Crystal Synthesis

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Solid-State Interconversions of Coordination Networks and Hydrogen-Bonded Salts

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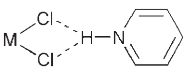
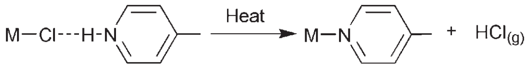
Much of modern materials science is underpinned by the ability to prepare crystalline phases of transition-metal compounds. Most such solids have been prepared by solution methods (e.g. for coordination framework materials[1] and salts of complex ions[2]) or by high-temperature (ceramic) methods for ionic solids (of monoatomic ions, oxides, etc.).[3] We report herein a range of modest-temperature, solid-state methods for the preparation of crystalline metal complexes in which the transformations between phases are achieved by chemical and mechanochemical procedures without the use of solutions. Such methods have been cited as providing "green" approaches to crystalline materials by minimizing solvent use, at least in this stage of the synthesis.[4]

We have developed and applied a strategy for crystal synthesis based on molecular tectonics using charged building blocks (tectons).[5] In this approach, the crystalline product salts contain complex ions—typically anionic metal complexes and organic cations. The peripheral functional groups of the component tectons are chosen to allow control of their supramolecular interactions; in particular the ligands of complexes are hydrogen-bond acceptors such as halides, and the cations are protonated nitrogen bases such as pyridines. The resultant pyridinium perchlorometalate crystal structures therefore contain NH⋯Cl-M interactions in well-defined arrangements such as **A**.



A

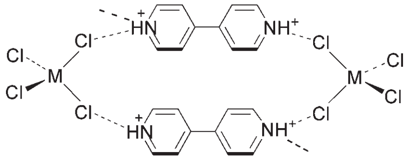
We have reported the solid-state reactivity of such phases and shown that thermally induced dehydrochlorination of the 4-picolinium salts of platinum(II) and palladium(II) tetrachloride dianions leads to the formation of 4-picoline coordination complexes (Scheme 1).[6]



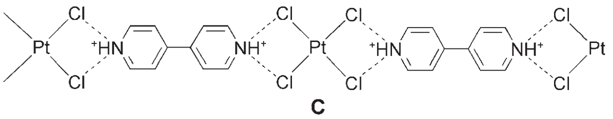
Scheme 1. Dehydrochlorination of a chlorometalate pyridinium salt to afford a metal pyridine complex.

Herein we show that: 1) this approach can be applied to prepare crystalline coordination networks of the ubiquitous 4,4′-bipyridine (4,4′-bipy) ligand, 2) in some circumstances mechanochemical dehydrochlorination and direct mechanochemical approaches may also be used to prepare these phases, and 3) hydrogen-bonded salt phases may be prepared either by chemical treatment of the coordination networks or by mechanochemical means to give high yields of products and in one case afford access to a phase not available by solution methods.

As noted above, the preparation of coordination networks (also termed metal–organic frameworks or coordination polymers) has usually been achieved by solution (often solvothermal) chemistry.[1] Many coordination networks contain transition-metal ions such as Co^{II} or Zn^{II} bridged by 4,4′-bipyridine ligands (ca. 250 with Co or Zn and over 800 with transition metals published to date) and have anionic coligands. We therefore sought to widen the range of synthetic methods offering access to such archetypal coordination networks by attempting dehydrochlorination of the 4,4′-bipyridinium salts of $[CoCl_4]^{2-}$, $[ZnCl_4]^{2-}$, and $[PtCl_4]^{2-}$ (**1**, **2**, and **3**, respectively). The salts were prepared from solution by literature methods.[5] The crystal structures of the cobalt and zinc salts are isomorphous (**B**), while the platinum salt **3** has the ribbon polymer structure **C**.[5]



B



C

Thermogravimetric analysis (TGA) of the salts $[4,4'\text{-}H_2bipy][MCl_4]$ (M = Co **1**, Zn **2**, Pt **3**) shows the loss of two equivalents of HCl in all three cases, with the mass losses centered at 220, 321, and 323 °C, respectively. Bulk products of this thermal process were prepared by heating samples of **1**, **2**, and **3** under N_2 for approximately 3 h at 250, 300, and 300 °C, respectively, to produce phases **4**, **5**, and **6**, respectively, in quantitative yield. The products were characterized by elemental analysis and X-ray powder diffraction.

