Design of non-molecular coordination solids from aqueous solution: $[\text{Cu}^{\text{II}}\text{L}_n\text{X}(\text{H}_2\text{O})]$, where $\text{X}=\text{SO}_4$, Cl or H_2O and $\text{L}=\text{pyrazole}$, imidazole or glutamic acid and $n=1$ or 4

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Abstract. We have successfully crystallized four new non-molecular coordination solids utilizing the synthons $-\text{Cu}-\text{OSO}_3-$ and $-\text{Cu}-\text{Cl}-$ in the presence of four organic ligands: $[\{\text{Cu}(\text{pz})_4\text{SO}_4\}\{\text{Cu}(\text{pz})_4\text{SO}_4(\text{H}_2\text{O})\}]\cdot\text{H}_2\text{O}$ **2**, $[\text{Cu}(\text{imi})_4\text{SO}_4]\cdot\text{H}_2\text{O}$ **3**, $[\text{Cu}(\text{imi})_4(\text{NO}_3)_2]\cdot\text{H}_2\text{O}$ **4** and $[\text{Cu}(\text{glu})\text{Cl}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ **5**. Use of glutamic acid resulted in two chiral coordination polymers **5** and $[\text{Cu}(\text{glu})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ **6** depending on the copper source. The paper provides chemical insights to the supramolecular aggregation of a crystal driven by the various competing intermolecular forces.

Keywords. Non-molecular coordination solids; supramolecular aggregation; coordination polymers.

1. Introduction

Non-molecular solids such as coordination polymers (CPs) and metal organic frameworks (MOFs) have been attracting considerable importance since Yaghi *et al.* reported the first family of MOFs with large porosity and high surface areas.¹ Majority of CPs and MOFs are grown from solution either under ambient or solvothermal/hydrothermal condition. A significant structural feature of all these solids is the occurrence of extended metal-ligand interactions analogous to supramolecular synthons² with varying dimensionality. Robson was the first one to recognize metal-ligand interaction as an effective tool to build multi-dimensional coordination polymers.³ Yaghi exploited the utility of coordination linkages such as metal-carboxylate and metal-nitrogen to construct porous 3-D MOF solids.^{4,5} In recent years, these zeolite-analogues turned out to be promising materials with greater flexibility and provisions to incorporate multiple functionality.⁶ In contrast to organic solids, crystallization of metal organic solids is quite complex and involves several competing reactions with different rates. To interpret a crystal synthesis, it is important to analyze the aggregation process leading to a crystal nucleus in terms of ‘chemically reasonable molecular bricks’ from a chemical soup.

Our group has developed a retrosynthetic approach to interpret the supramolecular aggregation during the crystallization of several metal organic solids.^{7–10} We demonstrated its usefulness with many examples drawn from literature and crystals grown in our own group to construe the molecular events preceding crystallization by invoking possible ‘chemical bricks’ that eventually lead to the final condensed product from a solution. The present work is an attempt to investigate the structural landscape of the system $\text{Cu}^{\text{II}}\text{X}_n$ ($\text{X}=\text{SO}_4$ or Cl)–ligand– H_2O with an objective to explore the role of the synthons $-\text{Cu}-\text{OSO}_3-$ or $-\text{Cu}-\text{Cl}-$ in engineering extended structural units of the type $-\text{X}-\text{Cu}-\text{X}-\text{Cu}-$. Further, we wanted to probe the competing nature of these with the desirable synthon $-\text{L}-\text{Cu}-$ which is responsible for the formation of CPs and MOFs. Our earlier analysis of several copper organic solids suggested that synthons of the type $-\text{Cu}-\text{OSO}_3-$ and $-\text{Cu}-\text{Cl}-$ also compete with $-\text{Cu}-\text{L}-$ (L-multidentate organic compound) in engineering non-molecular solids.^{8,9} A CSD analysis showed 11 and 19 hits respectively for extended $-\text{Cu}-\text{OSO}_3-$ and $-\text{Cu}-\text{Cl}-$ interactions in non-molecular copper organic solids.¹⁰ In this paper, we discuss our recent results on the crystallization of a few copper-based coordination solids grown on the basis of our rationale and describe its crystal structures providing molecular insights. The choice of sulphate and chloride anion is particularly significant as they can influence supramolecular assembly in two ways: either

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it directly coordinates with copper or may occur as counter anion. The organic ligands chosen were both non-bridging (pyrazole, imidazole and 1,10-phenanthroline) and bridging (glutamic acid). Our previous experiences showed that the use of ligands like 4,4'-bipyridine or pyrazine favoured extended –Cu–L–Cu– linkages resulting in coordination polymers. In a few cases, the bridging ligands compete with halide ions to form extended interactions.^{11,12} In this paper, we discuss the structural chemistry of four new coordination solids including one chiral coordination polymer providing molecular insights.

