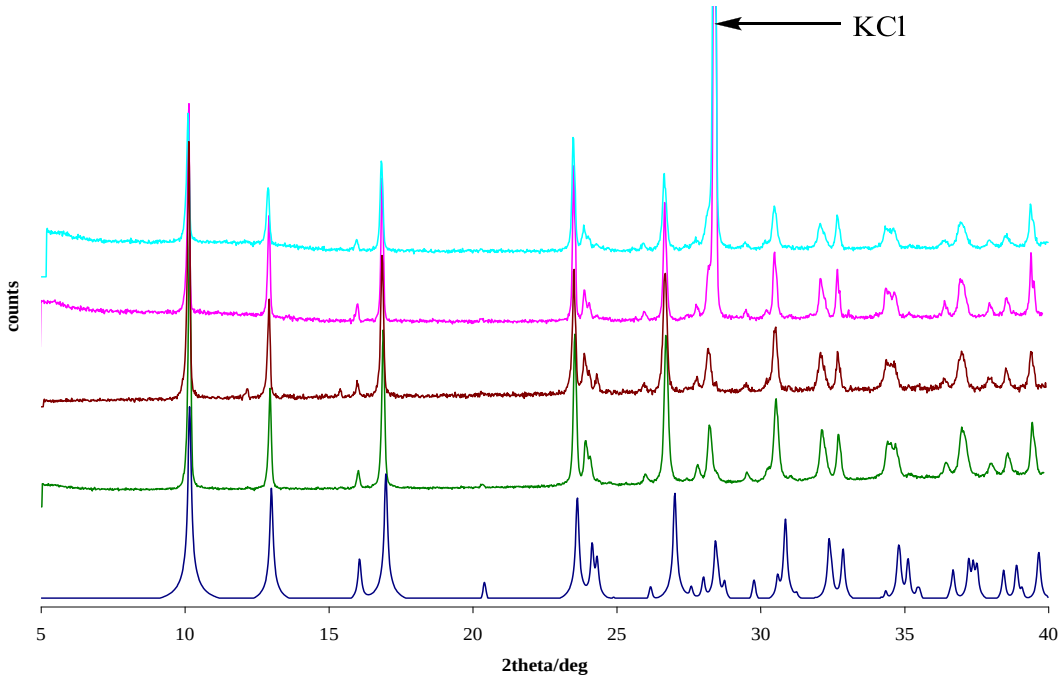

XRPD for $[H_2Pz]_2[ZnCl_4]$ **3**. Red = calculated from **3** (RT); green = mechanochemical; pink = vapour absorption; blue = calculated from **3** (LT).



