Crystallization Behavior of Coordination Polymers. 1. Kinetic and Thermodynamic Features of 1,3-Bis(4-pyridyl)propane/MCl₂ Systems

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ABSTRACT: A series of one-, two-, and three-dimensional (1D, 2D, and 3D) coordination polymers has been crystallized from solution as well as in gelled media, by controlled reaction of the flexible ligand 1,3-bis(4-pyridyl)propane with MCl₂ salts (M = Mn, Fe, Co, Ni, Cu, Cd, Zn). Attention was paid to the role of kinetic and thermodynamic control upon selection of the final products and that can be obtained with different optimized crystallization techniques. It is shown that the correct use of crystallization techniques allows tuning of the metal to ligand ratio and absolute concentrations and, hence, control of the crystallization of metal—organic frameworks, including their solvent-mediated phase transitions.

Introduction

Recent years have witnessed a surge of interest in supramolecular chemistry,¹ and, in particular, there is hope for future technological applications² of coordination polymers, a specific class of supramolecular objects also known as metal—organic frameworks (hereafter MOFs).³,⁴ The intriguing variety of architectures and topologies⁵ exhibited by MOFs are explored in crystal engineering,⁶ as they can reveal interesting properties for opto-electronic⁷ and magnetic⁸ functional materials, molecular sieving,⁹ ion exchange,¹⁰ catalysis¹¹–¹³ as well as stable and highly porous scaffolds¹⁴ for sorption of volatile organic compounds and gas storage.¹⁵–¹⁸ Attempts to build novel and useful coordination networks rely upon almost all metal cations available in the periodic table of elements, that is, transition, post-transition, lanthanide,¹⁹–²¹ and actinide²¹ metals. The counterpart of ligands shows an even wider variety of choices being based on multifunctional organic or inorganic moieties, displaying diversified local stereochemistries supposedly able to force the self-assembling of MOFs to follow a pre-established structural motif as wished by crystal engineers.²²–²⁴ Many structurally relevant MOFs which do have promising properties for key technological applications and high commercial value²⁵ have been synthesized starting from nitrogen-based multifunctional ligands.³,¹⁶c,d,²⁶ Among them, pyridine-based ligands differing in length, flexibility, and conformational freedom produced a variety of supramolecular networks with different metal cations.¹²

While the structural characterization of MOFs by X-ray diffraction is well established, there is no comparable understanding of their solution chemistry, under ambient or solvothermal conditions.²⁷,²⁸ Particularly unclear are the molecular recognition and assembling steps which eventually lead to a coordination polymer. This failure partly stems from the complexity of chemical equilibria involving these polymers which fragment upon solubilization, and whose high molecular weight frameworks arise from mostly unknown solution species,²⁹ apart from a few noteworthy oligomeric entities.³⁰,³¹ Thus, no accurate model for the network formation from solution is presently available; chemical synthesis usually is performed following a buy-and-mix strategy. However, it is also largely acknowledged that the final outcome of reactants mixing can be driven by subtle kinetical and thermodynamical details of the chemical processes. As several authors noticed, supramolecular inorganic coordination frameworks represent a dynamic challenge for structural chemists.³²,³³ Starting from the mother solutions, the overall supramolecular synthesis of MOFs includes molecular recognition and self-assembly of solution species through nucleation of crystalline phases, growth of mature crystals, and possibly phase transitions according to the relative kinetic prevalence and thermodynamic stability. Therefore, solution coordination chemistry is deeply entangled with nucleation and growth mechanisms of MOFs crystals to determine the final products and their properties, through a complicated interplay between kinetics and thermodynamics.

We have previously synthesized coordination polymers with reversible uptake/release of guest solvent molecules, for example, compounds [Cu₃(bpp)₃(SO₄)₄(EGOH)(H₂O)]₄(SO₄)⋅EtOH⋅2.5H₂O⋅34 (bpp = 1,3-bis(4-pyridyl)propane; EtOH = ethanol) and [Cu(bipy)₂(CF₃SO₃)₂]⋅2CH₂Cl₂⋅H₂O.³⁵ (bipy = 4,4′-bipyridyl); both exhibit interesting microporous behavior arising from novel 3D architectures associated with cavities or tunnels, respectively, from which guest molecules can be easily and reversibly removed due to some degree of flexibility³⁶ of the metal—organic framework. Moreover, the self-assembly of polymeric networks from different Ag(I) salts and the flexible ligand 1,3-bis(4-pyridyl)propane (bpp) has been systematically investigated in order to obtain basic information useful for the crystal engineering of coordination frames upon variation of the counterions.³⁷