2. Experimental

2.1 Synthesis

All the chemicals were bought and used without further purification. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.375 g, 1.5 mmol) was dissolved in 17 mL of water and the organic ligand (1.5 mmol) was added to this aqueous solution while being stirred. The resultant solution was then transferred to Teflon-lined stainless steel digester and heated at 150°C for 3 days. The contents were cooled to room temperature and allowed for crystallization at room temperature. For the synthesis of **1**, $[\text{Cu}(1,10\text{-phen})\text{SO}_4(\text{H}_2\text{O})_2]$, 1,10-phenanthroline (0.270 g, 1.5 mmol); for the synthesis of **2**, $[\{\text{Cu}(\text{pz})_4\text{SO}_4\}\{\text{Cu}(\text{pz})_4\text{SO}_4(\text{H}_2\text{O})\}]$, H_2O , pyrazole (0.102 g, 1.5 mmol) and for the synthesis of **3**, $[\text{Cu}(\text{imi})_4\text{SO}_4]$, imidazole (0.102 g, 1.5 mmol)

were used as organic ligands. Blue coloured single crystals suitable for X-ray diffraction study were obtained in all the three cases. For the synthesis of **4**, $[\text{Cu}(\text{imi})_4(\text{NO}_3)_2]$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.360 g, 1.5 mmol) was used as copper source and imidazole (0.102 g, 1.5 mmol) was used as organic ligand under similar conditions as for the synthesis of **1**, **2** and **3**. Synthesis of **5**, $[\text{Cu}(\text{glu})\text{Cl}(\text{H}_2\text{O})]$ was carried by grinding as well as slow evaporation method. Here $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g, 1 mmol) was taken as copper source and glutamic acid (0.147 g, 1 mmol) was used as organic ligand. We employed D, L and DL glutamic acid in our synthesis. The reactants were ground in a mortar and pestle, dissolved in 10 mL water and kept for crystallization. Dark blue coloured single crystals suitable for X-ray diffraction were obtained after 4–5 days. When we used D or L glutamic acid, crystallization yielded either right-handed or left-handed helices as confirmed by structural analysis. However, use of racemic DL acid resulted in spontaneous resolution leading to a mixture of right-handed and left-handed helices. Schemes 1 and 2 summarize the experimental condition for the growth of all solids reported in this study.

2.2 X-ray crystallography

X-ray diffraction study of a crystal mounted on a capillary was carried out on a BRUKER AXS SMART-APEX diffractometer with a CCD area detector ($\text{MoK}\alpha$: 0.71073 Å, monochromator: graphite).¹³

Table 1. Crystal data and structural refinements for the solids **1**–**5**.

Parameter	1	2	3	4	5
Formula	C12 H8 Cu N2 O6 S	C24 H32 Cu2 N16 O10 S2	C12 H16 Cu N8 O4 S	C12 H16 Cu N10 O6	C5 H8 Cl Cu N O5
Formula weight, g.mol ^{−1}	371.82	895.90	431.95	459.90	261.12
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	C2/c	P 2 ₁ /c	C2/c	Pna2 ₁	P2 ₁ 2 ₁ 2 ₁
a (Å)	14.876(4)	14.073(4)	9.2180(17)	13.888(5)	5.2793(14)
b (Å)	13.839(3)	16.617(5)	17.631(3)	9.815(4)	7.967(2)
c (Å)	7.0214(17)	15.367(4)	10.5455(19)	13.397(5)	20.909(6)
α (°)	90	90	90	90	90
β (°)	108.624(4)	90.20(3)	93.447(3)	90	90
γ (°)	90	90	90	90	90
V (Å ³)	1369.79	3593.59	1710.78	1826.15	879.436
Z	4	4	4	4	4
d _{calc} (g.cm ^{−3})	1.803	1.656	1.677	1.673	1.972
μ _{MoKα} , (cm ^{−1})	1.778	1.376	1.437	1.253	2.776
R1(I > 2σI)	0.0435	0.1757	0.0409	0.0941	0.0324
WR2(all)	0.1081	0.3336	0.1035	0.1714	0.0843
GOF	1.153	1.181	1.088	1.107	1.084
CCDC/CSD No.	996530	996531	996532	996533	996534

Scheme 1. Crystallization of non-molecular solids engineered through the synthon $-\text{Cu}-\text{O}-\text{SO}_2\text{O}-$.