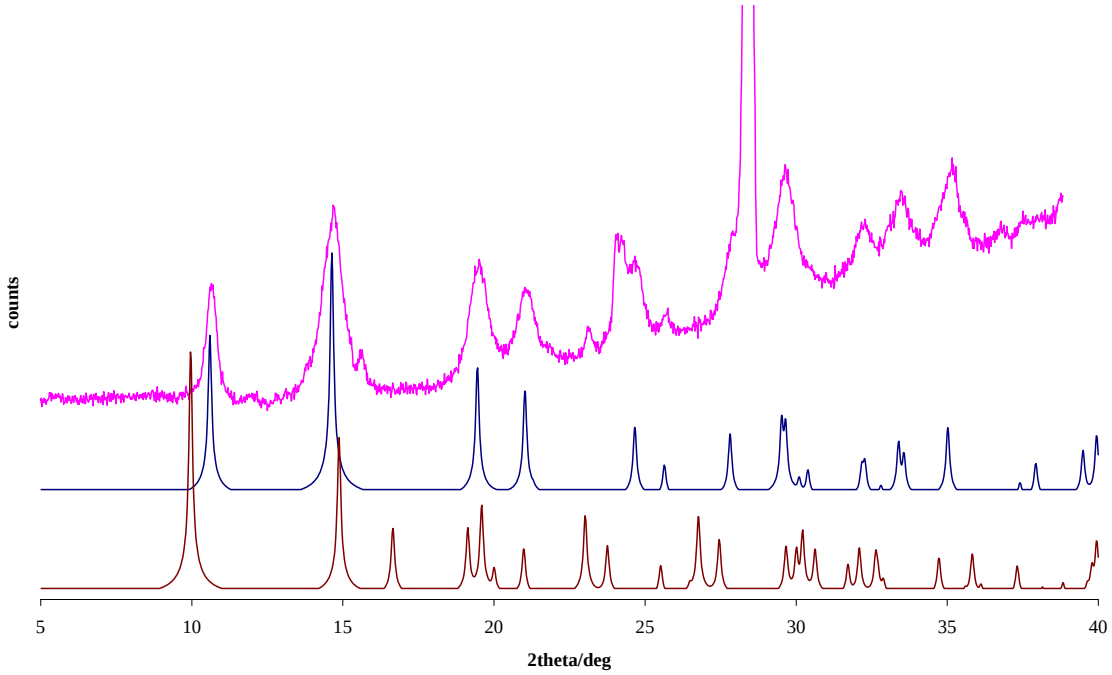

XRPD for $[ZnCl_2(Hpz)_2]$ **4**. Red = calculated from **4** (RT); green = mechanochemical; brown = $H_2pzCl$ + $3Zn(OH)_2{\cdot}2ZnCO_3$; pink = **3** + 2KOH; turquoise = **3** + $K_2CO_3$; blue = calculated from **4** (LT).



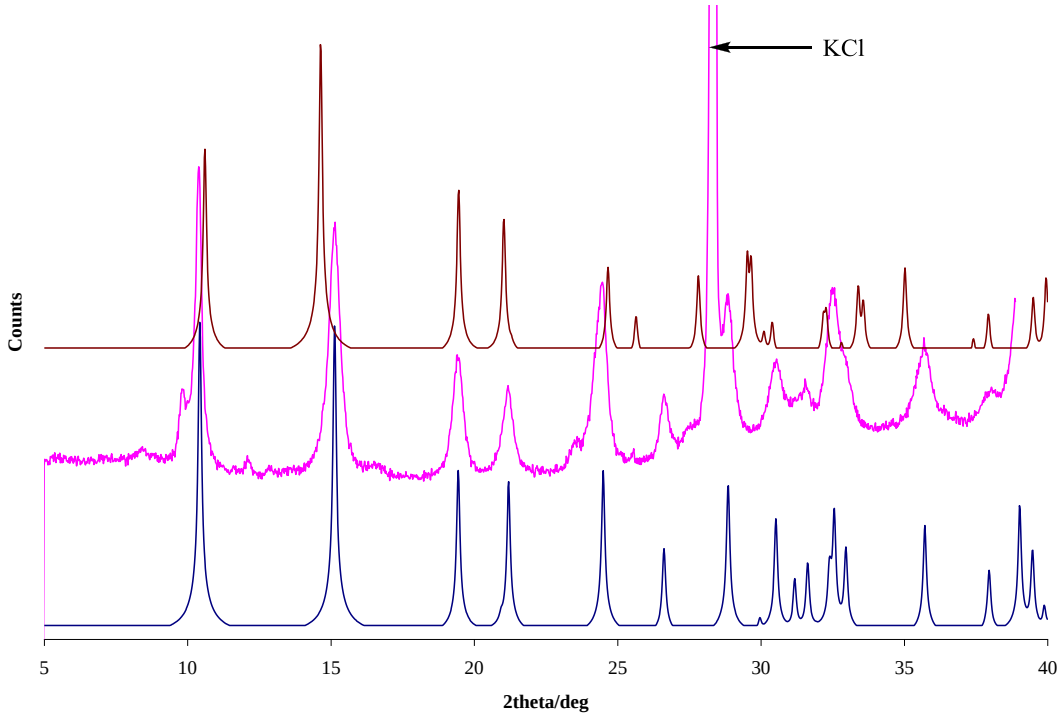

XRPD pattern for $[H_2pz]_2[CuCl_4]$ **5**. Green = mechanochemical; pink = HCl gas absorption.



