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

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Solid pyrazole reacts with HCl gas to form pyrazolium chloride [H_2pz]Cl, which reacts in the solid state, under grinding, with metal chlorides MCl_2 (M = Co, Zn, Cu) to form the pyrazolium tetrachlorometallate salts [H_2pz]$_2$[MCl_4] (M = Co **1**, Zn **3**, Cu **5**). Salt **5** cannot be made in solution, and upon standing at room temperature spontaneously emits HCl to give the coordination compound [$CuCl_2$(Hpz)$_2$] (**6**). Compounds **1** and **3** do not exhibit this behaviour, but can be ground together with bases such as KOH or K_2CO_3 to effect the elimination of HCl and afford their respective [MCl_2(Hpz)$_2$] compounds (M = Co **2**, Zn **4**). **2**, **4** and **6** can also be synthesised in the solid-state by direct reaction of the appropriate metal chloride with pyrazole, or by reaction of a basic metal salt such as the carbonate or hydroxide with pyrazolium chloride. **4** and **6** {and their nickel analogue [$NiCl_2$(Hpz)$_2$]} can be ground with a further two equivalents of base to make the known polymeric metal pyrazolates [M(pz)$_2$]$_n$ (M = Ni **7**, Cu **8**, Zn **9**); the same reaction appears to work for the cobalt analogue **2**, but the presumed product [Co(pz)$_2$]$_n$ **10** then decomposes by oxidation. The imidazolate complexes [M(im)$_2$] (M = Ni, **11**; Cu, **12**; Zn, **13**; Co, **14**) were similarly prepared by grinding the appropriate [M(Him)$_2$Cl$_2$] precursor with KOH.

Introduction

The scope of solid-state synthesis in molecular coordination chemistry has been long established but remains relatively under-exploited. Here we show that they offer access to framework solids (often termed MOFs) that are of high current interest but which are usually prepared by solvothermal routes. In recent work we have shown that coordination complexes and related complex salts can be interconverted and offer ready access to coordination compounds and framework solids that complement the routes available from conventional (solution) chemistry. Thus, we showed how complex salts of the form [H_2bipy][MCl_4] (bipy = 4,4′-bipyridine; M = Zn, Co, Fe, Pt)[1] and [H_2im]$_2$[MCl_4] (Him = imidazole, M = Zn, Co, Cu)[2] can be transformed into their corresponding coordination compounds [MCl_2(bipy)] and [MCl_2(Him)$_2$]. Herein we report studies of the complex salts [H_2pz]$_2$[MCl_4], and their interconversion with coordination compounds [MCl_2(Hpz)$_2$] (H_2pz = pyrazolium; Hpz = pyrazole; M = Co, Cu, Zn) and then pyrazolates [M(pz)$_2$] (pz = pyrazolate), to complement our recent report on similar transformations in palladium and platinum chemistry.[3]

The simplest and most thoroughly studied type of pyrazole complexes are [M(Hpz)$_n$X$_m$] where M is a transition metal or a metalloid and X is an anionic ligand (*e.g.* a halide) and *m* is the valence of the transition metal, often 2.[4] Such complexes are readily prepared by the reaction of the metal salts with pyrazole in neutral or slightly acidic media. In contrast, salts of the pyrazolium cation [H_2pz]$^+$ have received little attention. This is probably related to the low basicity of pyrazole, which has a pK_a of 2.5,[5,6] which implies that the pyrazolium cation is relatively prone to deprotonation to release neutral pyrazole compared with, for example, the isomeric imidazolium cation (pK_a = 14.5). The observation that deprotonation of the cations affords access to M–N bonded species prompted us to explore whether a second deprotonation could provide solvent-free access to the corresponding pyrazolates M(pz)$_2$ and (starting from imidazole compounds) imidazolates M(im)$_2$.

Results

Pyrazolium chloride

Exposure of neutral pyrazole to dry HCl gas in a sealed jar results in instant transformation of the white crystals into a cream-coloured powder, which crystal structure determination and microanalysis confirmed as [H_2pz]Cl. In the crystal structure, both nitrogen atoms on the pyrazolium cation are protonated, and are involved in NH···Cl hydrogen-bonding interactions which connect the cation and anion in a hydrogen-bonded ribbon along the crystallographic *b*-axis (Fig. 1). Details of all the crystal structures reported herein are given in Table 1, and tables of hydrogen bond lengths and angles are given in the ESI.†

Metal complexes

With the pyrazolium chloride salt in hand, the behaviour of pyrazole complexes and pyrazolium salts of divalent metals could be explored by analogy to the chemistry of [H_2im]$_2$[MCl_4]

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† Electronic supplementary information (ESI) available: Complete powder diffraction patterns for all methods of synthesis for all compounds, tables of hydrogen bond lengths and angles and crystal structure information as CIF files. CCDC reference numbers 771207–771209, 771210–771212 and 771212–771215. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00195c

Table 1 Summary of crystallographic data

Crystal data	**1** (LT)	**1** (RT)	**2**	**3** (LT)	**3** (RT)	**4** (LT)	**4** (RT)	**6**	**[H_2pz]Cl**
T/K	100(2)	293(2)	100(2)	100(2)	293(2)	100(2)	293(2)	100(2)	100(2)
Empirical formula	$C_6H_{10}N_4$-$CoCl_4$	$C_6H_{10}N_4$-$CoCl_4$	$C_6H_8N_4$-$CoCl_2$	$C_6H_{10}N_4$-$ZnCl_4$	$C_6H_{10}N_4$-$ZnCl_4$	$C_6H_8N_4$-$ZnCl_2$	$C_6H_8N_4$-$ZnCl_2$	$C_6H_8N_4$-$CuCl_2$	$C_3H_5Cl_2$-N_2
Formula weight	338.91	338.91	265.99	345.35	345.35	272.43	272.43	270.61	104.54
Colour	Blue	Blue	Pink	Colourless	Colourless	Colourless	Colourless	Green	Colourless
Morphology	Prism	Block	Block	Block	Block	Plate	Plate	Needle	Plate
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/m$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a/Å	7.5428(16)	7.6306(7)	17.896(4)	7.5495(15)	7.5750(18)	7.9436(5)	7.9779(14)	3.7606(8)	8.3797(7)
b/Å	12.724(3)	12.8943(13)	3.6423(7)	12.693(3)	12.585(3)	11.3609(2)	12.8943(2)	8.8887(18)	7.3935(8)
c/Å	13.045(3)	13.3727(14)	6.8331(14)	13.068(3)	13.302(3)	11.3094(2)	12.0866(2)	13.649(3)	8.7051(7)
α (°)	90	90	90	90	90	90	90	86.21(3)	90
β (°)	92.60(9)	92.822(4)	93.99(3)	92.66(3)	92.882(11)	90	90	86.88(4)	114.398(5)
γ (°)	90	90	90	90	90	90	90	78.56(3)	90
V/Å^3	1250.7(8)	1314.2(2)	444.32(16)	1250.9(3)	1294.1.(5)	1074.24(3)	1097.2(3)	445.80(2)	491.16(8)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Z	4	4	2	4	4	4	4	2	4
Data collected	12687	13390	1559	14060	34843	98981	19078	4999	3637
Unique data	2854	2964	587	2866	3755	3924	2514	2022	1136
R(int)	0.0239	0.0243	0.0297	0.0225	0.0347	0.0793	0.0300	0.0272	0.0237
R_1 (%)	2.26	3.17	2.74	1.67	4.75	3.62	2.05	5.55	3.41
Flack parameter						0.025(13)	0.279(9)		

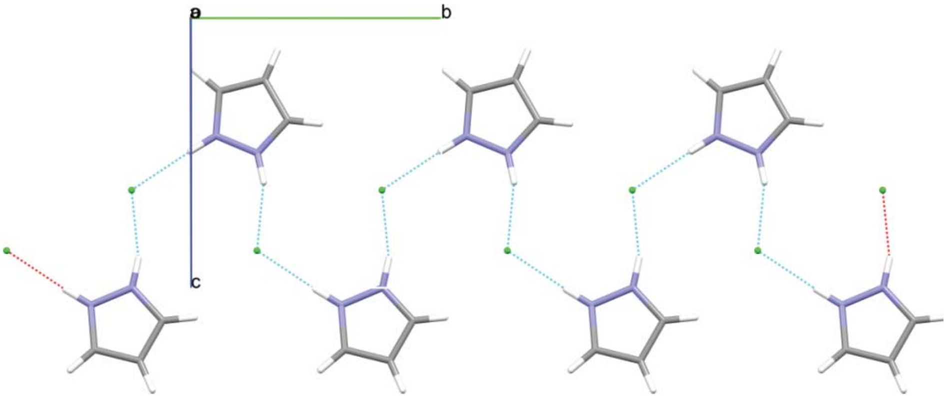


Fig. 1 The hydrogen-bonded ribbon in [H_2pz]Cl viewed down the crystallographic a-axis.

