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Notes

Synthesis of a new polymorph in [Cu(pyridine-2-carboxylate)$_2$] system

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Single crystal X-ray studies on a doubly carboxylate bridged $\{[Cu(pic)_2].2H_2O\}_n$ **(1)** (pic = pyridine-2-carboxylate) polymeric chains extending along the crystallographic *a* axis reveal that adjacent polymeric chains are joined by the lattice water chains running parallel to the polymeric chain leading to a 2D sheet in the (101) plane. The successive sheets are interdigitated and glued to each other by a novel C=O…π interaction into a 3D supramolecular motif. The complex **(1)** can be regarded as a pseudo-polymorph of $[Cu(pic)_2]_n$ which has been realized in two forms, violet **(2)** and blue-violet **(3)** from methanol.

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Crystals are 'supermolecules par excellence'[1]. Various molecular building blocks optimally pack in the crystalline solid state through preferred aggregation pattern called 'supramolecular synthon'. This molecular recognition is achieved through various weak, coordinative and covalent forces. Though most often this recognition pattern leads to unique lowest energy assembly in the solid state, sometimes variation in this recognition pattern leads to a number of assemblies which are closely spaced in energy giving rise to polymorphic systems. Polymorphism is the most challenging phenomena in crystal engineering but when polymorphs can be produced in a controlled manner they can provide detailed information regarding the molecular recognition pattern and the self-assembly process. Control of polymorphism has been achieved in various ways amongst which tuning of solvent [2] and control of *p*H [3] are important means of doing this.

There is hardly a compound which has raised more interest than water because of its fundamental importance[4]. Water molecules interact through strong hydrogen bonding which are highly directional and cooperative in nature. In recent years, there has been extensive investigation on the hydrogen bonded structure of ordered water clusters within the crystal hydrates and among these one-dimensional (1D) water topology has drawn a great deal of attention because of the possibility of using these systems as models for various fundamental biological processes such as transport of water, protons, and ions[5]. While 1D water chains are prevalent in many biological systems, it is extremely difficult to construct them artificially because the structural constraints required in stabilizing 1D water chains are yet to be fully understood. Only a few reports describe the formation of 1D water chains in synthetic hosts[6]. Therefore, structural investigations of 1D hydrogen-bonded water chains in various environments should be explored more extensively to better understand the structural constraints and the intrinsic nature of the 1D water chains.

Again, picolinic acid, generated in liver and kidneys is regarded as an important chelating agent. In recent years, research on transition metal chemistry of picolinic acid is receiving special attention from the pharmacological point of view, as useful systems to trace element supplementation or for the design of new metallopharmaceuticals[7].

Very recently a polymorphic systems having formula $[Cu(pic)_2]$ has been realized in two forms, violet[8] **(2)** and blue-violet[9] **(3)**, both of which have been synthesized in methanol solvent starting from different precursor materials. In an attempt to screen out other polymorphs of the same system we have used water as solvent. We report herein another polymorph, a blue variety **(1)**, which is established to be a pseudo-polymorph of the same system.

Experimental

Starting materials for the synthesis of **(1)**, i. e., pyridine-2-carboxylic acid (Aldrich), $CuCl_2.2H_2O$ (A.R. Loba, India) and NaOH (Merck India) were of reagent grade and used as received. Doubly distilled water was used as the reaction medium.

Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Infrared spectrum (400–4000 cm^{-1}) was recorded from KBr

pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. TGA and DTA curves were recorded simultaneously on a Perkin-Elmer (model Pyris Dimond) TG / DTA instrument in static dry nitrogen at the heating rate of 5 °C min^{-1}.

Synthesis of complex (1)

The complex **(1)** was prepared by reacting 2-picolinic acid (0.050 g, 0.4 mmol) with $CuCl_2.2H_2O$ (0.034g, 0.2 mmol) in water medium (25mL) at *p*H ~5, adjusted by adding 1 *M* NaOH, and refluxing for 4 hours. Blue rod-shaped crystals of **(1)** suitable for X-ray analysis were obtained after one week. Yield 5of the product was 6 % based on $[Cu(pic)_2]. 2H_2O$. Anal. Calcd. (%) for $C_{12}H_8CuN_2O_4$, $2(H_2O)$ (343.79): C, 41.89; H, 3.49; N, 8.14; Found (%): C, 41.88; H, 3.56; N, 8.10.

