

Crystallization of copper(II) sulfate based minerals and MOF from solution: Chemical insights into the supramolecular interactions

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Abstract. Crystallization of solids, molecular or non-molecular from solution is a supramolecular reaction. Nucleation of a lattice structure at supersaturation can be conceived to result from a critical nucleus, a high energy intermediate (supramolecular transition state). Conceptualization of a structure for the critical nucleus in terms of aggregation of tectons through non-covalent interactions provides chemical insights into the architecture of a solid. The retrosynthetic analysis of copper-based minerals and materials offers an elegant description for the crystal packing. It addresses the influence of the geometry, functionality and reactivity of copper tecton(s) in directing a specific supramolecular aggregation. The mechanistic approach provides guiding principles to chemists to account for the experimentally crystallized solids and a platform to practice structure-synthesis correlation. Rationalization of the same composition with different atomic arrangements (polymorphs), compositional variation leading to different pseudopolymorphs, degree of hydration (anhydrous to hydrated), water clusters, role of solvent, etc. can all be justified on molecular basis. Also, the method gives predictive components including directions to synthesize new solids. In a nutshell, the paper is an attempt to generalize the crystallization of inorganic solids from solution by recognizing supramolecular interactions between metal tectons and gain insights for designing new MOF.

Keywords. Crystallization; nucleation; supramolecular interaction; copper-based minerals; coordination polymer; MOF.

1. Introduction

Materials research for the past few decades have been dominated by 3d transition metal based non-molecular oxides, halides, chalcogenides owing to their rich structural chemistry and a range of electronic, magnetic, optical and catalytic properties.^{1,2} Most of these materials are obtained through conventional solid state route wherein the reaction is essentially diffusion-controlled leading to thermodynamically stable phases. However, in the recent past the focus has diverted towards another class of materials, organic inorganic hybrids³ that include coordination polymers (CP) and metal organic frameworks (MOF) wherein the hard properties of inorganic ceramics and the flexibility of soft organic matrix are being integrated to obtain functional materials.^{4–6} Unlike molecular synthesis, preparation of solids relies heavily on exploratory methods, and it is well-recognized that the complexity of the possibilities often defies predictability.^{7,8} In figure 1 we highlight the three major activities of the chemistry

of materials namely synthesis, structure and property at the corners of a triangle. Structure–property relationship is widely investigated for the past few decades; Yaghi's reticular synthesis of MOF is a notable example.^{9,10} While structure–synthesis correlation is rarely attempted due to lack of suitable mechanisms, designing or engineering a crystal to exhibit a particular set of properties for example, porosity towards gas storage and separation still remains an elusive dream.

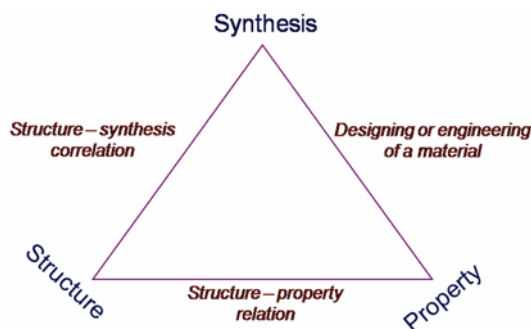


Figure 1. Three major activities of the chemistry of materials.

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With an objective to design zeolite mimics, several groups have exploited a synthetic strategy based on metal or metal cluster nodes coordinated through multidentate organic spacers.¹¹ Almost all CPs and MOFs are synthesized in a self-assembly process in which soluble metal species are reacted with suitable organic ligands that chelate/coordinate with metal. The most commonly employed ligands are carboxylate, polypyridyl ligands, polyazaheteroaromatic ligands such as imidazolate, pyrazolate, triazolate, and tetrazolate. This class of ligands affords the ability to bridge metal sites and is readily derivatized to provide bridging ligands with additional functionality. Interestingly, in many cases a crystal is achieved ‘by default’ rather than ‘by design’!¹² For true design and crystal engineering of a framework, one needs to assess the occurrence of different topologies (nets, grids, chains, sheets, helices, etc.) and solid state architectures in terms of chemically reasonable molecules reacting in the solution from which the crystals nucleate and grow. The terms like ‘self assembly’, ‘templating’ and ‘metal nucleation’ frequently employed in the literature will become more meaningful if we can understand the supramolecular reaction mediated in a solvent around the phase transition and how the chemical variables (pH, concentration, etc.) and external variables (temperature and pressure) influence the aggregation by the participating molecules. Almost five years ago we provoked a discussion by questioning ‘How molecules turn into solids?’ and responded by providing some intuitive mechanisms for the crystallization of selected MOFs.¹³ We further extended this mechanistic approach to many other systems including vanadates and molybdates and suggested molecular interpretation for the occurrence of water clusters, polymorphs, pseudopolymorphs, interpenetrated networks, hydration and solvation.^{14–19} Recently for the first time we employed the retrosynthetic analysis to interpret the packing of several minerals and materials crystallized from the system $\text{CuCl}_2\text{--H}_2\text{O--CuO}$ –organic in terms of supramolecular interactions.²⁰ The retrosynthetic analysis²¹ employed in our studies is an integrated approach involving the concepts of Corey’s synthon, Desiraju’s supramolecular synthon²² and Wuest’s tecton.²³ By proposing a structure for the critical nucleus, we were able to generalize the architectures of copper-based hydroxide and chloride minerals as well as copper organic solids built from molecular building blocks to account for different lattice with the same composition, variation in metal ligand

stoichiometry, degree of hydration and a link to chemical reactivity in the solution phase.^{12,20} This paper further explores the applicability of our pattern recognizing scheme to other phase diagrams like $\text{CuSO}_4\text{--H}_2\text{O--CuO}$, $\text{CuNO}_3\text{--H}_2\text{O--CuO}$ and $\text{CuCO}_3\text{--H}_2\text{O--CuO}$ and derive insights for the crystallization of MOF-based solids from reactions that employ copper salts as reactants. The objective is to uncover the mechanisms underpinning intermolecular interactions in the self assembly of inorganic solids including minerals and identify the pattern of crystal packing to engineer the crystallization of new MOFs.

2. Nucleation and crystallization of MOF solids from solution

Desiraju refers crystallization as a supramolecular reaction.²⁴ The crystallization process is considered to occur in two steps: nucleation and growth. Two recent articles have briefly discussed the issues related to nucleation and crystallization of solids from solution.^{25,26} In the context of crystal engineering, it means the stabilization of a particular arrangement of atoms and/or molecules from reacting species (solute as well as solvent molecules) at the supersaturation. In other words, the crystal structure of a solid represents a stable state where the intermolecular interactions are optimized to provide the most efficient packing – it may occur at the local minimum or global minimum on the energy landscape (figure 2). In the crystallization of molecular solids, intermolecular interactions influence their assembly and hence the crystal packing.²⁷ Many people have made significant contributions to the crystal packing analysis of molecular solids: Kitai-gorodsky’s close packing principle,²⁸ Etter’s principles for hydrogen bonded crystals,²⁹ Desiraju’s concept of supramolecular synthons,²² short-contact analysis of crystals, statistical analysis of intermolecular contacts, etc. are a few notable ones. Pattern recognition by manual inspection or database analysis still remains a convenient way to analyse crystal structures.³⁰ In contrast, crystal packing analysis of non-molecular solids (minerals, CP and MOF) is complex as both covalent and noncovalent interactions dominate.