(M = Zn, Co, Cu) salts and corresponding coordination compounds [$MCl_2(Him)_2$].[2]

Slow evaporation of a solution of $CoCl_2$ and two molar equivalents of pyrazole in concentrated aqueous HCl at room temperature led to the formation of blue prismatic crystals of [H_2pz]$_2$[$CoCl_4$] (**1**) suitable for single crystal X-ray diffraction. Crystal structure determination revealed an asymmetric unit containing discrete tetrahedral [$CoCl_4$]$^{2-}$ anions and two [H_2pz]$^+$ cations. The structure contains NH···Cl interactions, with the two pyrazolium cations each giving a chelating $R^2_2(7)$ hydrogen-bonding motif with the anion (Fig. 2).[7–9] **1** was also obtained in quantitative yield by grinding anhydrous $CoCl_2$ with two molar equivalents of pyrazolium chloride, or by exposure of microcrystalline [$CoCl_2(Hpz)_2$] **2** to dry HCl gas.

Grinding anhydrous $CoCl_2$ with two molar equivalents of pyrazole gave [$CoCl_2(Hpz)_2$] (**2**) as a pink polycrystalline powder, as did mechanochemical dehydrochlorination of **1** in the solid-state by grinding the salt with two molar equivalents of an "external base" (here KOH or K_2CO_3). We have previously reported that "internal" bases - the hydroxide, carbonate or equivalent salt of the appropriate transition metal - may be used as metal-containing starting materials that react with the hydrochloride adducts of the ligands [H_2im]Cl or [4,4′H_2bipy]Cl_2 in the solid state to yield the corresponding metal complexes of the ligands (Him or 4,4′bipy).[2] This approach can also be used to synthesize **2** by reaction of $Co(OH)_2$ or $CoCO_3$ and pyrazolium chloride. Composition of the products of these reactions (see the experimental section) was confirmed by elemental analysis and by comparison of the X-ray powder diffraction pattern with that generated from the single crystal structure. Single crystals of **2** suitable for X-ray structural analysis were obtained by slow evaporation of a water–acetonitrile (1 : 1 v/v) solution of the pink polycrystalline powder obtained in the solid-state reaction, and structural analysis revealed a chloride-bridged one dimensional polymeric structure, in which chains are formed by edge sharing between octahedral *trans*-$CoCl_4(Hpz)_2$ moieties (Fig. 3). Isostructural polymeric pyrazole compounds [$M(\mu\text{-}Cl)_2(Hpz)_2$] with double chloride bridges are known for M = Cd(II)[10] (CSD refcode: LEDQIV) and Mn(II) (CSD refcode: DCPZMN),[11] and an analogous imidazole compound [$CdCl_2(Him)_2$] (CSD refcode: CLIMCD) is known.[12]

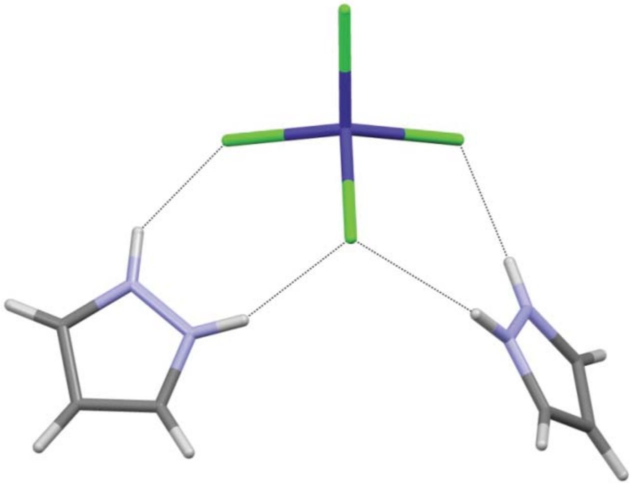


Fig. 2 The $R_2^2(7)$ N–H···Cl hydrogen-bonded supramolecular motif in $[H_2pz]_2[CoCl_4]$ (**1**).

Like its cobalt analogue, grinding $ZnCl_2$ with two molar equivalents of pyrazolium chloride led to the formation of crystalline $[H_2pz]_2[ZnCl_4]$ (**3**), as did exposure of $[ZnCl_2(Hpz)_2]$ (**4**) to vapours from concentrated aqueous HCl solution or dry HCl gas in a sealed jar. Slow evaporation of a concentrated HCl solution containing $ZnCl_2$ and two equivalents of pyrazole resulted in the formation of colourless crystals of **3** of suitable quality for X-ray structural analysis, which revealed a structure which is isomorphous with that of the cobalt analogue **1**, with almost identical unit cell parameters. Table 1 includes the crystal data for **1** and **3** at 100 K and 293 K.

Grinding together $[H_2pz]Cl$ and $2ZnCO_3{\cdot}3Zn(OH)_2$ in stoichiometric amounts (2 H_2pz: 1 Zn) successfully afforded $[ZnCl_2(Hpz)_2]$ (**4**) in quantitative yield with concomitant elimination of CO_2 and H_2O. Similarly, mechanochemical dehydrochlorination of **3** with KOH or K_2CO_3 also afforded **4** with KCl, water (removed *in vacuo*) and CO_2 (in the latter case) as by-products. Mechanochemical grinding of $ZnCl_2$ with two molar equivalents of pyrazole also resulted in the smooth formation of **4**. Colourless plate-like single crystals of **4** of suitable quality for X-ray structural analysis were obtained by slow evaporation of its solution in acetonitrile, and single crystal structure determination at 100 K revealed a structure in the orthorhombic space group $P2_12_12_1$. Unlike its cobalt analogue **2**, **4** is a tetrahedral monomer with the zinc coordinated to two chlorine atoms and two pyrazole molecules. In the crystal structure these tetrahedral building blocks are packed in such a way that one pyrazole ring from each $[ZnCl_2(Hpz)_2]$ complex stacks along the crystallographic *a*-axis, while N–H···Cl interactions form a hydrogen-bonded ribbon along the *b*-axis of the cell (Fig. 4). A similar structure has been reported for one of the crystal forms of dichlorobis(pyridazine-*N*) zinc(II), in which the zinc atoms are tetrahedrally coordinated to two chlorine atoms and two pyridazine ligands (CSD refcode: YAFYOU).[13]

Grinding anhydrous copper(II) chloride with two molar equivalents of pyrazolium chloride resulted in the formation of a crystalline, single phase reddish-brown powder of unknown structure, assigned as $[H_2pz]_2[CuCl_4]$ (**5**) on the basis of its elemental composition and chemical reactions. Using copper(II) chloride dihydrate instead, or exposure of the polymeric coordination compound $[CuCl_2(Hpz)_2]$ **6** to dry HCl gas afforded the same compound (Fig. 5).

Compound **5** was observed to lose 2 molecules of HCl when left to stand in air at room temperature. This process is accompanied by a colour change from brown to green. Elemental and X-ray powder diffraction analyses on the green product were consistent with it being the coordination compound **6**. The elimination process is complete in about 96 h (Fig. 6), and is fully reversible as exposure of the coordination compound $[CuCl_2(Hpz)_2]$ **6** (see below) to HCl gas causes it to revert back to the brown crystalline salt **5**. We have been unable to obtain the crystal structure of **5** as attempts to crystallize it from HCl solution yield instead a known salt of the dinuclear $[Cu_2Cl_6]^{2-}$ anion (CSD refcode: GADYUF).[14]

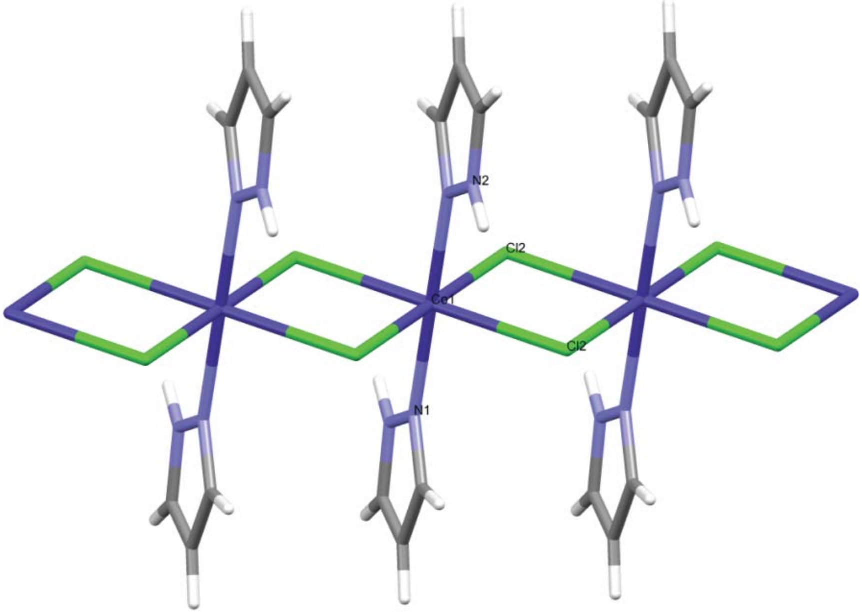


Fig. 3 The $\{Co(\mu\text{-}Cl)_2(Hpz)_2\}_n$ chain in **2**.