Frames were collected at $T = 293 \text{ K}$ by ω , ϕ and 2θ -rotation at 10 s per frame with SAINT.¹⁴ The measured intensities were reduced to F^2 and corrected

for absorption with SADABS.¹⁴ Structure solution, refinement and data output were carried out with the SHELXTL program.¹⁵ Non-hydrogen atoms were

Figure 1. (a) In **1**, extended $-\text{Cu}-\text{OSO}_3-\text{Cu}-$ interactions between copper phenanthroline complex units and bridging sulphate groups lead to neutral 1-D chains. (b) Adjacent chains interact through H-bonding between a pair of water molecules coordinated with copper and the uncoordinated sulphate oxygens. $\pi \cdots \pi$ interactions between phenanthroline groups facilitate further stability forming a sheet. (c) $\text{C}-\text{H} \cdots \text{O}$ interactions among sheets result in a 3-D network for **1**.

refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Structures were drawn with DIAMOND program.¹⁶ Crystal and refinement data of all new solids are summarized in table 1.

2.3 Other physical measurements

TG analysis were carried out using Perkin–Elmer TGA7 and DTA7 system on well ground samples of **5** and **6** in flowing nitrogen atmosphere with a heating rate of 10°C/min. While the solid **5** is unusually stable till 200°C, **6** loses water molecule at around 95°C (figure S1). PXRD showed the dehydrated products to be X-ray amorphous. Magnetic susceptibility measurements were performed with a SQUID magnetometer of Quantum Design Inc., USA. Diamagnetic corrections were estimated from Pascal's constants.

3. Results and Discussion

Crystallization from a solution containing copper sulphate and organic ligand (1,10-phenanthroline, pyrazole and imidazole) yielded two new non-molecular solids, [$\{\text{Cu}(\text{pz})_4\text{SO}_4\}\{\text{Cu}(\text{pz})_4\text{SO}_4(\text{H}_2\text{O})\}$]. H_2O and $[\text{Cu}(\text{imi})_4\text{SO}_4]$ **3** and one known solid $[\text{Cu}(\text{l},$

10-phen) $\text{SO}_4(\text{H}_2\text{O})_2]$ **1** (scheme 1). An interesting feature of the three solids is the occurrence of extended copper–sulphate interaction leading to 1-D chains. The chains, however pack differently depending on the nature of secondary non-covalent forces exhibited by the organic groups. The solid **1** is identical to the compound already reported in the literature except that our synthesis involves only reaction of copper source with the organic ligand.¹⁷ The previous report does not consider the extended interaction between copper and sulphate. In **1**, a strong H-bonding between a pair of water molecules coordinated with copper and the uncoordinated sulphate oxygens are responsible for almost linear metal–ligand chain (figure 1). This also facilitates $\pi \cdots \pi$ interactions between phenanthroline groups to form a sheet. C–H $\cdots$ O interactions between the sheets result in a 3-D network for **1**. The solid **2** is an interesting example of how the system optimizes crystal packing. The major directing force is still an extended $-\text{Cu}-\text{OSO}_3-\text{Cu}-$ interaction to form neutral 1-D chains (figure 2). However, the presence of pyrazole groups on copper dictates a different assembly to stabilize the chains. A discrete zwitterionic complex, $\{\text{Cu}(\text{pz})_4\text{SO}_4(\text{H}_2\text{O})\}$ enters the lattice to pack the chains efficiently through weak interactions ($\text{S}-\text{O} \cdots \text{H}_2\text{O}$ and $\pi \cdots \pi$). In **3**, we employed imidazole, an isomer of pyrazole. The 1:4 copper complex with the azole unit is the same as in **2**. Nevertheless, the $-\text{N}-\text{H}$ group in imidazole is favourable to H-bond with sulphate

Figure 2. (a) $\{\text{Cu}(\text{pz})_4(\text{SO}_4)\}$ units interact with sulphate groups to form neutral 1-D chains in **2**; the chains are similar to the one observed in **1**. (b) Discrete zwitterionic complex, $\{\text{Cu}(\text{pz})_4\text{SO}_4(\text{H}_2\text{O})\}$ in **2**. (c) The discrete neutral complex enters into the supramolecular assembly to stabilize adjacent chains by facilitating favourable interactions between $\text{S}-\text{O} \cdots \text{H}_2\text{O}$ and $\pi \cdots \pi$.