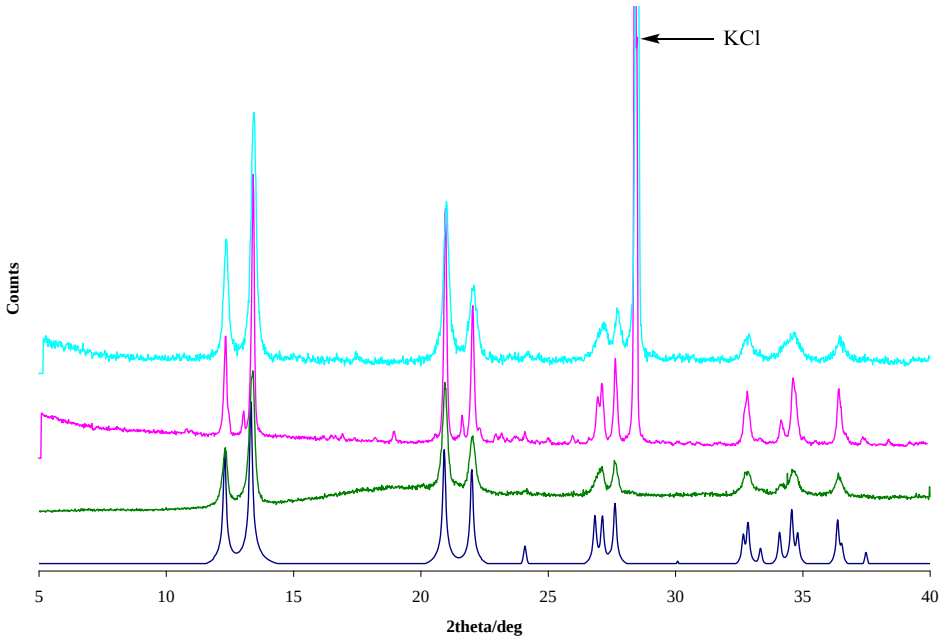

XRPD pattern for $[\{CuCl_2(Hpz)_2\}_n]$ **6**. Blue = calculated; green = mechanochemical; brown = $CuCO_3{\cdot}Cu(OH)_2$ + 4$[H_2pz]$Cl pink = **5** + 2KOH; turquoise = **5** + $K_2CO_3$.



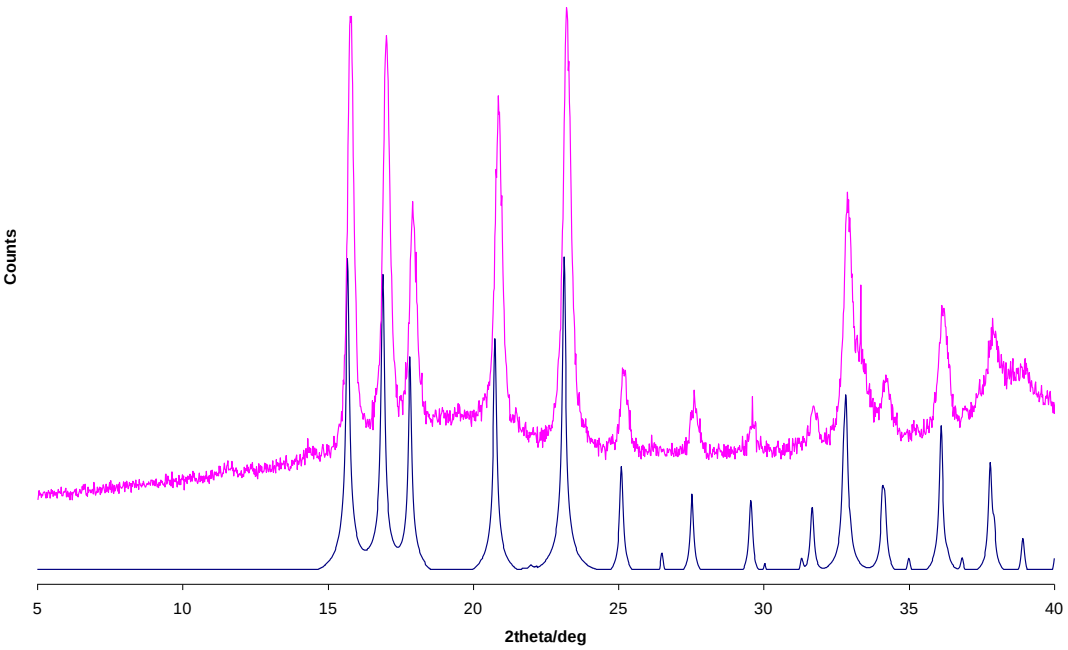

XRPD patterns for [{Ni(pz)$_2$}$_n$] **7**. Brown and blue = calculated from the crystal structures of β-[Ni(pz)$_2$] and α-[Ni(pz)$_2$] respectively; pink = [NiCl$_2$(Hpz)$_2$] + 2KOH.