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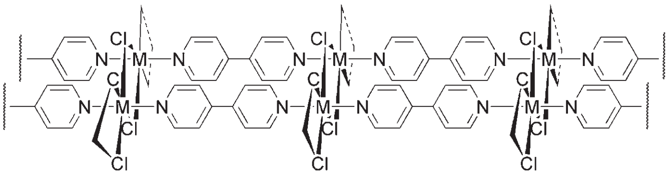
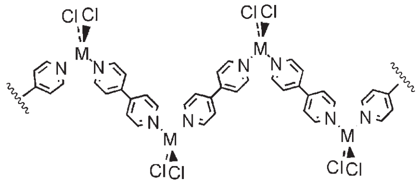
Phases **4** and **5** were readily identified by their X-ray powder patterns, which confirmed them to be the known coordination networks of composition [{MCl_2(4,4′-bipy)}$_n$]. The cobalt(II) compound **4**[7] has a two-dimensional network of form **D** in which octahedral cobalt ions are bridged by two pairs of *trans* chloride ligands to form chains, which are in turn bridged by 4,4′-bipy ligands to form neutral layers. Zinc compound **5** is known in three polymorphic forms, one of which has a structure similar to that of **4**. The other two polymorphs (one monoclinic and the other orthorhombic), which are formed concomitantly in the solution-based synthesis of **5**, have tetrahedral zinc centers (each with two terminal chlorides) linked by bridging 4,4′-bipy ligands into zig-zag polymers of form **E**.[8] Only the orthorhombic form results from our procedure. This selectivity is notable in view of the interconversion between polymorphs of **5** observed by Hu and Englert.



D



E

Phase **6** was less highly crystalline (Figure 1) and its structure was consequently less easily assigned. Its elemental analysis and IR spectrum were consistent with an empirical formula of [$PtCl_2$(4,4′-bipy)]. The powder pattern is, however, clearly not the same as those of **4** or **5**. Rather, it is similar to that of [{*trans*-$CuBr_2$(4,4′-bipy)}$_n$].[9] The structure of phase **6** was therefore modeled by using the unit-cell dimensions of the copper(II) bromide analogue, which has a chain structure, as a starting point, with two {*trans*-$PtCl_2$(4,4′-bipy)}$_n$ chains passing through this cell. Minimization of this model with the use of the Cerius2 universal force field led to the final structure shown in Figure 2, in which the bipyridyl rings are coplanar and are rotated by 54° from the Cl-Pt-Cl axis. The experimental and simulated powder diffraction patterns are shown in Figure 1. A good fit was obtained for the positions of the main reflections, but discrepancies in the intensities remain. These discrepancies might result from preferred crystallite orientation and anisotropic particle broadening. It would therefore appear that **6** is the [{*trans*-$PtCl_2$(4,4′-bipy)}$_n$] polymer (**F**) that might be anticipated from the dehydrochlorination of [4,4′-H_2bipy][$PtCl_4$] in a manner analogous to that noted above for [4-picolinium]$_2$[MCl_4]

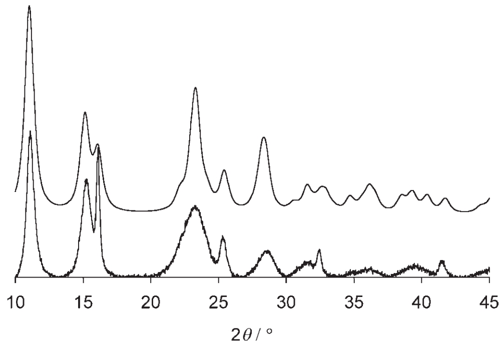
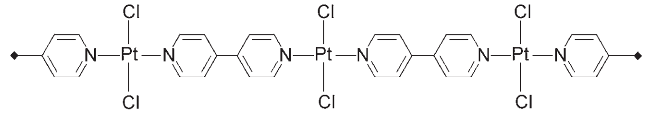