We have also studied the crystallization of inorganic polymers based on the flexible nitrogen ligand bpp and metal(II) chlorides, trying to improve understanding of the self-assembly...
processes of coordination networks. Reaction of aqueous CuCl₂ with bpp ligand under different conditions afforded a family of coordination polymers with one-, two-, and three-dimensional (1D, 2D, and 3D) polymeric network dimensionalities. A preliminary account on these systems has already been published mainly dealing with the structural features of the Cu(II)/bpp systems and improves the case study of the CuCl₂/bpp system and improves the selection of yields is reported in Table 2S in from gels and the very long times required to reach chemical equilibrium. A selection of yields is reported in Table 2S in from gels and the very long times required to reach chemical equilibrium.

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Synthesis of [Zn(bpp)Cl2] (6Zn). Crystals of polymeric Zn-bpp were grown by liquid–liquid diffusion method using both water and methanol as the solvent for reagents and 1:2 or 1:1 metal–ligand molar ratio (for example: ZnCl2 3.4 mg, 0.025 mmol, 2.5 mL of H2O/bpp 5.0 mg, 0.025 mmol, 2.5 mL of H2O; ZnCl2 3.6 mg, 0.026 mmol, 3.0 mL of H2O/bpp 5.1 mg, 0.026 mmol, 3 mL of MeOH).

Synthesis of [Cu(bpp)2Cl2]·THF (0.75H2O) (7Cu). Crystallization of compound 7Cu was accomplished by layering on a solution of bpp in tetrahydrofuran (THF) (4.6 mg, 0.030 mmol, 4 mL) an isopropylamine solution of CuCl2·2H2O (11.9 mg, 0.060 mmol, 4 mL). The mixture was left to stand at ambient temperature for one day to yield small prismatic light-blue crystals. The nature of the bulk material as pure 7Cu was confirmed by X-ray powder diffraction data compared with the pattern calculated from the single-crystal X-ray structure.

Determination of Phase Diagrams. The batch technique has been used to perform a screening of crystallization conditions and to build the phase diagram as a function of metal salts and ligand concentrations. Crystallization trials were rapidly set up in a standard 24-well plate made of polystyrene (aqueous systems) or polypropylene (methanolic systems). Each well was air-tightly sealed with a 22 mm diameter glass coverslip and vacuum grease. A set of solutions with different concentrations of metal salts and bpp ligand were prepared in deionized water or methanol. Crystallization trials were performed by mixing the appropriate amount of reagent solutions and pure solvent so that a final volume of 2.0 mL for each fixed concentration of the components was obtained. The concentrations of metal salt and bpp ligand were systematically varied along the x-axis and the columns of the plate. The samples were monitored, by using an optical microscope coupled to a CCD camera, until equilibrium conditions were reached.

An extensive study was carried out only for copper and cobalt chlorides in water and methanol solvent systems. For all other metal cations (Mn2+, Fe2+, Ni2+, Cd2+, Zn2+), the nature and purity of the products formed by precipitation from water or methanol were checked by XRPD analysis by comparing the experimental patterns with the simulated ones from the single crystal structures. Microcrystalline powder samples were prepared following a standard procedure: typically, a water (or methanolic) solution of bpp of appropriate concentration was added to an aqueous (or methanolic) solution of the metal salt while stirring. In water a 1:3 metal–ligand molar ratio was used while in methanol the reagents were mixed in 1:1 and 1:2 ratio according to the stoichiometry of the two cobalt species isolated from this solvent. Precipitate was formed and the reaction mixture was left to react for ~2 h. The precipitate was filtered through a Buchner funnel, washed with small portions of solvent and dried in air. A summary of the results and further details about crystallization conditions for each plate and powder samples are given as Supporting Information.

Gel Double Diffusion Experiments. Two similar crystallization experiments, based on the double diffusion technique, were carried out by using U-shaped tubes (5 mm i.d. and 130 mm long with two identical arms of 30 mm length). The tubes were filled up with agarose gel of high strength prepared at 1% (w/v) and then solutions of the pertinent 1D species. Precipitate was formed and the columns of the plate. The samples were monitored, by using an optical microscope coupled to a CCD camera, until equilibrium conditions were reached.

Phase Transformations. The crystal transformations among different MOFs were monitored by means of an optical microscope coupled to a CCD camera connected to a computer equipped with a framegrabber. Time-lapse acquisition for automatic archiving of image series was performed at a suitable frequency.

1D → 2D Transformation. A crystal of the 1D copper species 1Cu was placed in a small cell to which 0.2 mL of a 0.1 M CuCl2 aqueous solution was added. The transformation took place at 25 °C in about 4 h (Figure 3).