oxygens of adjacent neutral chains (figure 3). In all the three cases, we obtained only the same solid even when we altered the ligand to metal ratio. We performed another crystallization reaction starting with copper nitrate rather than sulphate. The solid **4** is a molecular solid and favourable H-bonding interactions such as $\text{N-H}\cdots\text{ONO}_2$ and $\text{C-H}\cdots\text{ONO}_2$ dictate the aggregation of the discrete complex, $\{\text{Cu}(\text{imi})_4(\text{NO}_3)_2\}$. The overall H-bonded assembly in **4** is shown in figure 4. Lack of good quality crystals and probable disorder resulted in poor statistics for **4**. Reaction of copper nitrate with 1,10-phenanthroline and pyrazole did not yield any new metal organic solids. It appears that a favourable $\text{N-H}\cdots\text{O}$ with imidazole unit is responsible for the isolation of **3**. Use of copper chloride resulted in known solids¹⁸ for pyrazole and imidazole, $[\text{Cu}(\text{pz})_4\text{Cl}_2]$ and $[\text{Cu}(\text{imi})_4\text{Cl}_2]$.

With an objective to crystallize new coordination polymers, we attempted reaction of copper sulphate and copper chloride with an amino acid, namely

glutamic acid which is chiral and multidentate. One side of glutamic acid is ideal for chelation with copper while the other side can be extended to form a CP. Glutamic acid showed different crystallization behaviour when it was reacted with copper chloride and copper sulphate (scheme 2). To start with, copper chloride and copper sulphate salts produced different pH when dissolved in aqueous solution. We did not alter pH of initial solution with any external source. In the case of copper chloride, initial pH was around 2 and crystallization led to a blue colour crystal, **5** after a few days. Single crystal X-ray analysis established the compound to be $[\text{Cu}(\text{glu})\text{Cl}(\text{H}_2\text{O})]$. Interestingly, when we increased pH of the initial solution above 5 using dilute NaOH, morphologically different blue colour crystal **6** was obtained. Single crystal X-ray analysis confirmed the solid **6** to be $[\text{Cu}(\text{glu})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$. The compound **6** was found to be exactly the same as the one reported earlier by Mizutani *et al.*¹⁹ Whenever we used copper sulphate or copper nitrate as the source,

Figure 3. (a) Neutral 1-D chains in **3** also occur through extended $-\text{Cu}-\text{OSO}_3-$ interactions similar to **1** and **2**. (b) H-bonding between N-H of the imidazole units and uncoordinated sulphate oxygen stabilizes adjacent chains. The different chains are represented in different colors.

Figure 4. (a) Discrete molecular unit $[\text{Cu}(\text{imi})_4(\text{NO}_3)_2]$ in **4**. (b) Intermolecular $\text{N-H} \cdots \text{ONO}_2$ and intramolecular $\text{C-H} \cdots \text{ONO}_2$ interactions results in the formation of H-bonded sheet. (c) Intermolecular $\text{C-H} \cdots \text{ONO}_2$ interactions further stabilizes the 3-D network in the molecular solid **4**.

we ended up obtaining only **6**. When we attempted a mechanochemical reaction between copper chloride and glutamic acid, we observed a few new peaks along

with reactants; the peaks were later identified to belong to **5**. Both **5** and **6** are 1-D coordination polymers crystallizing in the same chiral space group, $P2_12_12_1$

Scheme 2. Crystallization of 1-D coordination polymers engineered through the synthon $-\text{Cu}-\text{glutamate}-$. * Structure is identical to the phase already reported in the literature but obtained by a different route.¹⁹

Figure 5. Extended $-\text{Cu}$ -glutamate- $\text{Cu}-$ interactions are responsible for the occurrence of chiral coordination polymers in **5** and **6**. (a) In **5**, two independent helices occur, favoured through extended $-\text{Cu}$ -glutamate- $\text{Cu}-$ and $-\text{Cu}-\text{Cl}-\text{Cu}-$ running parallel to each other almost on the same plane (Hydrogen atoms and tail of glutamic acid are removed for clarity). (b) In **6**, the helices occur only through $-\text{Cu}$ -glutamate- $\text{Cu}-$ interactions as in solid **5**; however, the interaction is different in nature.