A lot of theories have been proposed for the occurrence of nucleation^{25,26} though no interpretation of the same is available in terms of molecular recognition and aggregation of chemically reason-

able molecules present in the solution. Nucleation is defined as the formation of dispersed nuclei from a homogeneous solution under supersaturation. Formation of a critical nucleus signals the separation of a solid phase from the solution. A critical nucleus thus represents the high energy intermediate, a liquid-like cluster or aggregate (supramolecular transition state) acting as a bridge between the solution and the solid. Classical nucleation theory considers the existence of a critical nucleus, corresponding to the maximum of energy versus radius curve. It is crucial to obtain information on its size and structure to understand early stages of crystallization. How does one link the crystal growth units in the solution to the molecular fragments observed in the solid state?³¹ In the absence of a suitable mechanism for the nucleation highlighting molecular aggregation at supersaturation, it is difficult to interpret the results

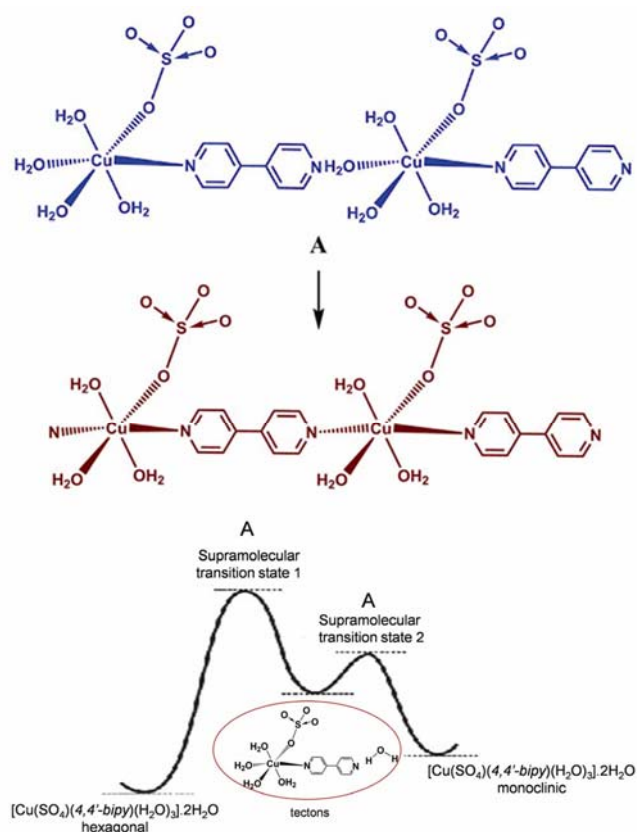


Figure 2. Energy profile diagram for the occurrence of copper organic polymorphs. The same set of tectons lead to two different critical nuclei as the supramolecular reaction pathway is altered by the reaction condition. Higher temperature favours the most stable hexagonal phase while milder condition results in the monoclinic symmetry. The structure differs in the way the water clustering occurs (refer figure 7).

obtained from various crystallization studies. Use of analytical probes such as mass spectrometry, FTIR, NMR for solution characterization and time resolved *in situ* diffraction studies for solid state structure were invariably found to be inconclusive in characterizing the intermediates or the critical nuclei.³² Thus it becomes necessary to propose a structure for the critical nucleus. In figure 3, we have provided the sequence of events that occur during the crystallization of a solid from a homogeneous solution: Dissolved molecules → complexes → dimers, oligomers or clusters → critical nucleus or supramolecular aggregate → the minute crystal → single crystal or

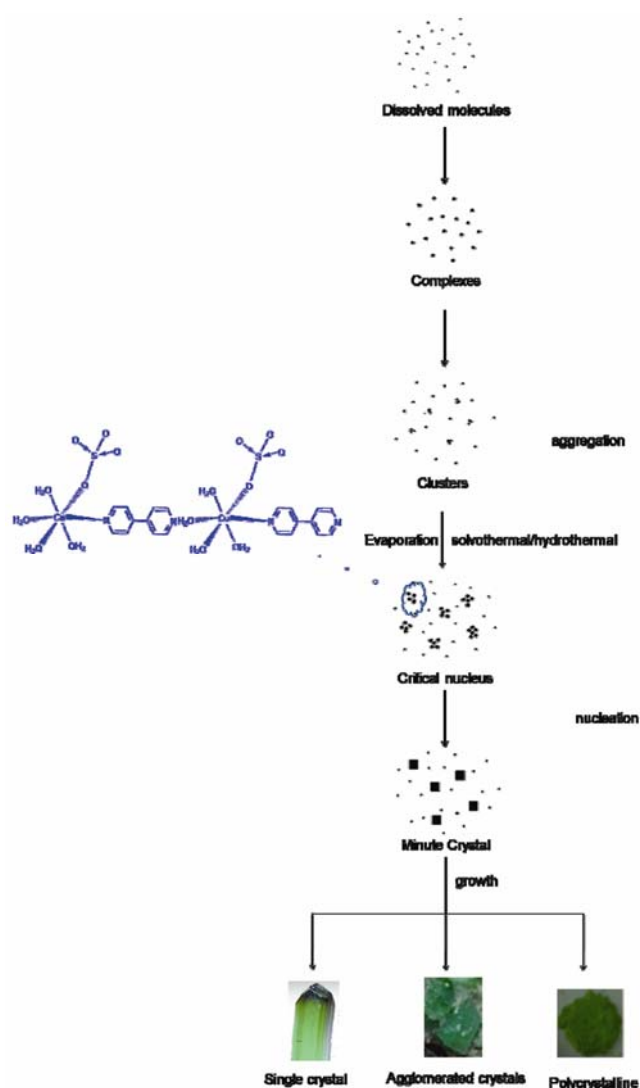


Figure 3. A schematic diagram representing the transformation of molecules in solution to a solid during crystallization reaction. Critical nucleus represents the supramolecular transition state. Nucleation refers to the stabilization of a minute crystal from a critical nucleus.

polycrystalline. Supersaturation must occur, at least locally in nano or subnano volume to drive nucleation and crystal growth. For nucleation to occur, molecular aggregates (clusters) of the soluble species (henceforth referred to as tectons) must continually form and dissociate because of local concentration fluctuations. In a supersaturated solution outside the metastable region, the rate of formation of aggregates exceeds that of their dissociation. Once the nucleus attains a critical size (hence critical nucleus), a minute crystal with a particular lattice structure is stabilized (see figure 3). Now the growth of the minute crystal (morphology) will be dominated by a different kinetics. Here the rate of integration of aggregates into an existing lattice structure exceeds that rate of releasing the aggregating molecules from the surface, a process again driven by the local fluctuations. Proposing a structure for the critical nucleus in terms of supramolecular aggregation of tectons is advantageous on several fronts. The presence and geometry of tectons can be established by employing various analytical techniques. Self assembly is easy to recognize as one can visualize the operation of long range forces (covalent or non-covalent) in a particular system. Chemical reactions occurring at molecular level such as hydrolysis, nature of the metal complex including geometry and metal/ligand ratio, hydrophilic or hydrophobic cavities forming between aggregating groups and hence water clusters or solvent inclusion will all become meaningful.