1D → 3D Transformation. A crystal of 1Cu was placed in a small cell to which pure ethanol was added. The transformation took place at 25 °C in about 5 min.

2D → 1D Transformation. Crystals of the 2D copper species 2Cu were spontaneously nucleated in a small cell by preparing an aqueous solution 4 mM and 12 mM with respect to CuCl2 and bpp, respectively. Subsequent appearance of 1Cu crystals starts within 15–30 min; equilibrium is reached at 25 °C in about 3–5 days with complete consumption of 2Cu crystals (see Figure 1S, Supporting Information).

2D → 3D Transformation. A crystal of 2Cu was placed in a small cell to which pure ethanol was added. The transformation took place at 25 °C in about 50 min.

Electroconduction Measurements. Solubilities of compounds 1Co, 1Ni, 1Cu, and 1Cd have been determined at 25.0 ± 0.1 °C using a thermostatic bath. Metal(II) chloride and bpp ligand solutions were mixed in a 1:3 M/L ratio and molar concentration sufficient to give a microcrystalline precipitate (1Cd) or crystals (1Co, 1Ni, 1Cu) of the corresponding 1D MOF species. Chemical equilibrium was reached after 3 weeks. Solubilities were determined by comparison of electroconductance value of the saturated solution after diluting 1:2 with deionized water against a set of standard solutions of the pertinent 1D species.

Single Crystal X-ray Structure Characterization. Crystal data for all the compounds are listed in Table 1S, Supporting Information. The data collections were performed with Mo Kα (λ = 0.71073 Å) on a Bruker APEX II CCD area-detector diffractometer for 1Co, 1Ni, 3Cd, 3Co, 3Fe, 3Mn, 3Ni, 6Co, and 7Cu and on an Enraf-Nonius CAD4 for 1Cd, by the ω-scan method. An empirical absorption correction was applied for the structures collected with the CCD detector, while the ψ-scan method was used for 1Cd. The structures were solved by direct methods (SIR97) and SHELX9755 and refined by full-matrix least-squares on F2 (SHELX-97)48 with WINGX interface.49 Anisotropic thermal parameters were commonly assigned to all the nondisordered nonhydrogen atoms except for the partially occupied atoms of the clathrate solvent molecules in some of the structures. In compounds 1Cd, 1Co, and 1Ni one of two independent ligands was found disordered and refined isotropically using two models with occupancies of 52 and 48% (1Cd), 50 and 50% (1Co), and 41% (1Ni). In the same structures the water molecules were refined anisotropically but with half occupancy. The hydroxyl H atom associated with the ethanol molecule in 3Mn was located an difference Fourier map and refined freely, with Uiso(H) = 1.2Ueq(O), while all the other ones were placed in geometrically calculated positions and thereafter refined using a riding model with the correct occupancy for disordered models. All the structure diagrams were performed using the TOPOS48 SCHAKAL96 programs.

Results and Discussion

As the nature of coordination polymers can be modified by the conformation of the chosen ligands, coordination geometry preferred by the metal, counterions, solvent system, and metal-to-ligand ratio, in the following sections we discuss the phenomenology and the interplay among some of the chemical parameters relevant to the selection of the crystalline species obtained after mixing of metal(II) chlorides and ligand bpp.50

The CuCl2/bpp/Water System. We already reported38 on the possibility to obtain a whole family of coordination polymers based on the couple CuCl2/bpp in water, with new interesting 1D, 2D, and 3D topologies (Figure 1) depending on the choice of several chemical parameters. The CuCl2/bpp system subsequently afforded another new species when the reaction was conducted in THF solutions (see next section). In ref 38, we also briefly explored the networking properties of the chlorides of other M2+ cations with suitable ionic radius and coordination stereochemistry that in principle can afford species isostructural to those obtained from CuCl2 (see Table 1).

By working with aqueous CuCl2, a 1D species ([Cu(bpp)3·Cl]-·2H2O, 1Cu), consisting of interdigitated zigzag chains...
containing dangling monocoordinated bpp ligands, and a 2D coordination polymer ([Cu(bpp)$_3$]Cl-1.5H$_2$O, 2Cu), that now can be better defined as a 3D array formed from inclined polycatenation of 2D square layers in the diagonal—diagonal mode (density of catenation DOC = (2/2))$^{54}$ have been obtained using different Cu/bpp ratios and concentrations. Independently from us another group prepared a 1D MnCl$_2$/bpp coordination polymer isostructural with our Cu(II) 1D system.$^{51}$ On the contrary, the presence of alcohols or other organic solvents (acetone, dichloromethane) leads to the formation of a 3D 4-fold interpenetrated diamondoid network ([Cu(bpp)$_3$]Cl$_2$-2.75H$_2$O, 3Cu) (see next section). Curiously, while in these systems phenomena of polymorphism and supramolecular isomerism are often encountered, this seems to be not the case here; indeed, compounds 2Cu and 3Cu have very similar composition differing only in the amount of solvated water molecules, but the chloride ions play a different role in these two species so that it is hard to consider them supramolecular isomers.