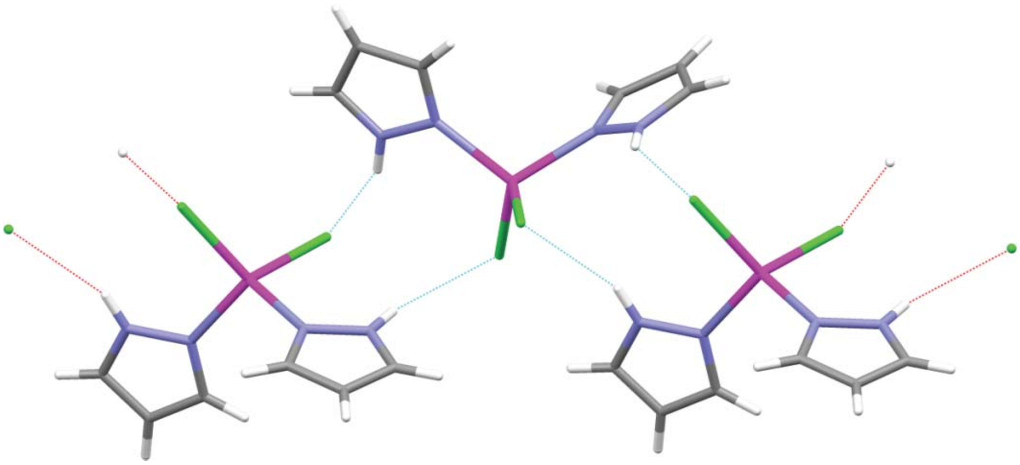


Fig. 4 The chain of $R_2^2(10)$ N–H···Cl hydrogen bond motifs in **4**, viewed down the *a*-axis.

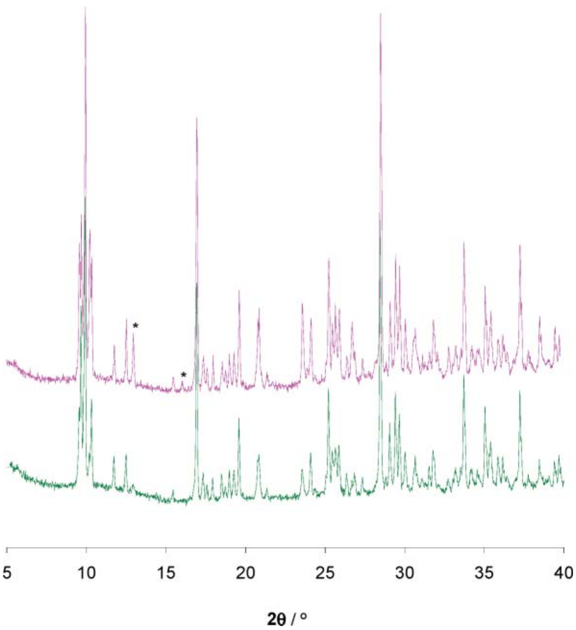


Fig. 5 XRPD patterns for samples of $[H_2pz]_2[CuCl_4]$ **5**. Green = mechanochemical synthesis; pink = from HCl gas absorption. * = peaks from **6**.

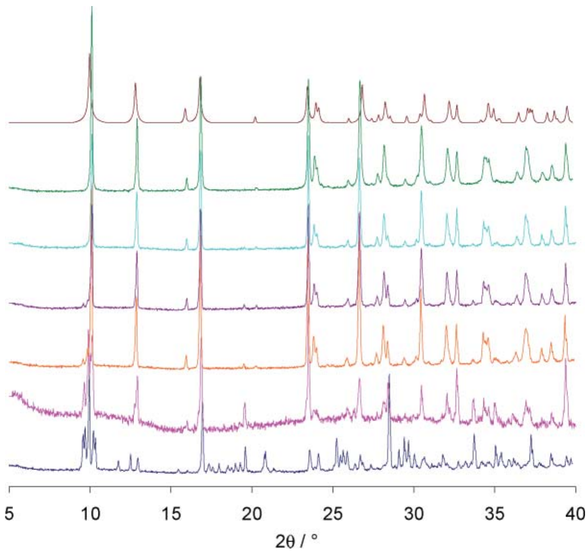


Fig. 6 XRPD patterns for the loss of HCl from $[H_2pz]_2[CuCl_4]$ **5**. Blue = 0 h; pink = 24 h; orange = 48 h; turquoise = 96 h; green = **6** (mechanochemical synthesis); brown = calculated from the crystal structure.

This is therefore an instance of differing reaction outcomes in solid and solution phases.

Grinding of either anhydrous $CuCl_2$ or $CuCl_2 \cdot 2H_2O$ with two molar equivalents of pyrazole resulted in the quantitative formation of $[CuCl_2(Hpz)_2]$ (**6**) as a green polycrystalline powder. Treatment of $CuCO_3 \cdot Cu(OH)_2$ (as an "internal base") with stoichiometric amounts of pyrazolium chloride also afforded **6**, with concomitant elimination of carbon dioxide and water. Similarly, grinding of KOH or K_2CO_3 with **5** resulted in the elimination of H_2O and CO_2 (in the case of K_2CO_3) and the formation of **6** and crystalline KCl as a by-product.

Single crystals of **6** suitable for X-ray structural analysis were obtained by slow evaporation of a water–acetonitrile (1 : 1 v/v) solution. Structure determination revealed that the structure consists of a chain of edge-sharing octahedral *trans*-$CuCl_4(Hpz)_2$ moieties (Fig. 7), and is therefore quasi-isostructural with **2** and its Cd(II)[10] and Mn(II)[11] analogues, though the Cu–Cl bond lengths in **6** are Jahn–Teller distorted, with two long Cu–Cl distances (2.8375(19) and 2.9354(19) Å) and two short distances (2.3495(17) and 2.3384(17) Å).

Pyrazolate compounds

It is possible to deprotonate pyrazole to produce the pyrazolate anion, $(pz)^-$, which will function as a ligand; many pyrazolate complexes are known, and are mostly obtained from solutions of pyrazole and a metal salt in the presence of a strong base as a deprotonating agent.[7,15,16] The need for a broader range of synthetic routes to species of this sort has been given added priority by recent discoveries in MOF chemistry, notably in zinc-imidazolate framework chemistry.[17] Given the success of the solid-state approach to pyrazolium and pyrazole compounds reported above, we decided to investigate whether it was possible

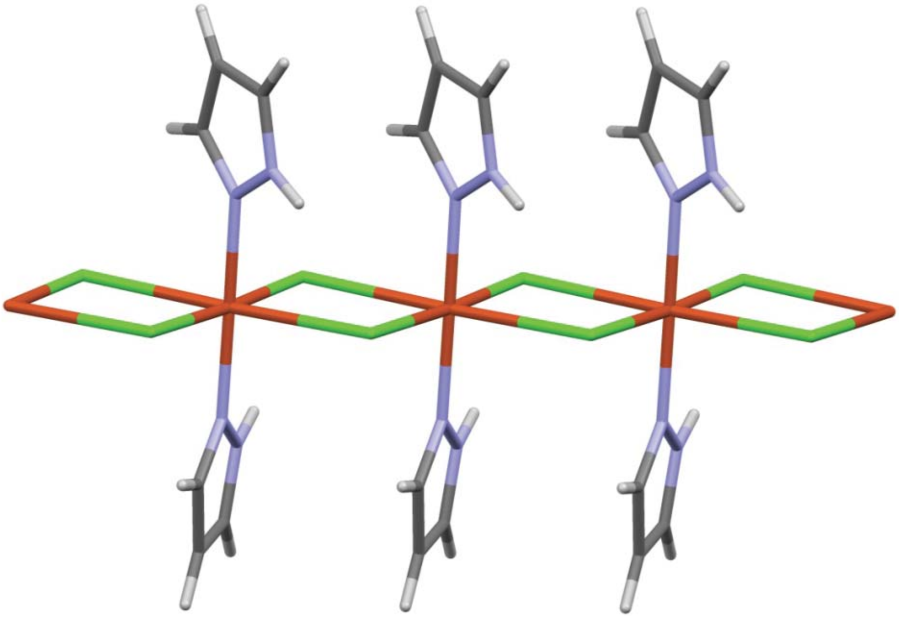


Fig. 7 The $\{CuCl_2(Hpz)_2\}_n$ chain in **6**.