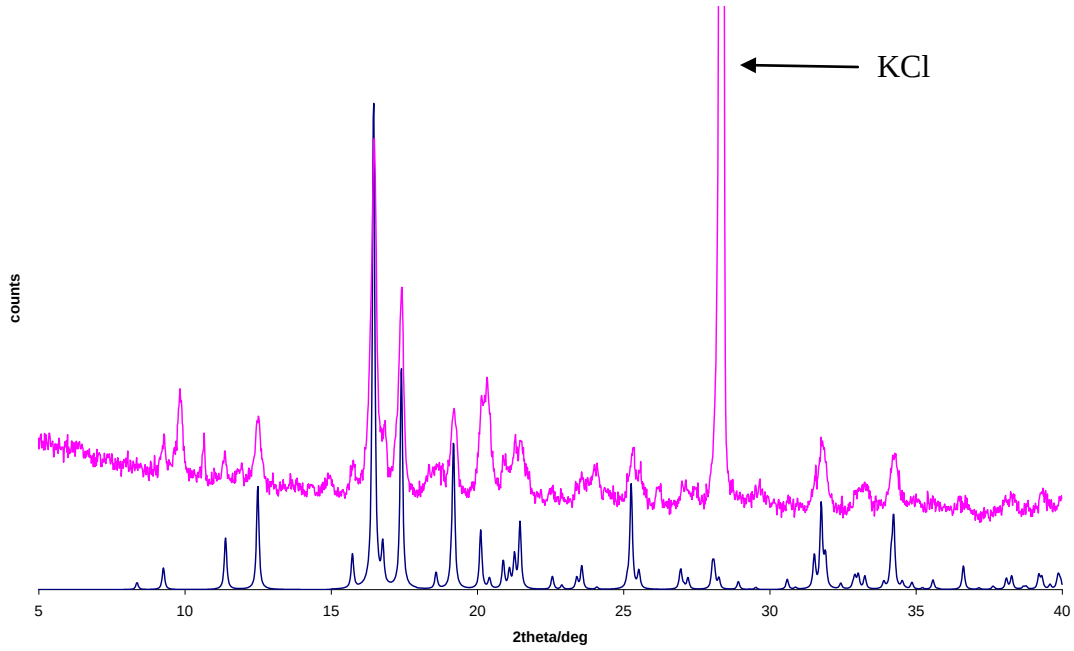

XRPD patterns for [{Cu(pz)$_2$}$_n$] (**8**) + 2KCl. Blue = calculated from the crystal structure; pink = **6** + 2KOH; brown calculated from the crystal structure of α-[Ni(pz)$_2$].