3. Drawing lessons from nature:

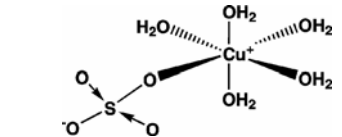
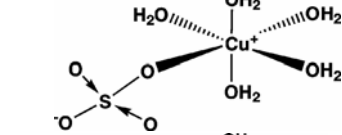
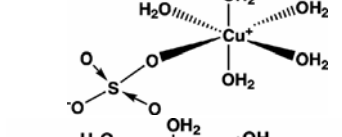
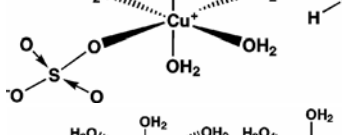
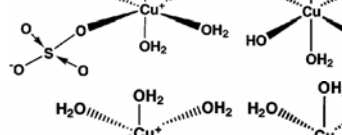
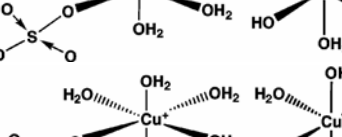
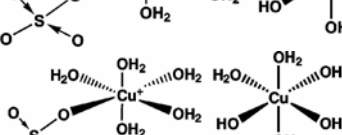
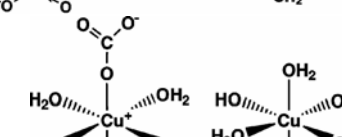
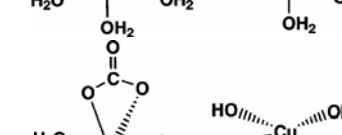
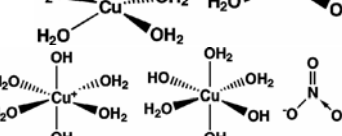
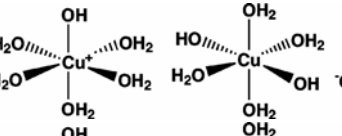
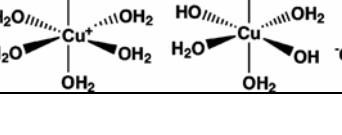

A retrosynthetic analysis of copper oxide-based minerals

Minerals are crystalline inorganic compounds grown in natural environment mostly from aqueous medium. Minerals represent position of equilibrium or stability of a solid in a particular system. A retrosynthetic analysis of its structure can provide us insight into the nature of intermolecular interactions responsible for the condensation of the reacting species or tectons to result into a particular crystal packing. In our recent paper,²⁰ we rationalised the stability of phases known in the ternary system $\text{CuCl}_2\text{--H}_2\text{O--CuO}$ as well as the MOF crystallized from organic containing system. Dissolution of these solids leads to charged and neutral copper aqua, chloro and hydroxide species. At supersaturation, such species aggregate (critical nucleus) and con-

dense to form the crystal – the bonds can be covalent, coordinate or non-covalent. In our analysis, a synthon refers to a H-bonded aggregate (e.g. $-\text{Cu--X}\cdots\text{OH}_2\text{--Cu}-$) that may favour a covalent $-\text{Cu--X--Cu}-$ ($\text{X} = \text{H}_2\text{O}, \text{Cl}, \text{OH}$) or non-covalent interaction during condensation. If such a synthon is associative favouring long range $-\text{Cu--X--Cu--X--Cu}-$ interaction, then the synthons are termed as supramolecular synthons. The retrosynthetic analysis allowed us to propose a structure for the critical nucleus by considering a supramolecular reaction that involves aggregation of appropriate tectons directed by supramolecular synthons. Proposal of structures for critical nuclei in the system $\text{CuCl}_2\text{--H}_2\text{O--CuO}$ postulates the condensation pathways for the copper tectons.²⁰ Such an analysis readily allows one to recognize the long range interactions (covalent as well as non-covalent) favouring a particular lattice structure and hence the crystallization of a hydrate, polymorph or pseudopolymorph of a mineral.

Can we extend this analysis to minerals known in other systems such as $\text{CuSO}_4\text{--H}_2\text{O--CuO}$, $\text{CuCO}_3\text{--H}_2\text{O--CuO}$ and $\text{CuNO}_3\text{--H}_2\text{O--CuO}$? Table 1 lists copper sulfate (carbonate and nitrate) based minerals crystallized from aqueous medium; a few are hydrated, some occur as polymorphs and pseudopolymorphs. As long as pH is below pKa of the reaction,³² $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Cu}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}_2\text{O}$, the tectons will be $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and SO_4^{2-} in the molar ratio 1 : 1 or $[\text{Cu}(\text{H}_2\text{O})_5\text{SO}_4]^0$ (overall charge of the aggregating species at the critical nucleus must be neutral). Figure 4 shows how supramolecular condensation between zwitter-ionic copper sulfate tectons take place in four different ways leading to the crystallization of the pseudopolymorphs, a textbook example. The phases represent a beautiful crystal engineering practiced by nature to account for the 1 : 1 stoichiometry of copper sulfate and the variation in the degree of hydration. A similar analysis is applicable for all phase diagrams involving salt hydrates.³³ The force of interaction (varying temperature at 1 atm or varying water pressure or humidity at 300 K) between self assembling molecules is evident by examining the different pathways for supramolecular condensation. Transformation of molecules into crystal is manifested in the way the sulfate ligand bridges with copper ions—complete covalent bonding in anhydrous CuSO_4 to coexistence of covalent and non-covalent interactions in the hydrated phases. The role of bridging ligands like chloride, hydroxide, sulfate, carbonate or nitrate will all become obvious if we carefully analyse crys-

Table 1. Various tectons involved in the formation of copper salt-based minerals crystallized from aqueous medium.

Copper tecton(s)	Composition	Reference
	[CuSO ₄] (Chalcocyanite)	1998 <i>Synth. Mineral. and Petro.</i> 39 201
	[CuSO ₄]·H ₂ O (Poitevinite)	1994 <i>Can. Mineral.</i> 32 873
	[CuSO ₄]·3H ₂ O (Bonattite)	1968 <i>Acta Cryst. B</i> 24 508
	[CuSO ₄]·5H ₂ O (Chalcanthite)	1934 <i>Proc. Roy. Soc. London, Series A: Math. Phys. Sci.</i> 146 570
	[Cu ₄ (OH) ₆ (SO ₄)] (Brochantite)	1997 <i>Acta Cryst. C</i> 53 1369
	[Cu ₃ (OH) ₄ (SO ₄)] (Antlerite)	1989 <i>Can. Mineral.</i> 27 205
	[Cu ₄ (OH) ₆ (SO ₄)(H ₂ O)] (Posnjakite)	1979 <i>Zeit. Kristall.</i> 149 249
	[Cu ₄ (OH) ₆ (SO ₄)(H ₂ O)]·H ₂ O (Wroewolfeite)	1985 <i>Am. Mineral.</i> 70 1050
	[Cu ₂ (OH) ₂ CO ₃] (Malachite)	1967 <i>Acta Cryst.</i> 22 146
	[Cu ₃ (OH) ₂ (CO ₃) ₂] (Azurite)	2001 <i>Phys. Chem. Mater.</i> 28 498
	[Cu ₃ (OH) ₅ NO ₃]·2H ₂ O (Likasite)	1986 <i>Neues Jahr. Mineral., Monat.</i> 101
	[Cu ₂ (OH) ₃ NO ₃] (Rouaite)	1983 <i>Zeit. Kristall.</i> 165 127
	[Cu ₂ (OH) ₃ NO ₃] (Gerhardtite)	1982 <i>J. Cryst. Spect. Res.</i> 12 507