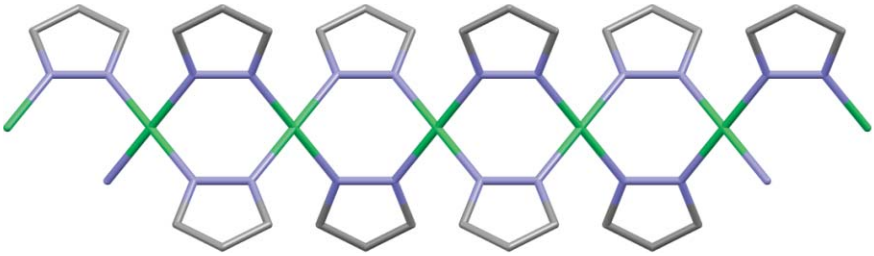


Fig. 8 The $[Ni(pz)_2]_n$ chain in α-**7**.

to synthesise pyrazolate compounds from pyrazole compounds by further deprotonation in the solid state.

Grinding $[NiCl_2(Hpz)_2]$ with 2 molar equivalents of KOH resulted in the formation of a yellow polycrystalline powder of $[Ni(pz)_2]_n$ (**7**) and crystalline KCl (two equivalents), as deduced by XRPD (Fig. 9) and elemental analysis. Compound **7** is known to exist in two polymorphic forms; α-$[Ni(pz)_2]_n$ (CSD refcode: AQOPUR01) was obtained from $Ni(CH_3COO)_2$, and β-$[Ni(pz)_2]_n$ (CSD refcode: AQOPUR) was obtained when NiO was used as a starting material.[7] Repeated syntheses *via* our solid-state KOH route always produced the α-$[Ni(pz)_2]_n$ polymorph (α-**7**). The polymeric chain seen in the structure of α-**7** is shown in Fig. 8; as in β-**7**, the coordination geometry about the nickel(II) centre in α-**7** is square planar. Fig. 9 compares the observed powder pattern for α-**7** with those calculated from the single crystal structure determinations for the α- and β-$[Ni(pz)_2]_n$ polymorphs. It is evident from the broad diffraction peaks in Fig. 9 that the samples of α-**7** prepared by the mechanochemical route have only moderate crystallinity; there are also some peaks present at around $2\theta = 16$ and 24° due to an unidentified crystalline side product.

In a similar fashion, mechanochemical treatment of $[CuCl_2(Hpz)_2]$ (**6**) with two molar equivalents of KOH led to formation of the crystalline polymeric compound $[Cu(pz)_2]_n$ (**8**), with an immediate colour change from green to beige. The preparation of this compound from an acetonitrile solution of $Cu(CH_3COO)_2 \cdot H_2O$ and pyrazole has been reported;[16] this gives a product which is hydrated and pink, but the water is quantitatively lost upon heating to form a quasi-isostructural, anhydrous, beige phase.[16] The product **8** obtained by the mechanochemical route is also beige, and elemental analysis indicates that no water was

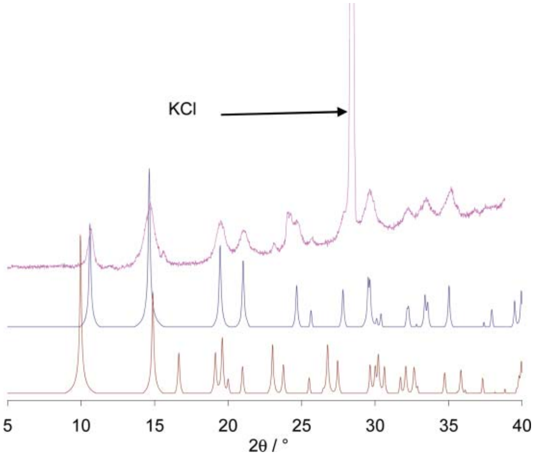


Fig. 9 XRPD patterns for **7**. Brown and blue = calculated from the single crystal structures of β-$[Ni(pz)_2]_n$ and α-$[Ni(pz)_2]_n$ respectively; pink = mechanochemical reaction of $[NiCl_2(Hpz)_2]$ + 2KOH.

present. Fig. 10 shows the powder pattern of **8** from the crystal structure[16] (CSD refcode: NAPBIQ) and an experimental XRPD pattern. Again, the crystallinity of the sample prepared in the solid-state is low, and there also some peaks visible in the powder pattern due to an unidentified crystalline side product.

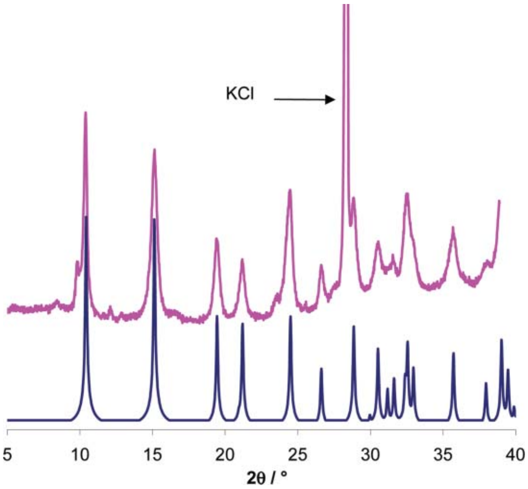


Fig. 10 XRPD patterns for $[Cu(pz)_2]_n$ (**8**) + 2KCl. Blue = calculated from the crystal structure NAPBIQ;[16] pink = product of grinding **6** + 2KOH.

Mechanochemical treatment of $3Zn(OH)_2{\cdot}2ZnCO_3$ with five molar equivalents of pyrazole led to the deprotonation of the pyrazole and the formation of crystalline, single phase, $[Zn(pz)_2]_n$ **9**, with concomitant elimination of CO_2 and H_2O. Similarly, grinding of $[ZnCl_2(Hpz)_2]$ (**4**) with two molar equivalents of either KOH or t-BuOK afforded **9** and KCl, with the elimination of water or t-butanol (removed *in vacuo*) respectively. Synthesis of **9** from solution and structural characterization by *ab initio* XRPD studies has been reported (CSD refcode: MAPCOV).[15] Fig. 11 and 12 show the crystal structure of **9** and the XRPD patterns from solid-state syntheses respectively; in this case, the crystallinity and purity of the products from the solid-state syntheses are better than in the cases of **7** and **8**. As in **7**, a M(μ-pz)$_2$ chain is present, although in **9** the metal adopts a tetrahedral coordination geometry.

We were unable to isolate either of the known polymorphs of $[Co(pz)_2]_n$ **10** by our solid state methods. Grinding $[CoCl_2(Hpz)_2]$ (**2**) with KOH or t-BuOK gave a violet paste which then turned into a brown powder, whose PXRD pattern contained only a large peak at $2\theta = 28°$, implying that KCl was the only crystalline phase present. Similarly, grinding pyrazole with $Co(OH)_2$ or $Co(CO)_3$ and a drop of water gave brown powders where the only diffraction peaks in the powder patterns were from the unreacted metal-containing starting material. We note that the purple compound $[Co(pz)_2]_n$ is susceptible to aerial oxidation to the brown cobalt(III) compound $[Co(pz)_3]_n$,[7] and it would seem likely that oxidation is also taking place in the cobalt reactions reported herein; no precautions against oxidation were taken.

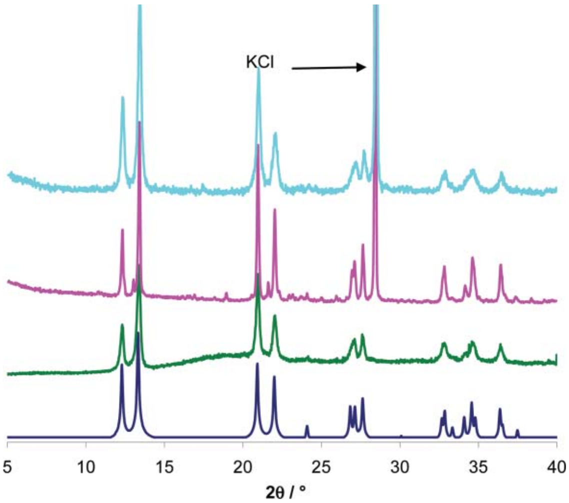


Fig. 12 Diffraction patterns for $[Zn(pz)_2]_n$ **9**. Blue = calculated from MAPCOV;[15] green = $3Zn(OH)_2{\cdot}2ZnCO_3$ + 10Hpz; pink = **4** + 2KOH; turquoise = **4** + 2t-BuOK.