Crystallographic data

The diffraction data for **(1)** were collected at 120(2) K on a four-circle diffractometer KM-4 (KUMA Diffraction, Poland) with a CCD detector equipped with an Oxford Cryostream Cooler (Oxford Cryosystems, UK), using monochromated Mo-K_α radiation (k = 0.71073Å) (monochromator Enhance, Oxford Diffraction, UK). The ω-scan technique with different κ and φ offsets for covering an independent part of reflections in the 3.13°–25° range was performed. The cell parameters were refined from all strong reflections. The data reductions were carried out using the CrysAlis RED (Oxford Diffraction, UK) program and analytical absorption corrections were applied. The structure was determined by direct methods and SHELXL-97[10] and refined anisotropically on F^2 using full-matrix least-squares procedure by SHELXL-97[11]. The data for publication were prepared by SHELXL and PARST[12]. Crystal data and refinement parameters of **(1)** one given in Table 1.

Results and discussion

The title complex, $\{[Cu(pic)_2].2H_2O\}_n$ **(1),** was prepared by reacting picolinic acid with $CuCl_2.2H_2O$ in water at *p*H ~5.0 maintained by adding 1 *M* NaOH solution and refluxing for 4 hours. Blue rod-shaped crystal of **(1)** was characterized by single- crystal X-ray structure analysis.

The complex **(1)** remained thermally stable at room temperature (≤ 30 °C) for an indefinite period of time, after which the compound underwent a gradual weight loss of 4.04 % on heating in the temperature range 75-120 °C with a small endo-peak at 83 °C

Table 1—Crystal data of $\{[Cu(pic)_2].2H_2O\}_n$ **(1)**

Formula	$C_{12}H_8CuN_2O_4$. $2(H_2O)$
Formula wt.	343.79
Crystal system	Triclinic
Space group	P-1 (No 2)
a, *b*, *c* (Å)	5.090(2) 7.480(4) 9.067(6)
α, β, γ (°)	75.89(5) 84.94(5) 71.96(4)
V (Å)	318.3(3)
Z	1
D(calc.) (g/cm^3)	1793
μ (mm^{-1})	1747
F(000)	175
Temp. (K)	120(2)
Radiation (Å)	MoKα [0.71073]
θ Min-Max (°)	4.1, 25.0
Total unique data, *R*(int)	2129, 1108, 0.012
Obs. data [$I > 20\ \sigma(I)$]	1086
R, wR_2, *S*	0.0281, 0.0763, 1.13

$w=1/[\sigma^2(Fo^2) + (0.040P)^2 + 0.500P]$, where $P= (Fo^2+2Fc^2)/3$

indicating the loss of *ca.* one water molecule, followed by another slow weight loss of ~ 4.4% up to temperature 290 °C indicating the loss of a second water molecule. From the gradual loss of water molecules occurring between 80 and 290 °C, it could be concluded that the water molecules are strongly hydrogen-bonded. The compound decomposed immediately after the removal of the second water molecule showing a large endo-thermal peak at *ca*. 310 °C in the DTA curve.

The IR spectrum of **(1)** showed stretching vibrations of the coordinated carboxylate groups at $\nu_{as}(COO)$ = 1610 cm^{-1} and $\nu_s(COO)$ = 1486 cm^{-1} with $\Delta\nu$ (COO^-) = 124 cm^{-1}, clearly indicating a bis-bidentate bonding nature of carboxylate group in the picolinate ligand[13-14,]. A broad peak observed at ~ 3300 cm^{-1} is due to the presence of water molecules.