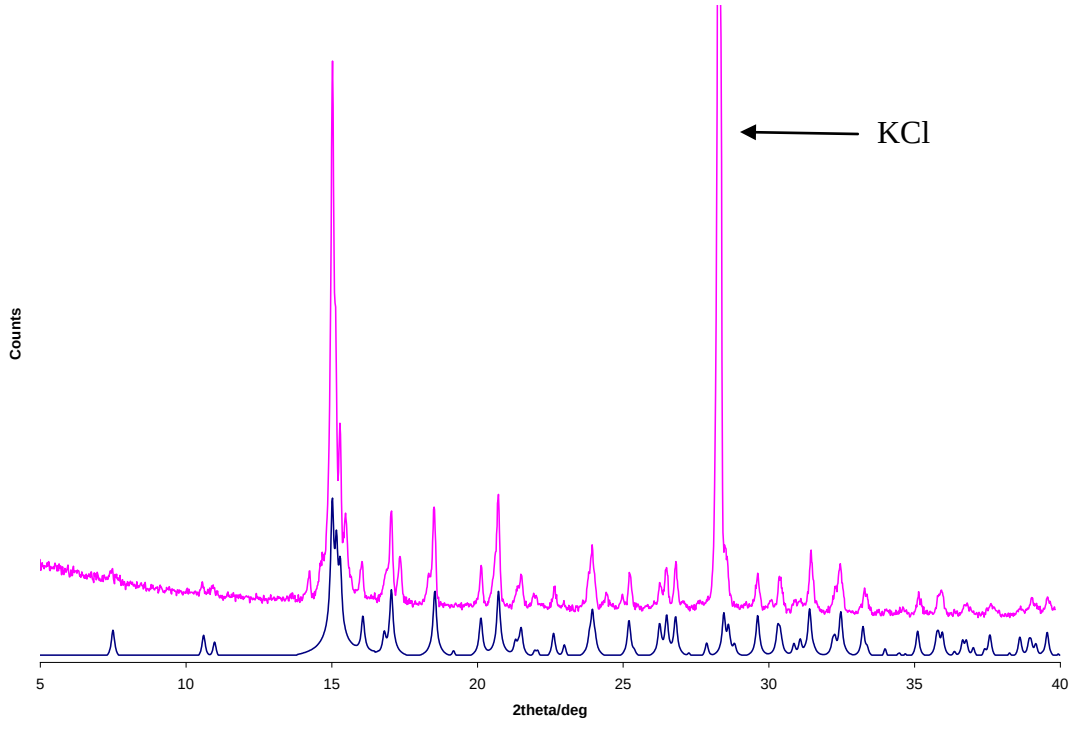

XRPD patterns for $[\{Zn(pz)_2\}_n]$ **9**. Blue = calculated from the crystal structure; green = $3Zn(OH)_2{\cdot}2ZnCO_3$ + 10Hpz; pink = **4** + 2KOH; turquoise = **4** + 2t-BuOK.



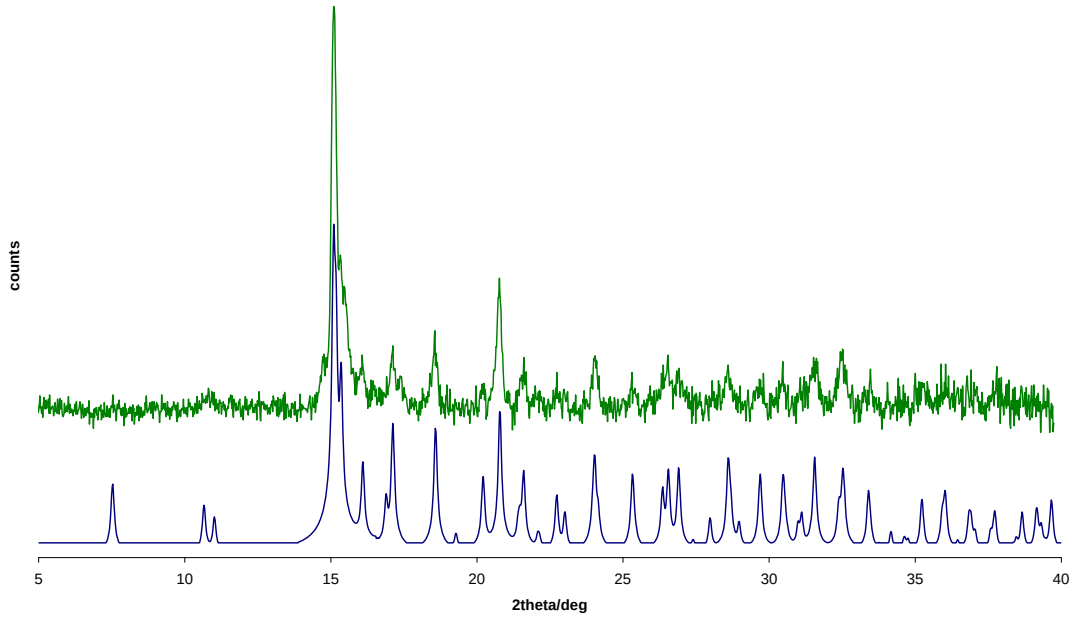

XRPD patterns for $[Ni(im)_2]$. **11** blue = calculated from ALIDUU; pink = $[Ni(Him)_2Cl_2]$ + 2KOH.




XRPD for $[Cu(im)_2]$ **12**. blue = calculated from CUIMDZ02; pink = $[Cu(Him)_2Cl_2]$ + 2KOH.




XRPD for $[Zn(im)_2]$ **13**. blue = calculated from IMIDZB01; pink = $[Zn(Him)_2Cl_2]$ + 2KOH.




XRPD for $[Co(im)_2]$ **14**. blue = calculated from IMZYCO01; green = $[Co(Him)_2Cl_2]$ + 2KOH.