During initial exploration of the behavior of aqueous solutions of CuCl$_2$ and bpp in a 1:2 ratio we obtained crystals of the 1D phase 1Cu by slow solvent evaporation at RT. While trying to improve size and quality of 1Cu crystals by varying crystallization conditions, that is, M/L ratio, absolute concentrations, and crystal growth technique (see later), we observed the formation of a new crystalline MOF (species 2Cu), easily recognized due to its deep blue color and different crystal morphology compared to 1Cu. However, upon standing for a few days in the presence of the mother solution the deep blue crystals of 2Cu disappeared leaving only pale blue crystals of 1Cu. Therefore, under the selected conditions, 1Cu was the thermodynamically stable product (showing indeed a lower solubility) whose formation is preceded by the nucleation of crystals of 2Cu, the kinetically favored species. This sequence of events follows Ostwald’s rule of stages$^{52}$ which allows the possibility that different crystalline species (e.g., polymorphs, or different hydrates or solvates) can nucleate sequentially starting from the least stable one that in turn transforms into a thermodynamically more stable species and so on until only the most stable species survive owing to its lowest solubility. Supersaturation conditions that provoke at first the nucleation of 2Cu followed by the more stable 1Cu (but see later for the opposite 1Cu to 2Cu transformation) are mirrored in the large number of small single crystals of 2Cu while crystals of 1Cu are generally heavily twinned rosettes. Nucleation of 2Cu occurs within minutes after mixing of reactants (e.g., CuCl$_2$ 4.0 mM and bpp 12.0 mM), while the subsequent solvent-mediated transformation into 1Cu requires several days to go to completion as monitored by means of time lapse optical microscopy (Figure 1S, Supporting Information).

![Figure 1. Coordination polymers obtained with the CuCl$_2$/bpp/ water system showing new interesting 1D, 2D, and 3D topologies.](image)

### Table 1. Summary of Crystallographic Data for Coordination Polymers Obtained from Different MCl$_2$/bpp/Solvent Systems