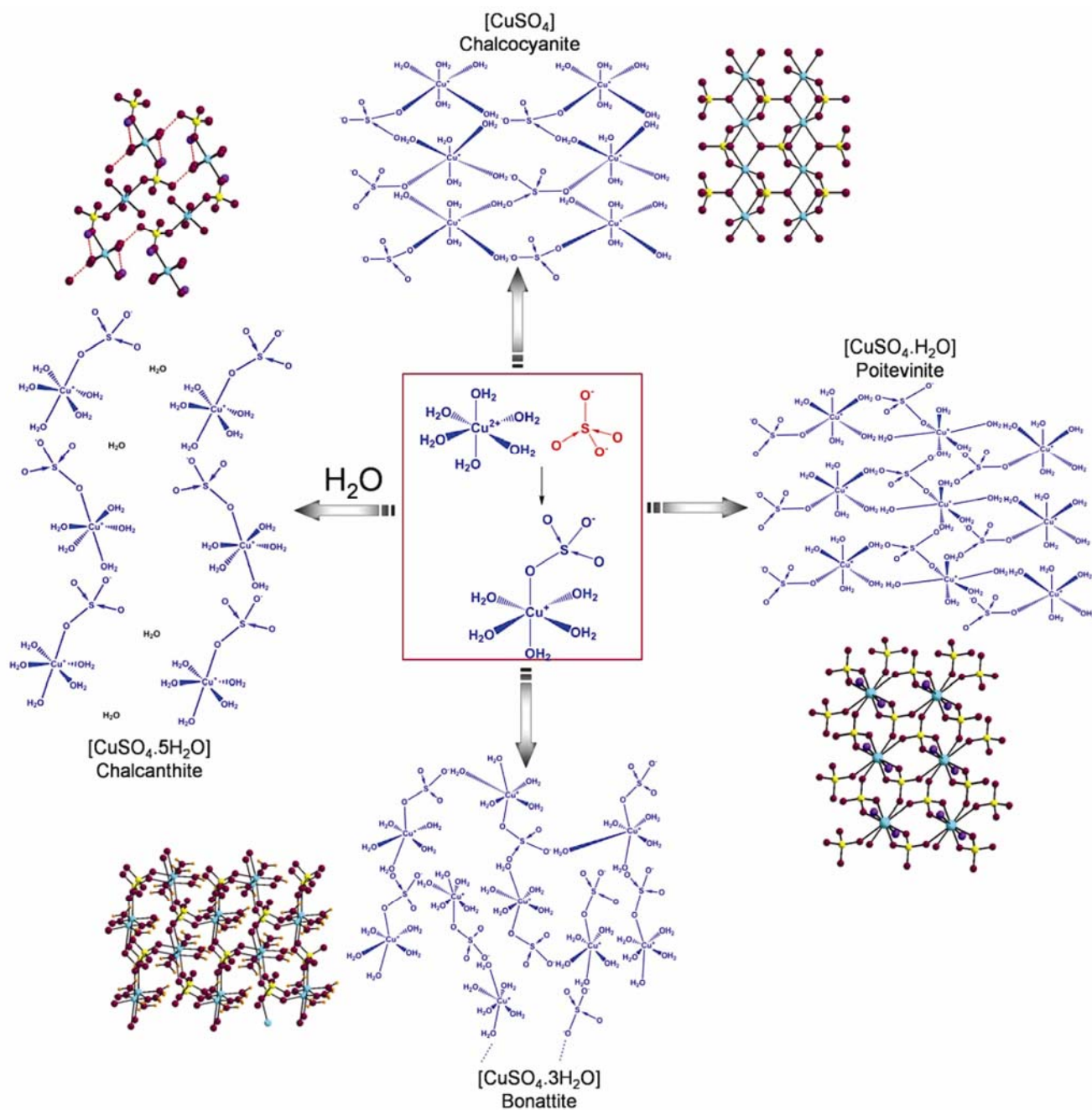


Figure 4. Crystal engineering of soluble zwitter ion, $[\text{Cu}(\text{H}_2\text{O})_5\text{SO}_4]^0$ (tecton) into different copper sulphate pseudopolymorphs. Notice how the external variables (temperature at 1atm or water vapour pressure at 25°C) induce different supramolecular aggregation and hence alternate pathways for condensation.

tallization in terms of tectons as building blocks. In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, effective packing requires an additional water molecule and hence water mediation.³⁴ Recently Zhang *et al.*³⁵ have grown an unusual zeolitic copper sulfate, $\text{Cu}_{12}(\text{SO}_4)_{12} \cdot 4\text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 1/3\text{H}_2\text{O}$ from a complex soup; such examples of a metastable phase is not uncommon in solid state chemistry. If pH is slightly altered to disrupt the

above equilibrium (addition of a mineral or organic base), the cupric hydrate will undergo hydrolysis forming $[\text{Cu}(\text{H}_2\text{O})_5(\text{OH})]^+$ and $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]^0$. However, the zwitter ion, $[\text{Cu}(\text{H}_2\text{O})_5\text{SO}_4]^0$ can not hydrolyse. These species can now induce a different supramolecular aggregation at the supersaturation with varying stoichiometries and hence the occurrence of pseudopolymorphs of anhydrous and