with an absolute structure parameter (Flack parameter) of ~ 0.00 . Crystal structures of **5** and **6** showed a remarkable self assembly induced by the counter anion as well as the organic ligand (figure 5). In **5**, two alternate helical chains are observed – one formed through extended $-\text{Cu}-\text{Cl}-\text{Cu}-$ and another through $-\text{Cu}-\text{L}-\text{Cu}-$. A significant characteristic is that both chloride and glutamate bridge adjacent copper ions forming two independent helical chains. Copper forms a chelate with N and a carboxylate oxygen while the other carboxylate oxygen is coordinated to a different copper thereby

leading to a helical chain (figure 5). The terminal carboxylic acid group of the amino acid stabilizes these sheets through a favourable H-bonding (figure 6). In **6**, the crystal structure shows a different helical chain. In this reaction, the building block during aggregation is $\{\text{Cu}(\text{glu})(\text{H}_2\text{O})_4\}^+$ with no Cl attached to copper. To compensate for charge compensation, the complex becomes zwitterionic releasing the proton from the terminal carboxylic acid group. Formation of 1-D

Figure 6. In **5**, the sheets containing the helices are further connected through a favorable H-bonding between the uncoordinated carboxylic acid unit and water molecule and oxygen coordinated to copper.

Figure 7. In **6**, the two sheets containing the helices are further connected through a favorable H-bonding one lattice water works as bridge between two coordinated water molecules.

Figure 8. Supramolecular condensation in solid **5** is analyzed through a retrosynthetic approach. The copper chelate, $\{\text{Cu}(\text{glu})\text{Cl}(\text{H}_2\text{O})_3\}$ is the building block in **5**. A favourable $-\text{Cu}-\text{glutamate}-\text{Cu}-$ and $-\text{Cu}-\text{Cl}-\text{Cu}-$ interactions are responsible for the particular assembly with a pair of independent helices observed in **5**.

Figure 9. Supramolecular condensation in solid **6** is analyzed through a retrosynthetic approach. The copper chelate, $\{\text{Cu}(\text{glu})(\text{H}_2\text{O})_4\}$ is the building block in **6**. The absence of Cl in the complex dictates a different assembly in **6**. Extended $-\text{Cu}-\text{glutamate}-\text{Cu}-$ is still the major directing force forming 1-D helical chains. In **6**, all carboxylate oxygens are involved in extended metal-ligand interactions.

helical chain is still a favourable direction to assemble. However, the system opts for the free carboxylate group at the tail for favourable coordination with neighbouring complex. To further strengthen the 1-D chains, a lattice water comes into play for efficient packing resulting in the overall composition for the solid **6** as $[\text{Cu}(\text{glu})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$. The structural chemistry of the solids **5** and **6** clearly demonstrate how a combination of different forces, a strong metal–ligand interaction and a directional weak H-bonding dictate the outcome of a crystallization reaction (figures 7, 8 and 9).

3.1 Magnetic properties

The temperature dependent magnetic susceptibilities of **5** and **6** were recorded over a range of 300–3K. χ_M^{-1} versus T plots for **5** and **6** are shown in figure 10. The observed effective magnetic moment at temperature 298 K for solid **5** and **6** are 2.58 and 2.14. The magnetic susceptibility data of **5** and **6** obey the Curie-Weiss law, $\chi_M = C/(T - \theta)$ ($C = 0.6730 \text{ emu mol}^{-1} \text{ K}$, $\theta = -10.80 \text{ K}$ for **5**, and $C = 0.5776 \text{ emu mol}^{-1} \text{ K}$, $\theta = -7.19 \text{ K}$ for **6**). The small Weiss constants in these complexes reveal the weak anti-ferromagnetic interactions. The magnetic moments calculated per copper(II) was found to be higher than the spin only value of 1.73 BM; this may be due to larger g values. A few coordination polymers show higher magnetic moments arising from g values greater than 2.0.²⁰ Detailed magnetic characterization on single crystals combined with ESR analysis and calculation is required to understand the origin of magnetic ordering in these compounds. It should be noted, a few non-molecular solids containing extended –Cu–Cl–Cu– chains seem to show interesting magnetic ordering: CuCl_2 is multi-ferroic²¹ and paratacamite, $[\text{Cu}_2\text{Cl}(\text{OH})_3]$ is ferrimagnetic below 2K.²²

Figure 10. Plot of χ_M^{-1} versus T for the solids **5** and **6**.

4. Conclusion

The examples described in this paper illustrate the importance of analyzing intermolecular interactions responsible for the isolation of a crystal from mother liquor. Metal–X (X-halide, sulphate, etc.) interactions are competitive synthons to produce extended structures or non-molecular solids and can be judiciously exploited to obtain desirable CPs and MOFs. Retro synthetic analysis provides chemical insights into the operation of various intermolecular forces which assemble a particular crystal structure. Influence of pH and metal source and participation of innocent species present in the mother liquor including solvent molecules in the supramolecular assembly may become obvious once we identify the chemically reasonable building blocks.

Supplementary Information

For supplementary information, see www.ias.ac.in/chemsci.

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