<table>
<thead>
<tr>
<th>compound</th>
<th>MOF</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>crystal system</th>
<th>sp group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Cd$^{a}$</td>
<td>1D</td>
<td>16.516(4)</td>
<td>26.779(6)</td>
<td>17.705(3)</td>
<td>1.5H$_2$O, (deg) crystal system sp group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Co$^{a}$</td>
<td>1D</td>
<td>16.580(3)</td>
<td>27.108(3)</td>
<td>17.126(6)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Cu$^{a}$</td>
<td>1D</td>
<td>17.191(1)</td>
<td>16.242(1)</td>
<td>26.859(2)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Fe$^{a}$</td>
<td>1D</td>
<td>16.517(2)</td>
<td>26.922(4)</td>
<td>17.221(2)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Mn$^{a}$</td>
<td>1D</td>
<td>16.571(3)</td>
<td>26.888(5)</td>
<td>17.525(3)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
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<tr>
<td>1Ni$^{a}$</td>
<td>1D</td>
<td>16.484(3)</td>
<td>26.901(3)</td>
<td>16.973(6)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Cu$^{a}$</td>
<td>2D</td>
<td>16.314(1)</td>
<td>18.211(1)</td>
<td>36.247(3)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Cd$^{a}$</td>
<td>3D</td>
<td>17.536(1)</td>
<td>17.536(1)</td>
<td>42.966(1)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Co$^{a}$</td>
<td>3D</td>
<td>17.187(1)</td>
<td>17.187(1)</td>
<td>42.299(3)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Cu$^{a}$</td>
<td>3D</td>
<td>17.221(1)</td>
<td>17.221(1)</td>
<td>40.965(2)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Fe$^{a}$</td>
<td>3D</td>
<td>17.081(2)</td>
<td>17.081(2)</td>
<td>42.554(5)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Mn$^{a}$</td>
<td>3D</td>
<td>17.201(2)</td>
<td>17.201(2)</td>
<td>42.697(4)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Ni$^{a}$</td>
<td>3D</td>
<td>16.991(4)</td>
<td>16.991(4)</td>
<td>41.947(9)</td>
<td>orthorhombic  Ibca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Co$^{a}$</td>
<td>1D</td>
<td>5.189(1)</td>
<td>12.980(1)</td>
<td>10.493(1)</td>
<td>monoclinic  P2$_1$/m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6Zn$^{a}$</td>
<td>1D</td>
<td>5.2254(4)</td>
<td>12.9371(9)</td>
<td>10.5425(6)</td>
<td>monoclinic  P2$_1$/m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7Cu$^{a}$</td>
<td>2D</td>
<td>22.062(9)</td>
<td>16.984(8)</td>
<td>15.647(7)</td>
<td>monoclinic  C2/c</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$This work. $^{b}$Ref 38. $^{c}$Ref 51. $^{d}$Ref 54.
This behavior is highly reproducible and has been checked several times. In the context of MOFs chemistry several other systems displayed crystal-to-crystal transformations. After this accidental discovery, we pursued a more rational approach by studying the influence of the Cu²⁺/bpp ratio and absolute concentration values on kinetics and final equilibrium composition. Considering that solid 1Cu and 2Cu have Cu²⁺/bpp ratios respectively of 1:3 and 1:2, a systematic exploration of Cu²⁺/bpp ratio and total concentration of reactants has been undertaken with the batch approach. Results for aqueous CuCl₂/bpp system are summarized in Figure 2 which extends up to ca. 15 mM for both CuCl₂ and bpp (solubility of bpp being of ca. 60 mM in water at RT). The equilibrium phase diagram clearly shows dominance of the 1D polymer over the 2D species starting from a bpp/CuCl₂ ratio of ~2, while the absolute concentration value has a negligible influence over stability regions of the two species. The phase diagram also shows the presence of the microcrystalline species Cu₄Cl₂(OH)₆ (4) identified by means of XRPD. This copper(II) hydroxochloride is produced when the Lewis basicity of bpp is overcome by its Brønsted–Lowry basicity at low ligand concentrations. From the point of view of kinetics, increasing the bpp/CuCl₂ ratio reduces the nucleation time for species 1Cu to an extent for which the preliminary nucleation and appearance of crystals of 2Cu becomes negligible or not discernible under the microscope at the highest magnification. Low ligand-to-metal ratios favor formation of 2Cu at the expense of 1Cu. Hence, when proper conditions are used, the 1 ↔ 2 reversible transformation can be driven to completion at will so that we are able to selectively nucleate and obtain pure crystal

![Figure 2. Equilibrium phase diagram for aqueous CuCl₂/bpp system with indication of the stability regions for 1D polymer 1Cu, 2D polymer 2Cu, and Cu₄Cl₂(OH)₆ (4) species as a function of [L]+[M] total concentration and [L]/[M] ratio (M = Cu²⁺, L = bpp).](image)

![Figure 3. Selected frames from a video microscopy record of the solvent mediated 1Cu → 2Cu transformation induced by a proper increase of the CuCl₂ concentration (time lapse between subsequent images is 15 min; crystal size is ca. 2 mm).](image)
samples of both species through equilibration. Indeed, based on our knowledge of chemical equilibria of aqueous CuCl₂/bpp system, it has been possible to drive to completion in about 4 h also the solvent-mediated $\text{1Cu} \rightarrow \text{2Cu}$ transformation as shown in Figure 3.

Since compounds $\text{1Cu}$ and $\text{2Cu}$ are characterized by different Cu/bpp stoichiometries the $\text{1Cu} \rightarrow \text{2Cu}$ transformation produces the release of the excess of bpp as a ghostly halo surrounding the transforming crystals (last frames in Figure 3). Clearly, the unidentified solution species leading to $\text{1Cu}$ or $\text{2Cu}$ depending on chemical conditions can be manipulated to move equilibrium by mass action law toward the desired product, independently from the kinetic features of the system previously described. A hint about the nature of the solution species that self-assemble to give $\text{1Cu}$ or $\text{2Cu}$ (the nucleation step in term of crystal growth mechanisms) has been collected by constructing a Job plot within U-shaped tubes and choosing experimental conditions on the basis of the phase diagram (Figure 2), it was possible to afford in the same crystallization tube the three species observed in water, that is, $\text{Cu}_4\text{Cl}_2(\text{OH})_6$ (4), $\text{2Cu}$, and $\text{1Cu}$ in order of increasing bpp to Cu ratio. On the right arm of the tube in Figure 6 was put an aqueous solution of CuCl₂ while on the left reservoir an aqueous solution of bpp was charged; the horizontal branch of the tube contained a 1% w/w agarose gel. Counter diffusion leads to concentration gradients of the two reactants which enabled us to obtain the aforementioned species in a single experiment according to the phase diagram, that is, 4 at very low, $\text{2Cu}$ at intermediate, and $\text{1Cu}$ at high bpp/Cu²⁺ ratios, respectively (Figure 6). This experimental setup is inter alia very useful to tailor reactants concentration in order to obtain good single crystals avoiding excessive nucleation, spherulitic, dendritic or twinned crystals, all representative of a very high supersaturation. By properly selecting concentrations, it has also been possible to drive the system toward production of pure samples of $\text{2Cu}$, without $\text{1Cu}$ or 4 as byproducts.