Imidazolate chemistry

In view of the reasonably successful preparation of metal(II) pyrazolates by solid state routes reported above, we investigated their imidazolate analogues. Thus, grinding $[NiCl_2(Him)_2]$ with two equivalents of KOH afforded a yellow polycrystalline powder containing $[Ni(im)_2]_n$ (**11**) (and KCl), which was washed with water to remove the KCl and dried *in vacuo*. Powder diffraction and elemental analysis confirmed that the nickel-containing product was crystalline, single phase α-$[Ni(im)_2]_n$ (**11**), one of the two known polymorphs (CSD refcode: ALIDUU).[18] Similarly, grinding $[CuCl_2(Him)_2]$ with two equivalents of KOH afforded a green polycrystalline powder containing $[Cu(im)_2]_n$ (**12**) and KCl.

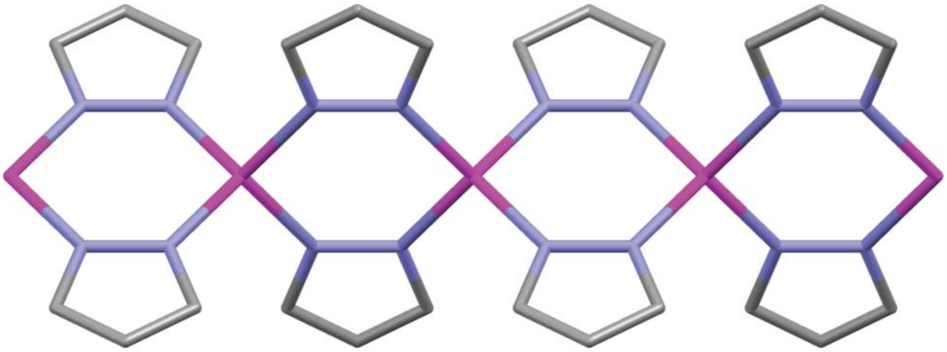


Fig. 11 A view of the polymeric chain in $[Zn(pz)_2]_n$ **9**.[15]

Powder diffraction (Fig. 13) and elemental analysis confirmed that the copper-containing product **12** was predominantly the G-$[Cu(im)_2]_n$ phase (CSD refcode CUIMDZ02), one of five known polymorphs, though peaks at $2\theta = 9.8$ and 20.5° indicate a small amount of the J-phase.[19]

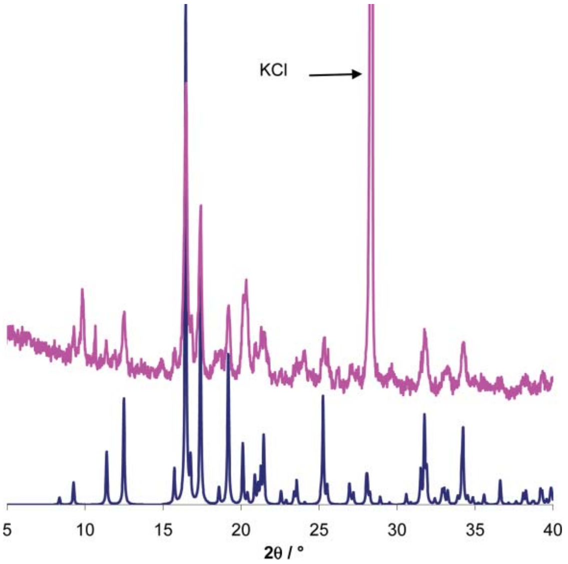


Fig. 13 Powder diffraction patterns for $[Cu(im)_2]_n$ (G-**12**). Blue = calculated from CUIMDZ02; pink = $[CuCl_2(Him)_2]$ + 2KOH.

Grinding $[ZnCl_2(Him)_2]$ with two equivalents of KOH afforded a white polycrystalline powder containing $[Zn(im)_2]_n$ (**13**) and KCl. Powder diffraction and elemental analysis confirmed that the zinc-containing product was crystalline, single phase $[Zn(im)_2]_n$ (**13**) (CSD refcodes IMIDZB01 and IMIDZB),[20] one of the many known (pseudo-)polymorphs and frameworks.[17,21] Finally, grinding $[CoCl_2(Him)_2]$ with two equivalents of KOH afforded a purple polycrystalline powder containing $[Co(im)_2]_n$ (**14**) and KCl. Powder diffraction (Fig. 14) and elemental analysis confirmed that the cobalt-containing product was crystalline, single phase $[Co(im)_2]_n$ (**14**), one of the many known (pseudo-)polymorphs (CSD refcode IMZYCO01; polymorph 4 using the numbering scheme from previous reports)[22,23] and frameworks.

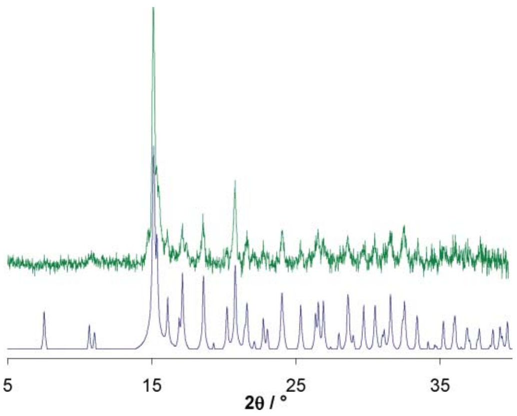


Fig. 14 Powder diffraction patterns for $[Co(im)_2]_n$ (**14**). Blue = calculated from IMZYCO01; green = $[Co(Him)_2Cl_2]$ + 2KOH.

Discussion and conclusions

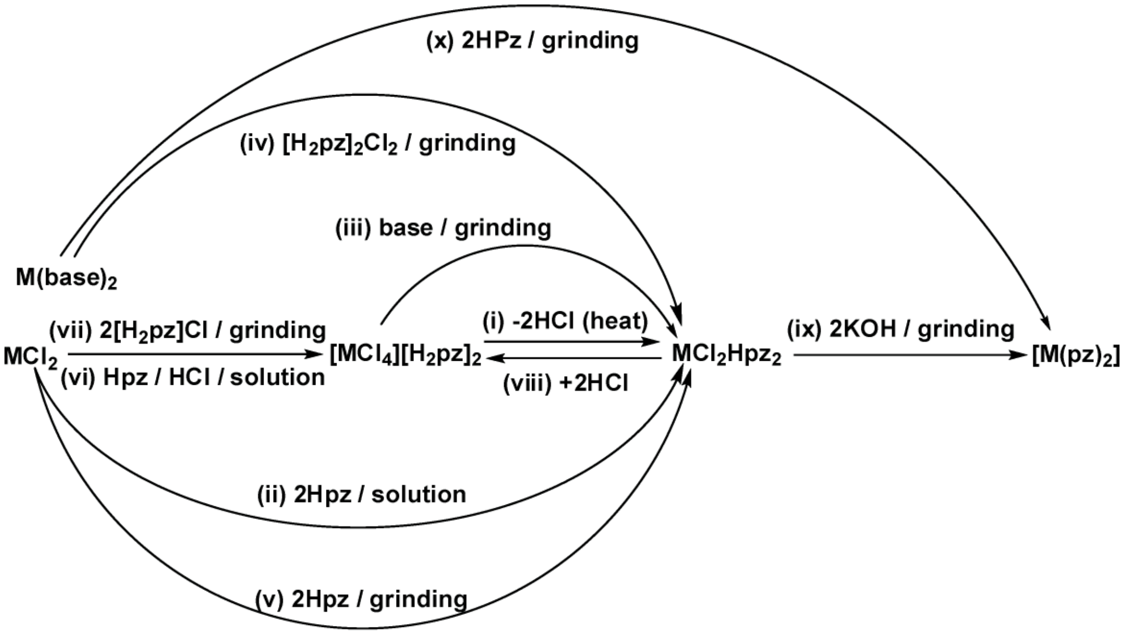
This work extends the range of hydrogen-bonded complexes that can be interconverted with coordination compounds (by mechanochemical dehydrochlorination, solid-gas (or vapour) reactions or accessed by mechanochemical reactions of metal dichlorides) in the solid-state to include pyrazole species. Both protonated and neutral pyrazole can be used as reagents in crystal synthesis, providing crystalline metal salts and coordination networks respectively. More importantly, these reactions can be achieved completely and selectively in the solid-state without recourse to the use of solvents. The reaction of pyrazolium chloride with metal chloride salts has enabled the selective solid-state syntheses of crystalline bis(pyrazolium) perchlorometallate $[H_2pz]_2[MCl_4]$ (M = Co **1**, Zn **3** Cu **5**) salts in quantitative yields. In particular it affords access to **5** (see Scheme 1, pathway vii) which is unobtainable in solution due to the formation of $[H_2pz]_2[Cu_2Cl_6]$, in which the Cu : H_2pz ratio is 1 : 1 rather than 1 : 2 in **6**. The cobalt and zinc salts **1** and **3** are isostructural and contain hydrogen-bonded $R^2_2(7)$ supramolecular motifs. The copper system **5** is different, but its structure is yet to be determined.