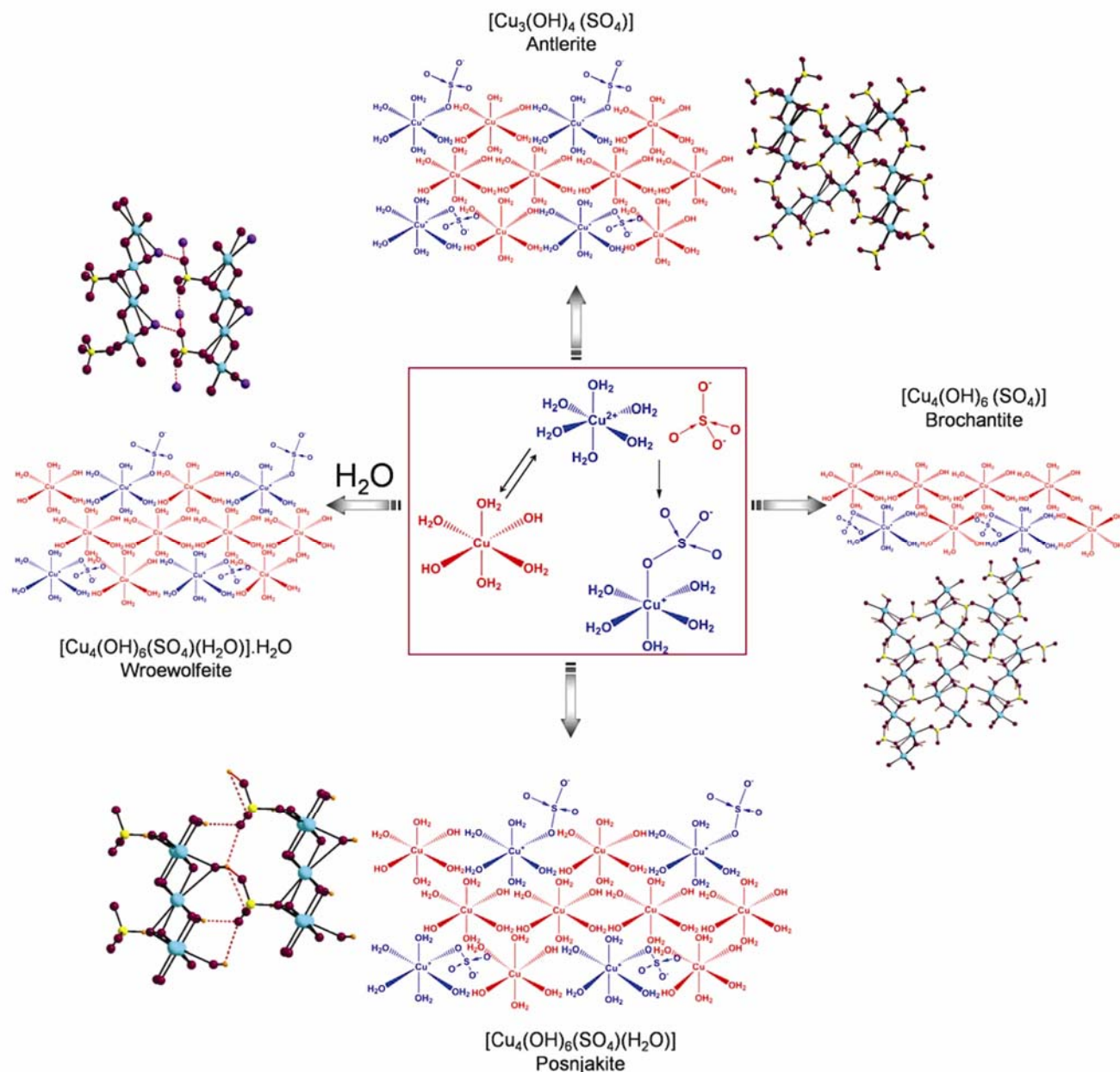


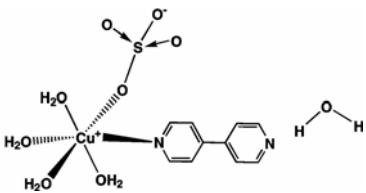
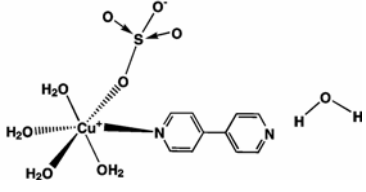
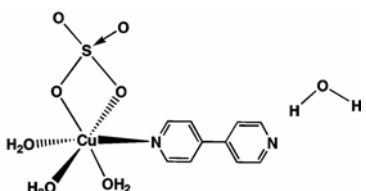
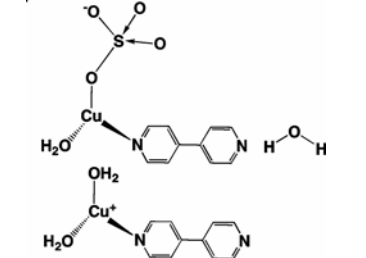
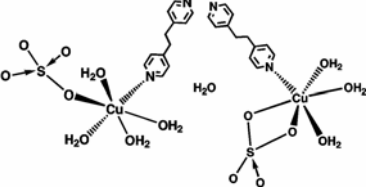
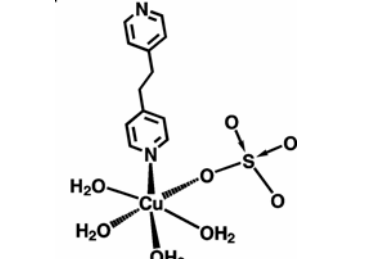
Figure 5. Local pH changes lead to the hydrolysis of the cupric hydrate and hence two different species $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]^0$ and the zwitter ion, $[\text{Cu}(\text{H}_2\text{O})_5\text{SO}_4]^0$ in the supramolecular reaction; the latter one cannot hydrolyze. Supramolecular aggregation of the two species with varying stoichiometries leading to the different pseudopolymorphs of anhydrous and hydrated copper hydroxy sulfates.

hydrated copper hydroxy sulfates (figure 5 and table 1).

In a similar way, the crystallization of polymorphs in the system $\text{CuNO}_3\text{--H}_2\text{O--CuO}$, and the two pseudopolymorphs (azurite and malachite) in the system $\text{CuCO}_3\text{--H}_2\text{O--CuO}$ can be rationalized (table 1) through the process of supramolecular condensation. The mechanism for the slow conversion of malachite

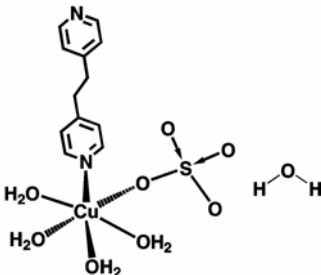
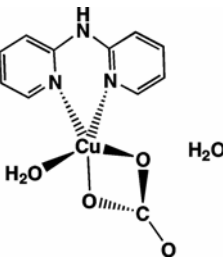
to azurite on exposure to moisturised CO_2 is a puzzle still to be solved. In all probability, the nucleation occurs through a dissolution followed by condensation and the driving force is the change in composition at the nucleating site. Our mechanistic approach can also explain why single crystals of CuCO_3 are difficult to achieve from aqueous solution; higher pH is required for the formation of carbonate tecton,

Table 2. Retrosynthetic analysis of copper sulphate/carbonate-based metal organic solids.