**Table 1**: Hydrogen-bonding geometry for **1** (LT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N1-H1A...Cl1[A] | 0.88 | 2.34 | 3.1537(18) | 153.5 |
| N2-H2A...Cl2[A] | 0.88 | 2.40 | 3.1497(18) | 143.3 |
| N3-H3A...Cl4[B] | 0.88 | 2.23 | 3.1012(17) | 170.6 |
| N4-H4A...Cl1[B] | 0.88 | 2.40 | 3.1391(18) | 141.1 |

Symmetry transformations used to generate equivalent atoms: [A] x,y-1,z [B] x-1/2,-y+3/2,z+1/2

**Table 2**: Hydrogen-bonding geometry for **1** (RT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(1)[A] | 0.86 | 2.35 | 3.159(2) | 157.2 |
| N(2)-H(2A)...Cl(2) [A] | 0.86 | 2.41 | 3.177(2) | 149.3 |
| N(3)-H(3A)...Cl(4) [B] | 0.86 | 2.25 | 3.109(2) | 172.7 |
| N(4)-H(4A)...Cl(1) [B] | 0.86 | 2.50 | 3.215(3) | 141.7 |

Symmetry transformations used to generate equivalent atoms: [A] x,y-1,z [B] x-1/2,-y+3/2,z+1/2

**Table 3**: Hydrogen bonds for **2** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(4)...Cl(2)[A] | 0.86 | 2.65 | 3.176(4) | 120.6 |
| N(2)-H(4)...Cl(2) [B] | 0.86 | 2.74 | 3.349(4) | 129.5 |

Symmetry transformations used to generate equivalent atoms: [A] x,y,z [B] -x,-y+2,-z+1

**Table 4**: Hydrogen-bonding geometry for **3** (LT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(1) [A] | 0.88 | 2.35 | 3.1586(14) | 153.5 |
| N(2)-H(2A)...Cl(2) [A] | 0.88 | 2.40 | 3.1478(13) | 143.0 |
| N(3)-H(3A)...Cl(4) [B] | 0.88 | 2.22 | 3.0964(13) | 171.2 |
| N(4)-H(4A)...Cl(1) [B] | 0.88 | 2.42 | 3.1481(15) | 140.7 |

Symmetry transformations used to generate equivalent atoms: [A] x,y-1,z [B] x-1/2,-y+3/2,z+1/2

**Table 5**: Hydrogen-bonding geometry for **3** (RT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(1) [A] | 0.86 | 2.34 | 3.146(5) | 156.7 |
| N(2)-H(2A)...Cl(2) [A] | 0.86 | 2.41 | 3.171(6) | 148.1 |
| N(3)-H(3A)...Cl(4) [B] | 0.86 | 2.24 | 3.097(5) | 173.5 |
| N(4)-H(4A)...Cl(1) [B] | 0.86 | 2.47 | 3.193(6) | 142.0 |

Symmetry transformations used to generate equivalent atoms: [A] x,y-1,z [B] x-1/2,-y+3/2,z+1/2

**Table 6**: Hydrogen-bonding geometry for **4** (LT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(2A)...Cl(1)[A] | 0.86 | 2.52 | 3.266(2) | 145.3 |
| N(4)-H(4A)...Cl(2)[B] | 0.86 | 2.45 | 3.251(2) | 156.0 |

Symmetry transformations used to generate equivalent atoms: [A] -x,y+1/2,-z+3/2 [B] -x,y-1/2,-z+3/2

**Table 7**: Hydrogen-bonding geometry for **4** (RT) [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(2A)...Cl(2) [A] | 0.86 | 2.50 | 3.303(2) | 155.2 |
| N(4)-H(4B)...Cl(1) [B] | 0.86 | 2.55 | 3.302(2) | 145.9 |

Symmetry transformations used to generate equivalent atoms: [A] -x,y-1/2,-z+1/2 [B] -x,y+1/2,-z+1/2

**Table 8**: Hydrogen-bonding geometry for **6** [Å, º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(2)-H(1A)...Cl(1)[A] | 0.88 | 2.74 | 3.340(5) | 126.9 |
| N(2)-H(1A)...Cl(1)[A] | 0.88 | 2.62 | 3.204(5) | 124.6 |
| N(4)-H(4A)...Cl(2)[B] | 0.88 | 2.48 | 3.017(5) | 120.3 |

Symmetry transformations used to generate equivalent atoms: [A] -x+2,-y+1,-z+1 [B] x+1,y,z

**Table 9**: Hydrogen bond geometry for **[$H_2$pz]Cl** [Å and º].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)...Cl(1) [A] | 0.88 | 2.20 | 3.0378(18) | 158.0 |
| N(2)-H(2A)...Cl(1) [B] | 0.88 | 2.20 | 3.0353(19) | 157.9 |

Symmetry transformations used to generate equivalent atoms: [A] x-1/2,-y+1/2,z+1/2; [B] -x+1,-y,-z+1