Like their imidazolium counterparts,[2] the thermal reactivities of the $[H_2pz]_2[MCl_4]$ complex salts studied herein are less well-behaved than the pyridinium derivatives we have studied previously.[1] For the cobalt and zinc complexes, thermogravimetric analysis did not show mass losses corresponding to extrusion of HCl, suggesting that thermal dehydrochlorination cannot afford the $[MCl_2(Hpz)_2]$ coordination compounds in these cases. This contrasts with the pyridinium derivative salts which were readily dehydrochlorinated to produce metal–pyridine complexes in the solid state.[24] The copper salt **5**, does however undergo reversible extrusion (Scheme 1, pathway i) of HCl at room temperature to give the coordination polymer $[CuCl_2(Hpz)_2]$ **6**. This behaviour is not observed with any of the other metals studied herein, but it is noteworthy that the imidazolium analogue of **6** ($[H_2im]_2[CuCl_4]$) was the only imidazole complex we have studied that afforded the coordination compound $[MCl_2(Him)_2]$ *via* thermal dehydrochlorination, and this therefore appears to be a characteristic of the copper systems. Similar behaviour has been reported by Espallargas *et al.*, who observed the reversible extrusion and uptake of HCl by (3-halopyridinium)$_2[CuCl_4]$ compounds.[25]

The reaction of "internal" bases {$M(OH)_2$ or equivalent} with pyrazolium chloride provides simple, fast and convenient access to crystalline coordination complexes $[MCl_2(Hpz)_2]$. It has also been shown here, for the first time, that K_2CO_3 can be used as a substitute for KOH in the mechanochemical elimination of HCl from $[H_2L]_2[MCl_4]$ to afford $[MCl_2(HL)_2]$ + 2KCl in quantitative yields. This is useful since K_2CO_3 is far less hygroscopic than KOH and as such much easier to handle. Direct access to the $[MCl_2(Hpz)_2]$ species by reaction of Hpz with the metal dichloride has also been demonstrated.

In general, the synthetic routes explored for most of the metals afforded the desired hydrogen bonded complexes, which were readily dehydrochlorinated mechanochemically to afford the metal-pyrazole complexes. Scheme 1 summarizes the overall transformations possible in the metal-pyrazole systems, highlighting the reactions that worked as designed and those which did not.

Furthermore, reaction of either $[MCl_2L_2]$ coordination complexes or $[HL]_2[MCl_4]$ salts (L = Hpz or Him) with external bases



M	i	ii	iii	iv	v	vi	vii	viii	ix	x
Co	X	√	√	√	√	√	√	√	?	
Zn	X	√	√	√	√	√	√	√	√	√
Cu	√	√	√	√	√	X	√	√	√	

Scheme 1 Interconversions of pyrazolium, pyrazole and pyrazolate compounds reported herein.

(such as KOH or K_2CO_3) has also afforded routes to a range of $[M(pz)_2]_n$ and $[M(im)_2]_n$ MOFs. Most of these compounds are highly polymorphic, but the solid-state methods generally seem selective, and mainly produce only one of the possible phases. Our results complement those of Fernández-Bertrán and Hernández, who have previously investigated the solid-state synthesis of imidazolates bv reaction of free imidazole with metal oxides and discovered that the reaction only works for d^{10} cations;[26,27] pre-coordination of the ligand (as in the present work) therefore expands the range of systems to which the solid-state methodology can be applied, and supports their hypothesis that the first stage in the reaction is coordination of the imine nitrogen to the metal rather than deprotonation of the pyrrolic NH group.

Overall it is clear that solid state methods are potent and rather general routes to crystalline coordination complexes of a variety of forms, including polymeric MOF-type materials, and it is remarkable that the transport (of metals and ligands and ions) that needs to occur in achieving crystallisation of phase pure materials is so readily achieved in these systems. It would seem that much of the chemistry that occurs is close to that in solution, and therefore that conventional wisdom learned from coordination chemistry (for example as regards the lability of metal–ligand bonds and the reactivity of metals towards aerial oxidation) remains useful in these solid-solid and solid-gas reactivity studies. That said there are clear differences in behaviour - it is sometimes possible to isolate species in the solid state that cannot be made from solution - and so there is complementarity of application.

Our aim in performing this and previous[3] work was to widen the range of coordination compounds and salts that can be synthesised simply by grinding together appropriate starting materials. Whilst many of the synthetic transformations reported herein generate the products pure and in quantitative yield, others form the coordination compounds, imidazolates or pyrazolates as mixtures with potassium chloride. We have not attempted further purification of these mixtures as we have deliberately limited the scope of this paper to solid-state chemistry and methods of analysis, but in many cases simply washing the mixture with water will remove the KCl by-product.

Experimental

Synthesis

Samples were ground by hand using an agate mortar and pestle in air to give solids with the expected elemental analysis and X-ray powder diffraction patterns. The time required in grinding (typically 20–30 s) is typically only that necessary to be sure that all the reagents have been thoroughly mixed. All other reagents were purchased from Aldrich, Strem or Lancaster and used without further purification. Product samples were dried in *vacuo* or in the oven at 50 °C.

$[H_2pz]Cl$. A vial containing 25 mg of pyrazole was placed in a sealed jar. This was flushed with dry nitrogen gas to evacuate any moisture present and then filled with dry HCl gas. The white crystals instantaneously became a creamy powder. Microanalytical data (%) Calculated for $C_3H_5N_2Cl$: C, 34.47; H, 4.82; N, 26.80. Found C, 34.58; H, 4.76; N, 27.11.

$[H_2pz][CoCl_4]$ (1). *Mechanochemical synthesis*: 129 mg (1 mmol) of anhydrous $CoCl_2$ and 209 mg (2 mmol) of pyrazolium chloride were ground in an agate mortar, forming a blue paste, which dries *in vacuo* into a crystalline powder of $[C_3H_5N_2]_2[CoCl_4]$.

Microanalytical data (%), Calculated for $[C_3H_5N_2]_2[CoCl_4]$: C, 21.26; H, 2.97; N, 16.53. Found C, 20.89; H, 2.99; N, 16.93. *HCl gas absorption*: A vial containing 25 mg of $[CoCl_2(Hpz)_2]$ (**2**) was placed in a sealed jar. This was flushed with dry nitrogen gas to displace any moisture present and then filled with dry HCl gas. The pink powder changed to blue after one hour of exposure. Microanalytical data (%) Calculated for $[C_3H_5N_2]_2[CoCl_4]$: C, 21.26; H, 2.97; N, 16.53. Found C, 21.06; H, 2.94; N, 16.23. *Solution synthesis*: 136 mg (2 mmol) of pyrazole was dissolved in conc. HCl (5 ml) and $CoCl_2\cdot 6H_2O$ (238 mg, 1 mmol) was added. The solution was allowed to evaporate at room temperature and, after a few days, blue crystals were obtained. Microanalytical data (%) calculated for $[C_3H_5N_2]_2[CoCl_4]$: C, 21.26; H, 2.97; N, 16.53. Found C, 20.95; H, 3.07; N, 16.12.

$[CoCl_2(Hpz)_2]$ (2). *Mechanochemical synthesis*: 129 mg (1 mmol) of anhydrous $CoCl_2$ and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of a pink polycrystalline powder. Microanalytical data (%) calculated for $[(C_3H_4N_2)_2CoCl_2]$: C, 25.37; H, 3.55; N, 19.73. Found C, 24.79; H, 3.20; N, 19.82. *Reaction of pyrazolium chloride with* (*i*) *$Co(OH)_2$*: 209 mg (2 mmol) of pyrazolium chloride was ground with 93 mg (1 mmol) of $Co(OH)_2$ forming $[\{CoCl_2(Hpz)_2\}_n]$ as a pink powder, which was dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CoCl_2]$: C, 13.09; H, 3.03; N, 21.06. Found C, 26.83; H, 3.22; N, 20.98. (*ii*) *$CoCO_3$*: 209 mg (2 mmol) of pyrazolium chloride was forcefully ground with 119 mg (1 mmol) of $CoCO_3$ forming $[\{CoCl_2(Hpz)_2\}_n]$ as a pink powder, which was dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CoCl_2]$: C, 13.09; H, 3.03; N, 21.06. Found C, 13.04; H, 3.08; N, 21.30. *Mechanochemical elimination with*: (*i*) *KOH*: 34 mg (0.1 mmol) of **1** was ground with 11 mg (0.2 mmol) of KOH resulting in the formation of a pink powder. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CoCl_2]$ + 2KCl: C, 17.36; H, 1.94; N, 13.50. Found C, 17.19; H, 2.12; N, 13.69. (*ii*) *K_2CO_3*: 34 mg (0.1 mmol) of **1** was ground with 14 mg (0.1 mmol) of K_2CO_3 resulting in the formation of a pink powder. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CoCl_2]$ + 2KCl: C, 17.36; H, 1.94; N, 13.50. Found C, 17.67; H, 2.15; N, 13.07. *Crystal synthesis*: A small amount of the pink powder of **2** was dissolved in acetonitrile and the solution allowed to evaporate slowly at room temperature. After a few days pink crystals of the title compound were obtained.