Figure 4. Job plot for the CuCl₂/bpp aqueous system with indication of the average composition of solution species at $\chi_{\text{Cu}} \sim 0.28$, that is, intermediate between the stoichiometry of $\text{1Cu}$ and $\text{2Cu}$.

Figure 5. Scheme illustrating the reversible solvent mediated chemical transformation $\text{1Cu} \leftrightarrow \text{2Cu}$.
The same experimental setup can be used to produce morphodromes, that is, a detailed study of dependence of crystal morphology on supersaturation or ratio between reacting species, a feature that can be of relevance for technological applications of MOFs. It must be mentioned that morphology of crystals can become a delicate issue when planning practical applications of crystalline materials, for example, for catalysis or gas sorption. These results, in view of the fact that no general and reliable models for the formation of coordination networks from solution are presently available, can be a useful guide for careful exploration and optimization of conditions for synthesis of crystalline coordination polymers. An illustrative example of the severe difficulties when trying to reproducibly synthesize and study the archetypal structure MOF-5 are discussed in a recent paper.27 Also temperature plays a fundamental role on determining kinetics and thermodynamics of coordination polymer synthesis and we briefly discussed it in ref 38. Recently, temperature has been exploited to select the final product and polymer topology through variation of conformation of a flexible ligand.59

The CuCl2/bpp/Organic Solvent Systems. Other crystallization trials involved use of organic solvents (methanol, ethanol, isopropanol, acetone, dichloromethane) for dissolving the ligand bpp and copper chloride. Presence of an organic solvent directs the self-assembling process toward the 3D species 3Cu, [Cu(bpp)1.5Cl2]-2.75H2O, that does not contain any solvated organic molecule within the cavities of the 3D metal framework.38 Therefore, it must be assumed that the organic solvent, without entering the coordination network, modifies the nature of the unknown solution species and/or their self-organization which eventually assemble into the interpenetrated structure of 3Cu. The role of methanol is well illustrated in a refined crystallization experiment with aqueous agarose gel which, thanks to composition gradients, in particular those involving methanol, produced both species 3Cu and 2Cu on sides of the growth tube where bpp concentration was higher or lower, respectively (Figure 7). Hence, beyond the presence of the organic solvent also the bpp/Cu2+ ratio comes again into play on determining which species can nucleate and develop into mature crystals.

Aiming at a better control of chemical equilibria involving our polymeric coordination species, we tried to transform 1Cu and 2Cu, obtained in the absence of organic solvents, into 3Cu by selecting the proper conditions. Indeed, crystals of 1Cu and 2Cu were unstable in the presence of pure organic solvents such as methanol, ethanol, or methylene chloride. As an example, upon immersing a crystal of 1Cu in ethanol we could observe its quick conversion into microcrystalline aggregates pseudomorphic of the starting crystal and whose composition was showed by XRPD to be that of 3Cu (Figure 8). Analogously, 2Cu can be converted into 3Cu with the same procedure but with a process that takes longer times to reach equilibrium. Therefore, as highlighted in Scheme 1, we could devise procedures to reversibly convert 1Cu into 2Cu and vice versa, together with conversion of 1Cu and 2Cu into 3Cu.

Parallel to formation of 3Cu, crystallization from organic solvents produced also a yellow sparingly soluble, and almost amorphous, powder (5Cu), represented by the yellow zones in the phase diagram and appearing at low total concentrations and bpp/Cu ratios. The formation of compound 5Cu has been observed in several preparations involving organic solvents such as methanol, isopropanol, or amyl acetate, but it has been possible isolate it in a crystalline pure form only by the method described above. In any case, the analysis of crystallization trials performed using a wide selection of conditions and configurations has confirmed that a low ligand-to-metal molar ratio favors unknown species 5Cu as evidenced by the phase diagram. The elemental analysis of the yellow phase58 indicated that the stoichiometric composition for 5Cu corresponds to a 1:1 combination of ligand and metal ion. These results and the similarities between the copper diagram in methanol and the cobalt one led us to hypothesize that the structures of yellow 5Cu and the blue 1D-polymer 6Co, containing cobalt ions tetrahedrically coordinated, could be closely related. Indeed, there are many examples of tetrahedral Cu(II) complexes containing N-donor ligands, some of which, but not all, show a yellow color. Unfortunately, other derivatives, as pyridinium salts of copper halide,58 could precipitate under the experimental conditions used, so we cannot be sure about the polymeric nature of the yellow phase.