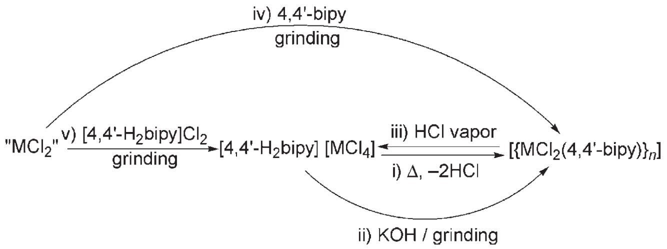
Figure 1. Powder diffraction pattern of *trans*-[{$PtCl_2$(4,4′-bipy)}$_n$] (**6**) (calculated, with full full width at half maximum set to 0.8°, upper; observed, lower).

Figure 2. Computed geometry of *trans*-[{$PtCl_2$(4,4′-bipy)}$_n$] (**6**).



F

Chemical dehydrochlorination of **1** and **2** may also be achieved readily by mechanochemical means (Scheme 2ii). Grinding of **1** with (nominally dry) KOH in air led to a color change from blue to turquoise over a period of minutes. Powder X-ray diffraction of the crude products indicated that crystalline **4** and KCl had been formed. Dehydrochlorination (without significant color change) was similarly achieved by grinding **2** with KOH to form a mixture of **5** and KCl. The



Scheme 2. Interconversion of crystalline phases (M = Co, Zn, Pt, or Fe): i) thermal dehydrochlorination; ii) grinding with KOH; iii) exposure to HCl vapor; iv) grinding with 4,4′-bipy (with the addition of one drop of solvent in some cases); v) grinding with [4,4′-H_2bipy]Cl_2.

reverse reaction, in which hydrogen-bonded salt arrays are formed by exposure of coordination networks to HCl, may be readily achieved (Scheme 2 iii). Thus, exposure of a crystalline powder sample of the turquoise cobalt coordination network **4** to HCl vapor (in a sealed vessel) led to the quantitative (as characterized by X-ray powder diffraction) formation of the blue salt **1**.

Similarly complete conversion of zinc species **5** into **2** is achieved in minutes. In contrast, the conversion of **6** into **3** is negligible even over a period of days. The reactivity of molecular crystals towards gases is known (see, for example, reference [10]), and Braga, Grepioni and co-workers have noted the ability of organometallic crystals to absorb HCl reversibly, albeit without affecting the metal coordination sphere.[10a,c] Very recently, Brammer noted the reversible absorption of HCl by Cu^{II} coordination complexes.[10d]

The cobalt and zinc coordination networks **4** and **5** may be prepared by a more direct route (Scheme 2 iv). Grinding of anhydrous $CoCl_2$ with 4,4′-bipy in air did not readily afford **4**. However, grinding after the addition of a drop of ethanol yielded rapid conversion of the lilac mixture into the characteristically blue phase **4**. Such solvent-drop grinding or kneading[11,12] procedures have been used in industry and in recent studies of organic,[11] organometallic,[12] and coordination network solids.[13] Phase **5** was also prepared by a similar procedure (not requiring solvent addition) from $ZnCl_2$ and 4,4′-bipy. The success of this latter route prompted us to attempt the direct preparation of salts **1**–**3** by grinding metal dichloride precursors with [4,4′-H_2bipy]Cl_2. (Scheme 2 v). Kneading of anhydrous $CoCl_2$ with [4,4′-H_2bipy]Cl_2 in air rapidly afforded [4,4′-H_2bipy][$CoCl_4$] (**1**) (as did dry grinding of $CoCl_2 \cdot 6H_2O$), as characterized by X-ray powder diffraction and microanalysis. Colorless [4,4′-H_2bipy][$ZnCl_4$] (**2**) was prepared in a similar way, again without solvent addition. However, grinding $PtCl_2$ with [4,4′-H_2bipy]Cl_2 in air with or without the addition of solvents (including water, ethanol, and conc. HCl) did not lead to reaction or the formation of any phases other than the starting materials.