$[H_2pz][ZnCl_4]$ (3). *Mechanochemical synthesis*: 136 mg (1 mmol) of $ZnCl_2$ and 209 mg (2 mmol) of pyrazolium chloride were ground in an agate mortar forming **3** as a white crystalline powder which was then dried *in vacuo*. Microanalytical data (%), Calculated for $[C_3H_5N_2]_2[ZnCl_4]$: C, 20.87; H, 2.92; N, 16.22. Found C, 21.06; H, 2.96; N, 16.48. *HCl gas absorption*: A vial containing 44 mg of $[(C_3H_4N_2)_2ZnCl_2]$ **4** was placed in a sealed jar, which was flushed with nitrogen gas and then filled with dry HCl gas for 8 h. Microanalytical data (%), Calculated for $[C_3H_5N_2]_2[ZnCl_4]$: C, 20.87; H, 2.92; N, 16.22. Found C, 20.85; H, 3.02; N, 15.87. *Solution synthesis*: 136 mg (2 mmol) of pyrazole was dissolved in conc. HCl (5 ml) and $ZnCl_2$ (136 mg, 1 mmol) was added. The solution was allowed to evaporate at room temperature, and after a few days colourless crystals were obtained. Microanalytical data (%), Calculated for $[C_3H_5N_2]_2[ZnCl_4]$: C, 20.87; H, 2.92; N, 16.22. Found C, 20.42; H, 2.78; N, 16.03.

$[ZnCl_2(Hpz)_2]$ (4). *Mechanochemical synthesis*: 136 mg (2 mmol) of pyrazole and 136 mg (1 mmol) of $ZnCl_2$ were forcefully ground in an agate mortar, resulting in the formation of a white polycrystalline powder. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2ZnCl_2]$: C, 26.45; H, 2.96; N, 20.56. Found C, 26.92; H, 3.09; N, 20.97. *Mechanochemical elimination* (*KOH*): 70 mg (0.2 mmol) of $[C_3H_5N_2]_2[ZnCl_4]$ was ground with 22 mg (0.4 mmol) of KOH in an agate mortar. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2ZnCl_2]$ + 2KCl: C, 17.10; H, 1.91; N, 13.29. Found C, 16.65; H, 1.90; N, 13.33. *Mechanochemical elimination* (*K_2CO_3*): 35 mg (0.1 mmol) of $[C_3H_5N_2]_2[ZnCl_4]$ was ground with 14 mg (0.1 mmol) of K_2CO_3 in an agate mortar. The reaction proceeded with no apparent colour change. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2ZnCl_2]$ + 2KCl: C, 17.10; H, 1.91; N, 13.29. Found C, 17.55; H, 2.09; N, 13.49. *Reaction of pyrazolium chloride with $3Zn(OH)_2\cdot 2ZnCO_3$*: 500 mg (5 mmol) of pyrazolium chloride was ground with 275 mg (0.5 mmol) of $3Zn(OH)_2\cdot 2ZnCO_3$. The title compound was formed as a white powder following a mild effervescence. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2ZnCl_2]$: C, 26.45; H, 2.96; N, 20.56. Found C, 26.58; H, 2.97; N, 20.76. *Crystal synthesis*: A small amount of the white powder of **4** was dissolved in acetonitrile and the solution allowed to evaporate slowly at room temperature. After a few days plate-like colourless crystals of the title compound were obtained.

$[H_2pz][CuCl_4]$ (5). *Mechanochemical synthesis*: 134 mg (1 mmol) of anhydrous $CuCl_2$ and 209 mg (2 mmol) of pyrazolium chloride were ground in an agate mortar, forming a dark brown powder of $[C_3H_5N_2]_2[CuCl_4]$. Microanalytical data (%), Calculated for $[C_3H_5N_2]_2[CuCl_4]$: C, 20.98; H, 2.93; N, 16.31. Found C, 20.89; H, 2.82; N, 16.33. *HCl gas absorption*: A vial containing 25 mg of **6** was placed in a jar. This was flushed with dry nitrogen gas to displace any moisture present and then filled with dry HCl gas. The green powder changed to brown after a few minutes of exposure. Microanalytical data (%) Calculated for $[C_3H_5N_2]_2[CuCl_4]$: C, 20.98; H, 2.93; N, 16.31. Found C, 21.31; H, 3.41; N, 16.56.

$[CuCl_2(Hpz)_2]$ (6). *Mechanochemical synthesis*: 134 mg (1 mmol) of anhydrous $CuCl_2$ and 136 mg (2 mmol) of pyrazole were forcefully ground in an agate mortar, resulting in the formation of $[\{CuCl_2(H_2pz)_2\}_n]$ **6** as a green polycrystalline powder, which was dried *in vacuo*. The same product was obtained when $CuCl_2\cdot 2H_2O$ was ground with two molar equivalents of pyrazole. Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CuCl_2]$: C, 26.63; H, 2.98; N, 20.70. Found C, 26.76; H, 3.05; N, 21.02. *Mechanochemical elimination* (*KOH*): 34 mg (0.1 mmol) of **5** were forcefully ground with 11 mg (0.2 mmol) of KOH causing a colour change from dark brown to green. Excess water was removed *in vacuo*. Microanalytical data (%) for $[(C_3H_4N_2)_2CuCl_2]$ + 2KCl, Calculated: C, 17.17; H, 1.92; N, 13.35. Found C, 17.58; H, 2.32; N, 13.73. *Mechanochemical elimination* (*K_2CO_3*): 34 mg (0.1 mmol) of $[C_3H_5N_2]_2[CuCl_4]$ was forcefully ground with 14 mg (0.1 mmol) of K_2CO_3 causing a colour change from dark brown to green. Excess water was removed *in vacuo*. Microanalytical data (%) for $[(C_3H_4N_2)_2CuCl_2]$ + 2KCl, Calculated: C, 17.17; H, 1.92; N, 13.35. Found C, 17.51; H, 2.25; N, 13.75. *Reaction of pyrazolium chloride with $Cu(OH)_2\cdot CuCO_3$*: 418 mg (4 mmol) of pyrazolium chloride was ground with 221 mg (1 mmol) of $Cu(OH)_2\cdot CuCO_3$, forming a green powder of $[\{CuCl_2(H_2pz)_2\}_n]$, which was dried *in vacuo*.

Microanalytical data (%), Calculated for $[(C_3H_4N_2)_2CuCl_2]$: C, 26.63; H, 2.98; N, 20.70. Found C, 27.06; H, 3.06; N, 21.17.

$[Ni(pz)_2]_n$ (7). *Mechanochemical elimination*: 266 mg (1 mmol) of $[NiCl_2(Hpz)_2]$ was forcefully ground with 112 mg (2 mmol) of KOH in an agate mortar, causing a colour change from pale green to yellow. The yellow polycrystalline powder of $[(C_3H_3N_2)_2Ni]$ + 2KCl was then dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Ni]$ + 2KCl: C, 21.08; H, 1.77; N, 16.39. Found C, 21.45; H, 2.28; N, 17.15.

$[Cu(pz)_2]_n$ (8). *Mechanochemical elimination*: 271 mg (1 mmol) of $[CuCl_2(Hpz)_2]$ **6** was forcefully ground in an agate mortar with 112 mg (2 mmol) of KOH. An immediate colour change from green to beige was observed and the powder was dried in *vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Cu]$ + 2KCl: C, 20.78; H, 1.74; N, 16.16. Found C, 20.35; H, 2.38; N, 16.17.

$[Zn(pz)_2]_n$ (9). *Mechanochemical elimination* (*internal base*): 549 mg (1 mmol) of $3Zn(OH)_2{\cdot}2ZnCO_3$ and 68.08 mg (10 mmol) of pyrazole were ground in an agate mortar, forming a white polycrystalline powder, which was dried in *vacuo* to remove excess water formed. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Zn]$: C, 36.12; H, 3.03; N, 28.08. Found C, 36.10; H, 3.15; N, 28.28. *Mechanochemical elimination* (*external base*): (i) *Using KOH*: 272 mg (1 mmol) of $[ZnCl_2(Hpz)_2]$ **4** was forcefully ground with 112 mg (2 mmol) of KOH in an agate mortar, forming a white powder of $[Zn(pz)_2]$ + 2KCl. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Zn]$ + 2KCl: C, 20.67; H, 1.73; N, 16.06. Found C, 20.56; H, 1.99; N, 16.18. (ii) *Using t-BuOK*: 272 mg (1 mmol) of $[ZnCl_2(Hpz)_2]$ **4** was forcefully ground with 224 mg (2 mmol) of t-BuOK in an agate mortar, forming a white powder of $[Zn(pz)_2]$ + 2KCl and t-butanol (evaporated *in vacuo*). Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Zn]$ + 2KCl: C, 20.67; H, 1.73; N, 16.06. Found C, 20.47; H, 2.07; N, 15.97.