We also built the equilibrium phase diagram for the CuCl2/bpp/MeOH system with a batch procedure (Figure 9). Deviations from the correct 3:1 bpp/Cu stoichiometry of 3Cu produce significant variations of the crystal morphology, but the combined effects upon supersaturation hamper interpretation of morphodromes (Figure 9 right). The feature common to all growth conditions is that, on average, species 3Cu exhibits a fast growing [001] direction, along which the 4-fold interpenetrated networks stack on top of each other. This feature has also been observed in other diamantoid networks based on nitriles.

When using THF to dissolve ligand bpp the new species [Cu(bpp)1.5Cl2]·(THF)·0.75H2O (7Cu) has been obtained, exemplifying the different role for this solvent, that can be supposed to be an active templating agent. Compound 7Cu consists of a two-dimensionally extended hexagonal array (Cu···Cu 13.349 and 13.489 Å) with open pores that accommodate the noncoordinating THF and water molecules stacked along the [201] direction with an ABAB sequence. The copper atoms exhibit a distorted square pyramidal co-ordination geometry with the basal plane formed by two nitrogens of pyridyl groups and two chlorine atoms arranged in trans configuration, while another pyridine nitrogen occupies the apical position at a rather long distance 2.27(1) Å. The two independent bpp ligands display both a trans—trans (TT) conformation (N-to-N of 9.644 and 9.859 Å). A single layer of 7Cu is shown in Figure 2S in the Supporting Information.
The MCl₂/bpp/Water (M = Mn, Fe, Co, Ni, Cd) Systems. As preliminarily reported in ref 38 substitution of copper(II) chloride with other bivalent cations allowed us to isolate coordination polymers isostructural to 1Cu (Table 1), while no analogues of 2Cu have been recovered. This different behavior has to be related to the octahedral coordination of copper in 1Cu, a local stereochemistry easily available also for Mn, Fe, Co, Ni and Cd 2⁺ ions, at variance with the square pyramidal pentacoordination of copper in 2Cu which is found less frequently for the other 2⁺ cations. Differences in ionic radii induced only minor structural effects on the 1D polymers of Co(II), Ni(II), and Cd(II) even though their crystal structures are described in different crystal systems (Table 1). Electroconductance measurements of saturated solutions and comparison between crystallization trials indicate that for 1D polymers of formula [M(bpp)₂Cl₂]·2H₂O 1Cu, 1Cd, 1Co, 1Ni, 1Mn, and 1Fe the solubility order is Mn > Fe > Co > Ni > Cu > Cd. Values for the solubility at 25 °C for 1Co, 1Ni, 1Cu, and 1Cd are 2.81, 1.66, 0.73, and 0.51 mM, respectively.

Further insights about similarities and differences between copper and the other divalent cations were gathered from the experimental determination with the batch technique of the phase diagrams for MCl₂/bpp systems in water. As an example, concentrations had to be increased up to 50 mM for both bpp and Co 2⁺, about three times higher than that used for the less soluble copper polymer. A thorough analysis of batch experiments for the 1D polymer 1Co shows, compared to copper, a shrinking of the nucleation zone moved at higher concentrations. From a practical point of view, the increased solubility of all 1D networks with the exception of Cd, is reflected in more difficulties to obtain crystals on moving from copper to cobalt and nickel, the latter one being the most soluble system. Crystals of the derivative 1Ni could be obtained only from isothermal evaporation of solutions containing Ni 2⁺ cation and bpp ligand because there is no possibility to reach the critical concentration necessary for nucleation by simply mixing cation and ligand. On the contrary, trials in high density hydrogels evidenced for the cadmium derivative 1Cd a prompt...
crystallization due its very low solubility. In fact, crystallization of Cd must be carefully controlled in order to avoid dendritic or spherulitic growth owing to the very high supersaturation reachable in the mother solution. A high growth rate can be easily obtained producing several centimeters long dendritic crystals in a few minutes after contact of the bpp and CdCl₂ solutions.