We sought to exploit these new methods to prepare phases not accessible by solution methods. Notably, when $FeCl_2$ was treated in aqueous solution in air with HCl and 4,4′-bipy, a range of products resulted and [4,4′-H_2bipy][$FeCl_4$] (**7**) was not obtained.[14] The layer coordination network [{$FeCl_2$(4,4′-bipy)}$_n$] (**8**) is readily accessible by solution methods, and also by method (iv) in Scheme 2. With **8** in hand, **7** may then be prepared by exposure of **8** to HCl vapor. Remarkably, anhydrous [4,4′-H_2bipy][$FeCl_4$] (**7**) can then be recrystallized from aqueous solution. Its structure determination (Figure 3) confirms that **7** is isomorphous with **1** and **2**. Salt **7** can also be prepared by mechanochemical treatment of $FeCl_2 \cdot 4H_2O$ with [4,4′-H_2bipy]Cl_2.

In conclusion we note:

i) That the hydrogen-bonded complex salts [4,4′-H_2bipy][MCl_4] (M = Co **1**, Zn **2**, and Pt **3**) can be readily transformed into crystalline coordination networks [{MCl_2(4,4′-bipy)}$_n$] (M = Co **4**, Zn **5**, and Pt **6**) by thermal dehydrochlorination. For zinc species **5**, one of three known polymorphs is formed selectively.

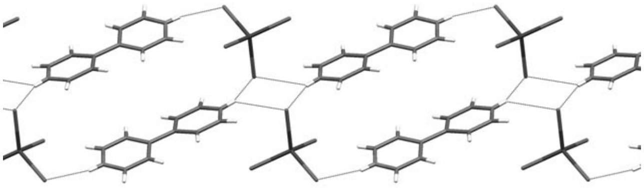


Figure 3. Crystal structure of [4,4′-H_2bipy][$FeCl_4$] (**7**).

ii) That this process may be reversed by exposure of the coordination networks to HCl vapor for **4**, **5**, and **8**, but not for **6**.

iii) That the coordination networks [{MCl_2(4,4′-bipy)}$_n$] (M = Co **4**, Zn **5**, and Fe **8**, but not Pt **6**) can be prepared by grinding of "MCl_2" with 4,4′-bipy.

iv) The availability of a wide range of "crystal-engineered" coordination networks formed by nitrogen ligands and of salts of anionic metal halide complexes of (poly)pyridinium and other protonated nitrogen bases offers the prospect of widely applying the hydrochlorination reaction and its reverse reaction, dehydrochlorination, under the control of crystalline environments.

v) Preliminary indications of the scope and limitations of these reactions are that solids containing less labile metals (herein platinum) are less likely to undergo reactions involving metal–ligand bond cleavage. The potential for structural control of reactivity is still to be explored. For example, the addition of HCl to different coordination network structures [{MCl_2(4,4′-bipy)}$_n$] (M = Co **4**, Zn **5**) gives rise to isomorphous salts [4,4′-H_2bipy][MCl_4] (M = Co **1**, Zn **2**), and, for M = Zn, the reverse reaction, thermal dehydrochlorination, is selective for the *Pnma* polymorph of **5** and for M = Co, Fe a different (layer) network is formed.

vi) The reactions reported herein would seem to be driven primarily by thermodynamic factors at both the molecular and extended crystalline array level (e.g. by formation and loss of HCl, by formation of metal–ligand bonds, formation of supramolecular interactions such as those in the hydrogen-bonded arrays in **1**–**3**, or by crystallization of KCl or of phases **1**–**8**).

vii) The remarkable facility of these systems—including those that are salts—for crystallization without the involvement of macroscopic solutions. The importance of the small (catalytic) amounts of solvent seems clear. In this work these amounts are sometimes stoichiometric—when water is present as a ligand coordinated to the metal or occluded in the reagent crystal structure—whereas on other occasions the solvent is added but in amounts insufficient to lead to macroscopic dissolution. We cannot rule out the importance of adventitious water from the atmosphere in facilitating apparently "dry" processes.