$[Ni(im)_2]_n$ (11). *Mechanochemical elimination*: 266 mg (1 mmol) of $[NiCl_2(Him)_2]$ was forcefully ground with 112 mg (2 mmol) of KOH in an agate mortar, causing a colour change from pale green to yellow. The yellow polycrystalline powder of $[(C_3H_3N_2)_2Ni]$ + 2KCl was washed with water to remove KCl and then dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Ni]$: C, 27.12; H, 3.03; N, 21.08. Found C, 27.18; H, 3.24; N, 21.17.

$[Cu(im)_2]_n$ (12). *Mechanochemical elimination*: 271 mg (1 mmol) of $[CuCl_2(Him)_2]^2$ was forcefully ground with 112 mg (2 mmol) of KOH in an agate mortar. The reaction proceeded with a colour change from light green into a dark green polycrystalline powder of $[(C_3H_3N_2)_2Cu]$ + 2KCl, which was dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Cu]$ + 2KCl: C, 20.78; H, 1.74; N, 16.16. Found C, 20.69; H, 2.01; N, 15.96.

$[Zn(im)_2]_n$ (13). *Mechanochemical elimination*: 272 mg (1 mmol) of $[ZnCl_2(Him)_2]^2$ was forcefully ground with 112 mg (2 mmol) of KOH in an agate mortar. The reaction proceeded with no significant colour change, forming a white polycrystalline powder of $[(C_3H_3N_2)_2Zn]$ + 2KCl, which was dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Zn]$ + 2KCl: C, 20.67; H, 1.73; N, 16.06. Found C, 21.15; H, 2.00; N, 16.56.

$[Co(im)_2]_n$ (14). *Mechanochemical elimination*: 266 mg (1 mmol) of $[CoCl_2(Him)_2]^2$ was forcefully ground with 112 mg (2 mmol) of KOH. The reaction proceeded with a significant colour change, from blue to purple polycrystalline powder of $[(C_3H_3N_2)_2Co]$ + 2KCl, which was washed with water to remove KCl and then dried *in vacuo*. Microanalytical data (%), Calculated for $[(C_3H_3N_2)_2Co]$ + H_2O: C, 34.14; H, 3.03; N, 26.54. Found C, 34.46; H, 3.29; N, 26.18. Note: The crystal structure does not contain water but the elemental analysis shows the apparent presence of one water molecule.

X-Ray single crystal analysis

Single crystal X-ray data (see Table 1) were collected at 100 K on a Bruker APEX diffractometer using Mo-Kα X-radiation and at 293 K for the room temperature versions of the $[H_2pz]_2[MCl_4]$ salts (M = Co, **1**; Zn, **3**) and for $[ZnCl_2(Hpz)_2]$ **4**. Data were corrected for absorption using empirical methods (SADABS)[28] based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. Crystal structures were solved and refined against all F^2 values using the SHELXTL suite of programs.[29] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Extinction corrections for **1** (RT) and **3** (LT) were applied using the *Zachariasen* method.[30]

X-Ray powder diffraction analysis

All crystalline phases were analysed at room temperature by powder X-ray diffraction on a Bruker D8 diffractometer using Cu-Kα X-radiation. Unless stated in the text the experimental patterns matched those calculated on the basis of the relevant single crystal structure determination at room temperature indicating phase purity, excepting the powder patterns of the products of mechanochemical eliminations (reactions with KOH, K_2CO_3 or t-BuOK) which show an extra peak at $2\theta = 28°$ due to the presence of KCl.

Thermogravimetric analysis

Thermal analysis of the samples was carried out on a TA Q500 V6.4 Build 193 instrument under N_2 flow over the temperature range 20–700 °C at variable (high resolution mode) heating rate and analyzed by TA Universal analysis 2000 software, or on a Perkin-Elmer STA 6000 simultaneous thermal analyzer between 50 and 500 °C at the heating rate of 5 °C min^{-1}. Data was analyzed using Pyris thermal analysis software.

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References

1 C. J. Adams, H. M. Colquhoun, P. C. Crawford, M. Lusi and A. G. Orpen, *Angew. Chem., Int. Ed.*, 2007, **46**, 1124.
2 C. J. Adams, M. A. Kurawa, M. Lusi and A. G. Orpen, *CrystEngComm*, 2008, **10**, 1790.

3 C. J. Adams, M. F. Haddow, R. J. I. Hughes, M. A. Kurawa and A. G. Orpen, *Dalton Trans.*, 2010, **39**, 3714.
4 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
5 J. Reedijk, *Heterocyclic Nitrogen-donor Ligands in Comprehensive Coordination Chemistry: the synthesis, reactions, properties & applications of coordination compounds*, Pergamon Press, Oxford, 1987.
6 M. A. Halcrow, *Dalton Trans.*, 2009, 2059.
7 N. Masciocchi, G. A. Ardizzoia, S. Brenna, G. LaMonica, A. Maspero, S. Galli and A. Sironi, *Inorg. Chem.*, 2002, **41**, 6080.
8 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
9 M. C. Etter, J. C. Macdonald and J. Bernstein, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1990, **46**, 256.
10 P. B. da Silva, R. C. G. Frem, A. V. G. Netto, A. E. Mauro, J. G. Ferreira and R. H. A. Santos, *Inorg. Chem. Commun.*, 2006, **9**, 235.
11 S. Gorter, A. D. Vaningen and G. C. Verschoo, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1974, **B 30**, 1867.
12 R. J. Flook, H. C. Freeman, F. Huq and J. M. Rosalky, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1973, **B 29**, 903.
13 G. Bhosekar, I. Jess, Z. Havlas and C. Näther, *Cryst. Growth Des.*, 2007, **7**, 2627.
14 U. Casellato and R. Graziani, *Z. Kristallogr. -New Cryst. Struct.*, 1998, **213**, 363.
15 N. Masciocchi, G. A. Ardizzoia, A. Maspero, G. LaMonica and A. Sironi, *Inorg. Chem.*, 1999, **38**, 3657.
16 A. Cingolani, S. Galli, N. Masciocchi, L. Pandolfo, C. Pettinari and A. Sironi, *J. Am. Chem. Soc.*, 2005, **127**, 6144.
17 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186.
18 N. Masciocchi, F. Castelli, P. M. Forster, M. M. Tafoya and A. K. Cheetham, *Inorg. Chem.*, 2003, **42**, 6147.
19 N. Masciocchi, S. Bruni, E. Cariati, F. Cariati, S. Galli and A. Sironi, *Inorg. Chem.*, 2001, **40**, 5897.
20 R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem.*, 1980, **464**, 187.
21 Y.-Q. Tian, Y.-M. Zhao, Z.-X. Chen, G.-N. Zhang, L.-H. Weng and D.-Y. Zhao, *Chem.–Eur. J.*, 2007, **13**, 4146.
22 Y.-Q. Tian, C.-X. Cai, X.-M. Ren, C.-Y. Duan, Y. Xu, S. Gao and X.-Z. You, *Chem.–Eur. J.*, 2003, **9**, 5673.
23 Y.-Q. Tian, Z.-X. Chen, L.-H. Weng, H.-B. Guo, S. Gao and D. Y. Zhao, *Inorg. Chem.*, 2004, **43**, 4631.
24 C. J. Adams, P. C. Crawford, A. G. Orpen, T. J. Podesta and B. Salt, *Chem. Commun.*, 2005, 2457.
25 G. M. Espallargas, L. Brammer, J. van de Streek, K. Shankland, A. J. Florence and H. Adams, *J. Am. Chem. Soc.*, 2006, **128**, 9584.
26 J. F. Fernández-Bertrán, M. P. Hernández, E. Reguera, H. Yee-Madeira, J. Rodriguez, A. Paneque and J. C. Llopiz, *J. Phys. Chem. Solids*, 2006, **67**, 1612.
27 J. Fernández-Bertrán, L. Castellanos-Serra, H. Yee-Madeira and E. Reguera, *J. Solid State Chem.*, 1999, **147**, 561.
28 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
29 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
30 S. R. Hall, F. H. Allen and I. D. Brown, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1991, **47**, 655.