Tectons	Composition	Cell parameters	Reference
	$[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$	Hexagonal $P6_5$ $a = 11.2058(2) \text{ \AA}$ $c = 21.5947(5) \text{ \AA}$ $V = 2348.35(8) \text{ \AA}^3$ $Z = 6$	1998 <i>Chem. Mater.</i> 10 2091 2009 <i>Inorg. Chim. Acta</i> 362 2435
	$[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$	Monoclinic Cc $a = 10.189(10) \text{ \AA}$ $b = 19.760(18) \text{ \AA}$ $c = 7.455(3) \text{ \AA}$ $\beta = 100.36(10)^\circ$ $V = 1476(2) \text{ \AA}^3$ $Z = 4$	2000 <i>Cryst. Eng. Comm.</i> 2 1
	$[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$	Monoclinic $C2/c$ $a = 20.0305(4) \text{ \AA}$ $b = 9.8326(3) \text{ \AA}$ $c = 11.9363(3) \text{ \AA}$ $\beta = 101.136(3)^\circ$ $V = 2306.61(11) \text{ \AA}^3$ $Z = 8$	2006 <i>Inorg. Chem. Comm.</i> 9 42
	$[\text{Cu}_2(\text{SO}_4)(4,4'\text{-bipy})_2] \cdot 6\text{H}_2\text{O}$	Monoclinic $P2_1/c$ $a = 10.9225(3) \text{ \AA}$ $b = 17.1588(5) \text{ \AA}$ $c = 14.3282(4) \text{ \AA}$ $\beta = 110.252(5)^\circ$ $V = 2519.34(12) \text{ \AA}^3$ $Z = 4$	2006 <i>Inorg. Chem. Comm.</i> 9 42
	$[\text{Cu}(\text{SO}_4)(\text{bpe})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$	Triclinic $P-1$ $a = 9.399(3) \text{ \AA}$ $b = 9.496(3) \text{ \AA}$ $c = 10.073(4) \text{ \AA}$ $\alpha = 62.11(2)^\circ$ $\beta = 106.030(1)^\circ$ $\gamma = 73.00(2)^\circ$ $V = 751.9(5) \text{ \AA}^3$ $Z = 2$	2003 <i>Cryst. Eng. Comm.</i> 5 190
	$[\text{Cu}(\text{SO}_4)(\text{bpe})(\text{H}_2\text{O})]$	Monoclinic Pn $a = 7.2851(2) \text{ \AA}$ $b = 9.9062(3) \text{ \AA}$ $c = 9.1407(2) \text{ \AA}$ $\beta = 98.207(1)^\circ$ $V = 652.91(3) \text{ \AA}^3$ $Z = 2$	1998 <i>Chem. Mater.</i> 10 2091

(Contd...)

Table 2. (Contd...)

Tectons	Composition	Cell parameters	Reference
	$[\{\text{Cu}(\text{bpe})_2\}\{\text{Cu}(\text{bpe})(\text{H}_2\text{O})_2(\text{SO}_4)_2\}]\cdot 2\text{H}_2\text{O}$	Monoclinic <i>Pn</i> $a = 22.9863(1) \text{ \AA}$ $b = 13.4707(1) \text{ \AA}$ $c = 13.4902(1) \text{ \AA}$ $\beta = 106.030(1)^\circ$ $V = 4014.71(5) \text{ \AA}^3$ $Z = 8$	1998 <i>Chem. Mater.</i> 10 2091
	$[\text{Cu}(\text{CO}_3)(\text{dpa})]\cdot 3\text{H}_2\text{O}$	Monoclinic <i>P2₁/c</i> $a = 11.209(1) \text{ \AA}$ $b = 7.107(1) \text{ \AA}$ $c = 17.339(1) \text{ \AA}$ $\beta = 100.891(1)^\circ$ $V = 1356.37(10) \text{ \AA}^3$ $Z = 4$	2001 <i>Cryst. Eng. Comm.</i> 34 1

(4,4'-*bipy* = 4,4'-bipyridyl, *bpe* = bis(4-pyridyl)ethane, *dpa* = dipyridylamine).

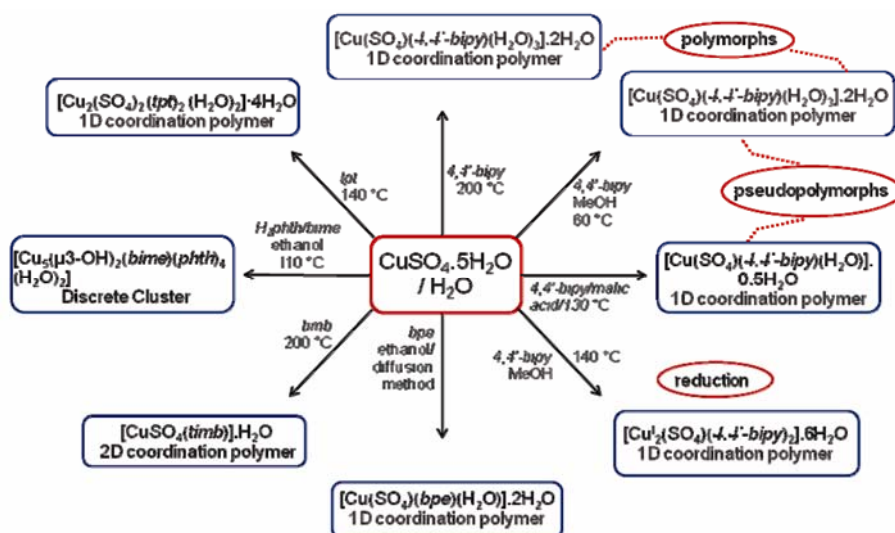


Figure 6. Crystallization of a few selected copper-organic solids from the system $\text{CuSO}_4\text{--H}_2\text{O--org.}$ Solid state architectures, compositional variation and water aggregation can be accounted for on molecular level by considering the supramolecular aggregation of appropriate tectons (refer table 2).

$[\text{CuCO}_3(\text{H}_2\text{O})_5]^0$ while the rate of formation of the hydroxide tecton $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]^0$ will be very high at this pH.

4. Chemical insights into the crystallization of copper based metal organic solid

Crystallization of a metal organic solid can be considered as a modification of the above systems: $\text{CuX}_2\text{--}$

$\text{H}_2\text{O--organic}$ ($\text{X} = \text{Cl}, \text{OH}$ or NO_3) or $\text{CuX--H}_2\text{O--organic}$ ($\text{X} = \text{SO}_4$ or CO_3). Here the solution (aqueous or non-aqueous) is made by dissolving a copper salt along with a chelating organic molecule. Three possibilities can occur in the solution: (i) copper can form a complex or a chelate, (ii) soluble cupric species or its complex can condense into a stable cluster and (iii) copper(II) may undergo reduction by organic group to form Cu(I) species. At super-