The planned synthesis of crystals—termed crystal engineering or synthetic crystallography—is a major goal of modern chemistry. Its successful achievement requires the development of a broad spectrum of methods for the preparation of crystalline phases. It is clear for molecular solids, and now also for salts of complex ions, that crystalline phases can be readily interconverted with minimal or no addition of solvent being required to facilitate the crystallization process.

Experimental Section

Crystal synthesis: Syntheses were carried out in air using standard glassware. The salts [4,4′-H_2bipy]Cl_2, [4,4′-H_2bipy][$CoCl_4$] (**1**), [4,4′-H_2bipy][$ZnCl_4$] (**2**), and [4,4′-H_2bipy][$PtCl_4$] (**3**), and coordination network solids [{$CoCl_2$(4,4′-bipy)}$_n$] (**4**), [{$ZnCl_2$(4,4′-bipy)}$_n$] (**5**), and [{$FeCl_2$(4,4′-bipy)}$_n$] (**8**) were prepared from solution by literature methods. Further details of these and other syntheses and analyses noted below are given in the Supporting Information.

1: Mechanochemical synthesis: 4,4′-[H_2bipy]Cl_2 (229 mg, 1 mmol) and $CoCl_2$ (129 mg, 1 mmol) were ground in an agate mortar for 20–30 seconds with the addition of a drop of water. The lilac-colored mixture became a turquoise paste, which on drying became a blue powder. Vapor absorption: A vial containing [{$CoCl_2$(4,4′-bipy)}$_n$] (20 mg) was placed in a sealed jar containing concentrated aqueous HCl. In one hour, the light turquoise powder became blue.

4: Mechanochemical synthesis: 4,4′-bipy (156 mg, 1 mmol) and $CoCl_2$ (129 mg, 1 mmol) were ground in an agate mortar with a drop of ethanol. The initially lilac-colored mixture became a turquoise paste, which on drying became a turquoise powder. The same product was obtained by forcefully grinding $CoCl_2{\cdot}6H_2O$ with 4,4′-bipy. Thermal elimination: [4,4′-H_2bipy][$CoCl_4$] (36 mg, 0.1 mmol) was heated to 230 °C in a round-bottomed flask for two hours, with stirring. The blue powder became light turquoise. Mechanochemical elimination reaction: [4,4′-H_2bipy][$CoCl_4$] (36 mg, 0.1 mmol) was ground with KOH (11 mg, 0.2 mmol). Upon grinding, the blue powder became light turquoise (after less than 1 minute). Preparations of **2** and **5–8** were carried out by analogous procedures.

X-ray crystallography: Single-crystal X-ray data for [4,4′-H_2bipy]-[$FeCl_4$] (**7**) were collected at 100 K with a Bruker APEX diffractometer: $C_{10}H_{10}N_2FeCl_2$, $M_r = 355.85$, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.6796(15)$, $b = 19.842(4)$, $c = 9.3816(19)$ Å, $\beta = 108.81(3)°$, $V = 1353.2(5)$ Å^3, $Z = 4$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $\mu = 1.881\ mm^{-1}$, $T = 100$ K, 3091 unique data, $R1 = 0.0426$. CCDC 616410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

X-ray powder diffraction and computational modeling studies: Powder diffraction data were obtained at room temperature by using $Cu_{K\alpha}$ radiation in the Bragg–Brentano mode. Computational modeling studies were carried out by using the Cerius2 package (Accelrys, Cambridge version 3.5, universal force field reparameterized (bond lengths, bond angles, and torsion angles) by reference to the structure of [*trans*-$PtCl_2(Py)_2$][15]). Energy minimization of the crystal within a constrained unit cell gave the model shown in Figure 2: [{*trans*-$PtCl_2$(4,4′-bipy)}$_n$] (**6**), $a = 12.45$, $b = 11.00$, $c = 4.05$ Å, $\beta = 110.0°$, space group $C2/m$, $V = 521$ Å^3, $d_c = 2.69\ g\,cm^{-3}$. Further details are provided in the Supporting Information and with the crystallographic information (.cif) file.

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