The MCl₂/bpp/Organic Solvent (M = Mn, Fe, Co, Ni, Cd) Systems. Similarities among Cu and Mn, Fe, Co, Ni, and Cd 2⁺ cations were further investigated by using an aliphatic alcohol (methanol, ethanol, isopropanol) as solvent for both MCl₂ and bpp or alternatively an alcohol for dissolving the metal salt and dichloromethane to dissolve bpp. In this way, it has been possible to obtain crystalline coordination polymers akin to 3Cu for all metal cations studied. Solubility ranking for these 3D metal–organic networks is analogous to that discussed for the 1D polymers crystallizing from water as confirmed by the reaction yields obtained from methanol at high concentrations of the reagents and at metal/bpp molar ratio of 1:2. The formation of pure products in all cases (with exception of Cd) was checked by XRPD analysis, by comparing the experimental patterns with the simulated ones from the single crystal structures. These results evidence once more the necessity to explore for any solvent system chosen as reaction media a wide range of concentrations and reagents molar ratio. In fact, data collected for the phase diagram of the CoCl₂/bpp/methanol system with the batch technique evidenced a shift toward higher concentrations with respect to the case of copper, together with a higher bpp/M ²⁺ molar ratio. Analysis of the crystallization batch (Figure 10) revealed also the presence of the new species 6Co characterized by blue crystals appearing just beneath the metastable zone of the 3D polymer 3Co.

Also the prismatic morphology of species 6Co is clearly different from that typically bipyramidal (with or without the (100) pinacoid) of the 3D polymer 3Cu but also for Ni, Cd, Mn, and Fe. The crystal structure of 6Co has the formula [Co(bpp)Cl₂] and is isomorphous to the published 1D polymer [Zn(bpp)Cl₂]₄ obtained via hydrothermal synthesis using a mixture of ZnCl₂ in H₂O and bpp ligand in ethanol. This species, which is probably related to compound 7Cu discussed in the case of copper, consists of festoon chains of Co atoms interconnected by bpp ligands in TT conformation. The distorted tetrahedral coordination geometry of cobalt cations are completed by two chloride anions. To confirm the primary role of the tetrahedral coordination around the metal ion in the assembly of Zn and Co 1D polymers, we have reprepared the Zn-bpp compound 6Zn, in both powder and single crystal forms, following a more conventional way of crystallization (i.e., using the liquid–liquid diffusion method) than the hydrothermal reaction used by Yao and co-workers. We have found that the better solvent system to prepare this compound in a suitable crystalline form for X-ray diffraction measurements is water and a combination of water and methanol.

Conclusion

We discussed kinetical and thermodynamical features of the crystallization behavior of MOFs based on MCl₂ salts and the ligand 1,3-bis(4-pyridyl)propane. Our systematic approach, using different crystallization techniques, to explore conditions enabling the synthesis of new MOF systems is of general application to a variety of coordination polymers. In particular, the self-assembly of coordination networks and the phase transformations here described between species with different metal to ligand ratios and/or clathrated solvents are
intimately related to kinetic and thermodynamic factors active during the crystallization processes. We showed that MOF species which are kinetically favored can be substituted by the thermodynamically stable product and conversion among different species can be performed after proper chemical knowledge has been gained.

The present work, while not resolving the very nature of the self-assembling processes leading to polymeric coordination networks, shows, however, that it is possible to finely tune and control the synthetic route toward a desired MOF. The capability to explore extensively the physicochemical variables of the metal–ligand solution equilibria is a major improvement over a simple buy-and-mix approach.


Supporting Information Available: X-ray crystallographic information files (CIF) for compounds 1Cd, 1Co, 1Fe, 1Ni, 3Cd, 3Co, 3Fe, 3Mn, 3Ni, 6Co, 7Cu. Figure 1S showing crystallization of 2Cu followed by its transformation into 1Cu. Figure 2S with details of the structure of 7Cu. Figures 3S and 4S showing batch crystallization results for 1,3-bis(4-pyridyl) propane + CuCl₂·2H₂O in methanol and CoCl₂·6H₂O in water, respectively. Table 1S with crystal data and Table 2S with a summary of microcrystalline powder samples prepared with bppy and Fe, Ni, Cd, Zn chlorides in water and methanol. This information is available free of charge via the Internet at http://pubs.acs.org.

References


(13) Caveat should be noted to avoid the misuse of solution spectroscopy in the rationalization of structural features of the extended solid-state species: IR and NMR solution data, indeed, can only give information about the fragments of the dissolution process.


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(58) Elemental analyses were carried out at the Microanalytical Laboratory of the University of Milano. Calcd. for [Cu(bpp)Cl2]: C13 H 14 CuN 4 Cl2: C, 46.93; H, 4.24; N, 8.42%. Found: C, 42.27; H, 4.25; N, 7.45%.