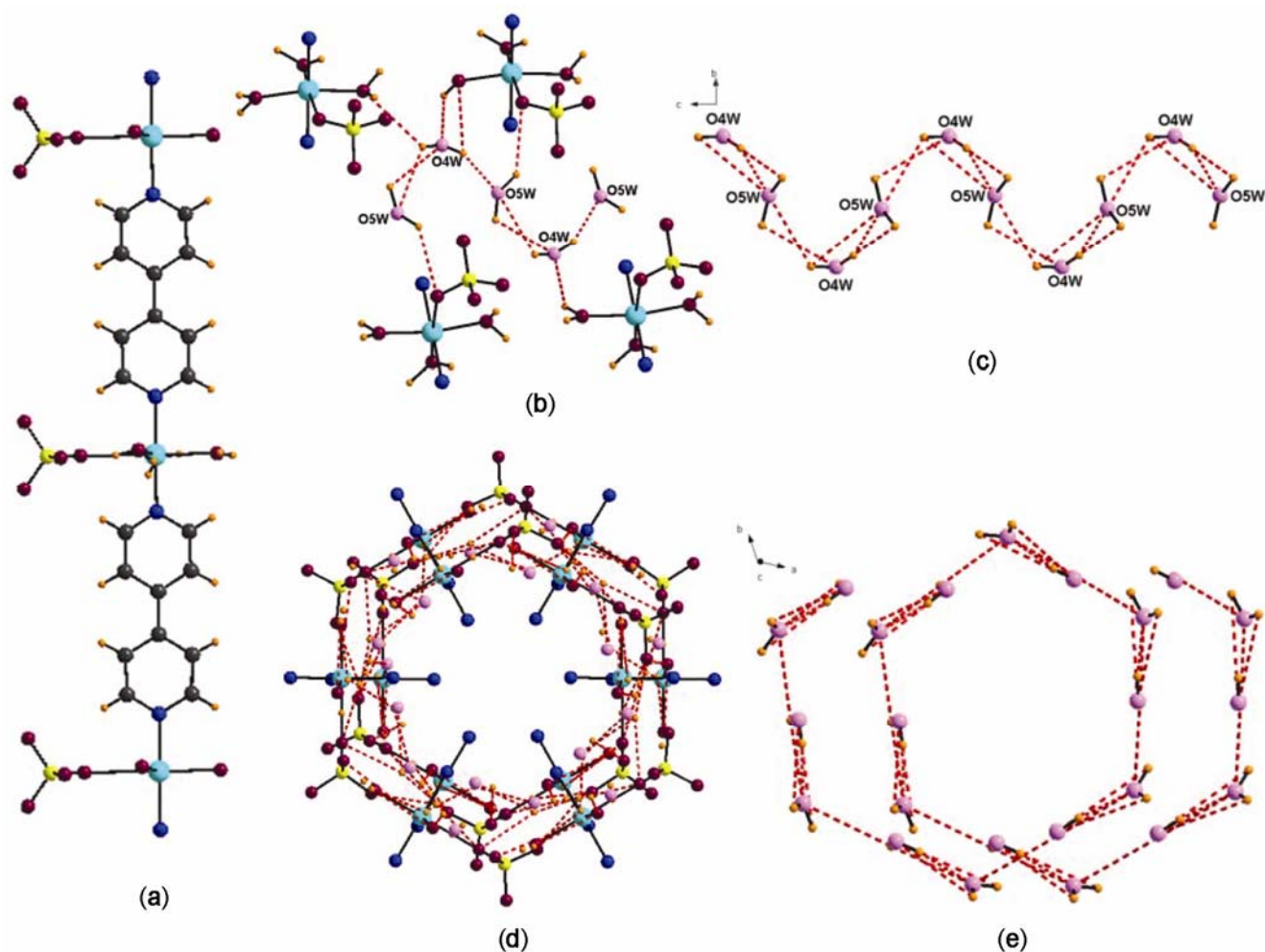


Figure 7. Crystallization of both hexagonal and monoclinic phases of the composition $[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ is a compromise of dominating covalent interactions forming 1D coordination polymers (a) and extended water interactions between mediating water molecules. In both phases the water chains interact with sulfate and coordinated water molecules. The higher temperature probably forces a stronger nonbonding interaction that results in a helical water chains for the hexagonal phase. (Carbon atoms are removed for clarity in (b) and (d)).

saturation, any one or more of these soluble species can aggregate through supramolecular interactions and eventually result in a particular crystal. To make a meaningful structure–synthesis correlation, it is essential to examine the crystal packing of a structure through condensation of appropriate tectons. Recently we reported how different condensation pathways lead to the crystallization of copper organic solids based on copper chloride and hydroxide.^{12,20} In this paper, we have examined the system $\text{CuSO}_4\text{--H}_2\text{O--org}$ (table 2). Crystallization of metal organic phases from the system $\text{CuSO}_4\text{--H}_2\text{O--4,4'-bipy}$ is an interesting case for examination. Four phases have been isolated of which one is Cu^{I} based (figure 6). The two polymorphic hydrates (hexagonal and monoclinic) observed for the composition

$[\text{CuSO}_4(4,4'\text{-bipy})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ is an elegant example of crystal engineering demonstrated between same set of molecules at two different condition. In both solids, the dominating assembly is the formation of 1D linear coordination polymers. However, the difference in space symmetry is dictated the way the two mediating water molecules interact with the chains (figure 7). Hydrothermal reaction at higher temperature forces stronger non-bonding interactions and hence a hexagonal symmetry; a helical symmetry (6_1) connects copper chains as well as the extended mediating water molecules. A milder condition, however results in a weaker interaction and hence lower monoclinic symmetry (figure 7). In the other monoclinic phase, $[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$, the tecton has a bidentate

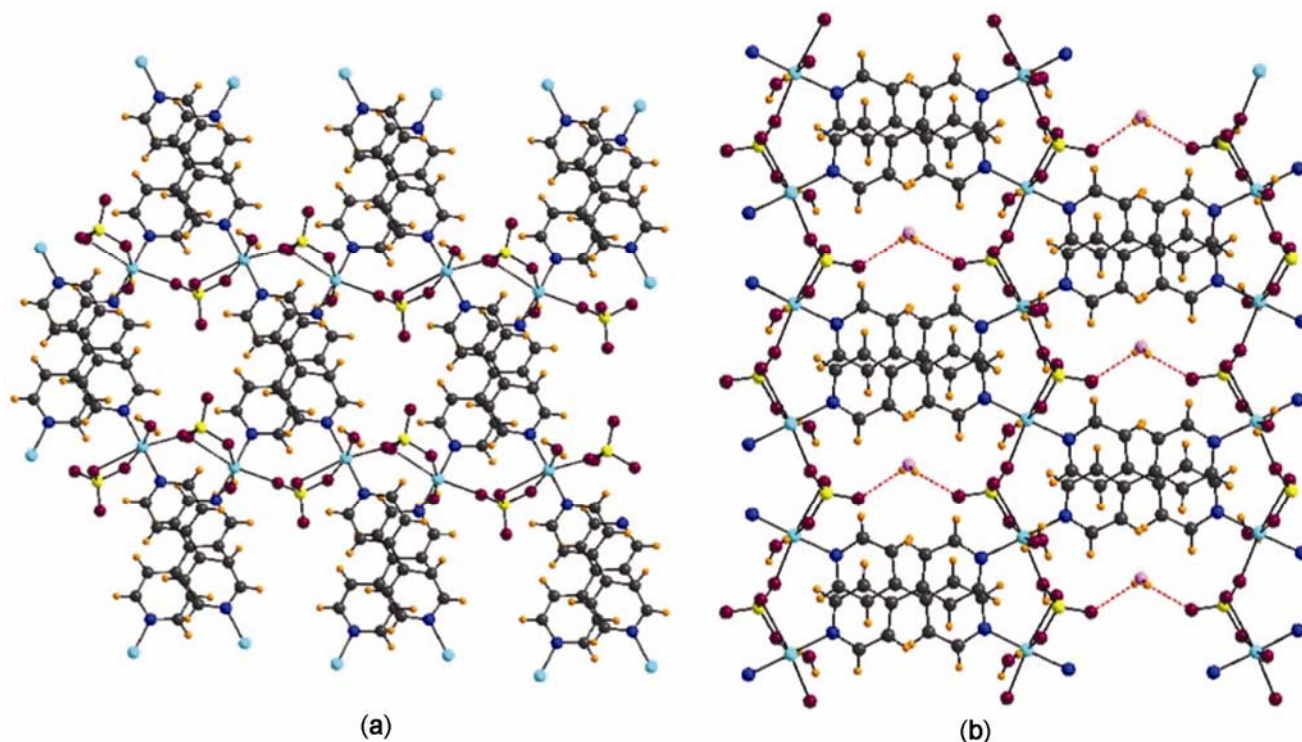


Figure 8. Crystallization of $[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$ is due to the formation of the tecton, $[\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})]_4^0$ wherein the sulphate is a bidentating ligand. Cu coordination is fulfilled by two nitrogens of 4,4'-bipy, three oxygens of sulfate groups and one water molecule. (a) 2D sheet formed by $\{\text{Cu}(\text{SO}_4)(4,4'\text{-bipy})(\text{H}_2\text{O})\}$ chains linked through sulfate groups. (b) Water mediation stabilizing the 3D structure.

sulfate group; the 1D chain still dominates the packing but the sulfate groups condenses with two water molecules of the copper coordination and hence the composition with lesser number of water around copper. The structure also shows the presence of one mediating water molecule that connects a pair of chains (figure 8).

Unlike chloride and sulfate, carbonate based metal organic solids are quite rare. There are only two examples known. $[\text{CuCO}_3(\text{dpa})]$ (*dpa* = dipyridylamine) wherein the copper (*dpa*) complex is extended into chains through bidentating and monodentating carbonate groups (table 2). A similar structure also exist for the solid $\text{CuCO}_3(\text{NH}_3)_2$.³⁶ A discrete complex based solid, $[\text{Cu}_4(\text{CO}_3)_2(\text{tppnol})_2](\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (*Htppnol* = *N,N,N'*-tris-(2-pyridylmethyl)-1,3-diaminopropan-2-ol) is also known.³⁷ By appropriate choice of organic groups, it is possible to prepare new metal organic solids of the composition $\text{CuCO}_3(\text{org})$. Probing chemistry issues concerning the formation of metal organic carbonates at the molecular level may have long term implications to the conservationists for preserving old paint-

ings containing pigments such as auzrite as well for fixing carbon dioxide in air through new MOF.

Copper acetate is another salt that is commonly employed as copper source in the synthesis of copper-based MOF. Unlike carbonate or acetate, aromatic di- or tri-carboxylates are more versatile to provide multidimensional covalent linkages; the aromatic groups can further influence crystal packing through specific $\pi\cdots\pi$ and $\text{CH}\cdots\pi$ interactions. Table 3 lists some selected examples with a brief account of experimental condition employed for its crystallization. Solid state structures of copper-based carboxylates³⁸ are unique among the first row transition metals as the tectons with variable geometry dictates varying reactivity and self-assembling properties. A quick examination of the table suggests that the choice of the reactants and solvent assists to overcome the solubility of copper and organic in a medium. However, rationalization of the composition and solvent inclusion in the most celebrated examples like HKUST1 and MOF-505 (table 3) requires a detailed structure-synthesis correlation along the lines discussed above.

Table 3. Retrosynthetic analysis of copper-arylcarboxylate based MOFs and CPs.

Tectons	Composition	Experimental Conditions	Reference
	[Cu(<i>bdc</i>)(H ₂ O)]·H ₂ O	Cu(OAc) ₂ ·H ₂ O/ <i>bdc</i> /imidazole/2 : 2 : 1 in H ₂ O and <i>n</i> -propyl alcohol at 160°C for 5 days	2003 <i>Inorg. Chem. Commun.</i> 6 1249
	[Cu ₃ (<i>tma</i>) ₂ (H ₂ O) ₃] HKUST1	CuNO ₃ ·3H ₂ O/H ₃ TMA/2 : 1 in 50 : 50 H ₂ O : EtOH at 180°C for 12 h	1999 <i>Science</i> 283 1148
	[Cu ₂ (OH)(<i>tma</i>)(H ₂ O)]·2H ₂ O	CuNO ₃ ·3H ₂ O/H ₃ TMA/1 : 3 in H ₂ O at 120°C for 24 h	2003 <i>Chem. Lett.</i> 32 590
	[Cu(<i>tma</i>)(H ₂ O) ₃]	Diffusion of an aqueous solution of Cu(ClO ₄) ₂ into <i>tma</i> in ethanol	1988 <i>Acta Cryst.</i> C44 992
	[Cu ₂ (<i>btc</i>) ₂ (H ₂ O) ₃]·2H ₂ O	Cu(NO ₃) ₂ ·3H ₂ O/ <i>btc</i> anhydride/1 : 1 in 10 ml H ₂ O. pH was adjusted to 4.5 by triethylamine. The reaction was heated at 160°C for 5 days	2004 <i>Inorg. Chem. Commun.</i> 7 788
	[Cu ₃ (OH) ₂ (<i>btec</i>)]	CuCl ₂ ·2H ₂ O/H ₄ <i>btec</i> /imH/NaOH/1 : 1 : 1 : 2 in 1 : 1 (v/v) MeOH–H ₂ O at 140°C for 2 days	2002 <i>Inorg. Chem.</i> 41 6161
	[Cu ₂ (<i>btec</i>)(H ₂ O) ₄]·2H ₂ O	CuCl ₂ ·2H ₂ O/H ₄ <i>btec</i> /pyz/NaOH/2 : 1 : 2 MeOH–H ₂ O solution at room temperature	2002 <i>Inorg. Chem.</i> 41 6161
	[Cu(<i>btec</i>)(H ₂ O) ₃]·3H ₂ O	CuCO ₃ /H ₄ <i>btec</i> /1 : 2 in water at room temperature	2002 <i>Eur. J. Inorg. Chem.</i> 1115
	[Cu(<i>btec</i>) _{0.5} dmf]	A DMF solution of H ₄ <i>btc</i> (0.5 mmol) was added drop-wise into a methanol solution of CuCl ₂ (1 mmol). The solution left for crystallization	2007 <i>Z. Anorg. Allg. Chem.</i> 633 1735
	[Cu ₂ (<i>bptc</i>)(H ₂ O) ₂ (dmf) ₃](H ₂ O)] MOF 505	H ₄ <i>bptc</i> /Cu(NO ₃) ₂ ·2.5H ₂ O in DMF/ethanol/H ₂ O at 65°C for 24 h	2005 <i>Angew. Chem. Int. Ed.</i> 44 4745

(*bdc* = 1,3-benzenedicarboxylate, *tma* = benzene-1,3,5-tricarboxylate, *btc* = 1,2,4-benzene, H₄*btec* = 1,2,4,5-benzenetetracarboxylic acid tricarboxylate, H₄*bptc* = 3,3',5,5'-biphenyltetracarboxylic acid)

5. Conclusions

The intuitive mechanisms in terms of molecular recognition and aggregation in solution between tectons enables one to propose a structure for the critical nucleus, the high energy intermediate; this establishes the directions of possible self-assembly prognosis paving way for a rational synthesis–structure correlation. It is necessary to employ suitable experimental techniques (microscopic, spectroscopic, and other solution methods) to ascertain the interactions between molecules at higher concentrations and thus establish a link between molecular and colloidal species. Computer simulation studies are essential to gain as much information as possible on the molecular-scale interactions leading to nucleation of minute crystals.

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