Crystal structure of (1)

The crystal data of **(I)** are given in Table 1. The crystals of the title compound contain 1D–chain structure, in which the Cu(II) ions are chelated by two picolinate ions via their N,O donor atoms. The copper(II) centre in **(1)** (Fig. 1) has a distorted octahedral environment in which the basal plane is occupied by O1 oxygen atom, N7 nitrogen atom and their symmetry related , O1* and N7* (*= 1-*x*,1-*y*,1-*z*) of two picolinate ions. The axial positions are occupied by the carbonyl O2 atoms of picolinate from two adjacent Cu^{II} units. This gives rise to a doubly carboxylate bridged Cu^{II} polymeric chains which extends along the crystallographic *a* axis (Fig. 2). In

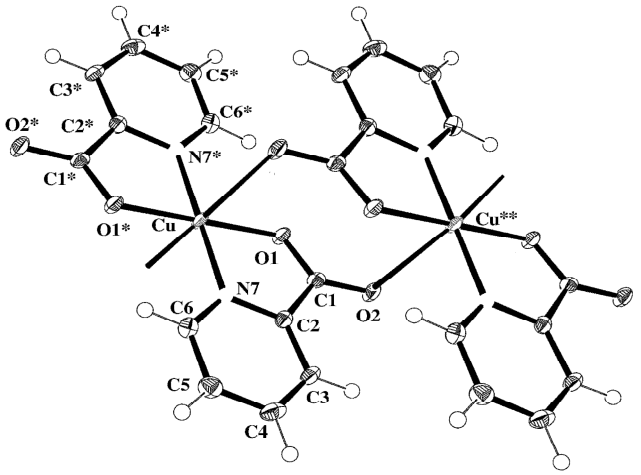

Fig. 1—ORTEP view of carboxylato- bridged $\{[Cu(pic)_2]\ 2H_2O\}_n$ (**1**) polymer.

the basal plane of the octahedron, (N7; N7*) and (O1; O1*) are mutually *trans*- to each other. The Cu-N7 (1.951(2) Å) and Cu-O1 (1.940(2) Å) distances are virtually identical but the axial Cu-O2** (2.692(3) Å) (** = -1+ *x, y, z*) distance is appreciably elongated. Cu-O1 distance is significantly shorter than the Cu-O2 distance, reflecting in part, the difference in donor strengths of the O1 and O2 atoms. Respective bond angles are O2**-Cu-O1 = 94.99(8)°, O1-Cu-O1* = N7-Cu-N7* = 180°, N7-Cu-O2** = 91.00(9)° (Table 2). The distance between successive Cu(II) centers along the polymeric chain is 5.090 Å. Bond distances and bond angles of (**1**) are given in Table 2.

Successive polymeric chains are glued to each other through lattice water assisted hydrogen bonding giving rise to supramolecular sheets (Fig. 2) in the (101) plane. In this cooperative interaction lattice water molecules (O21) in turn are nicely arranged into one dimensional *zig-zag* water chains. A particular water chain runs parallel in between two Cu-picoline coordination polymeric chains along the crystallographic *a* axis and are hydrogen bonded to the carboxylate oxygen atoms (O2) on either side of the polymeric chains. Water molecules act as donors and the carboxylate oxygen atoms act as acceptors. Along a particular water chain, distances between adjacent oxygen atoms are not unique; instead alternate successive oxygen atoms are separated by 2.784(4) Å [O21…O21* (*=3-x,1-y,-z)] and 2.815(4) Å [O21…O21** (**=2-*x*,1-*y*,1-*z*)] respectively. The contact distance between the water chain and the coordination polymeric chain [(O21)…(O2)] is 2.895(4)Å. The water stitched to supramolecular

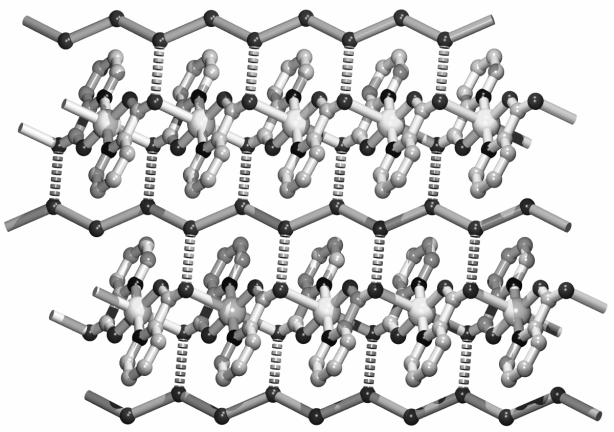

Fig. 2—Two-way zipping of coordination polymeric chains into a 2D supramolecular sheet by one dimensional chain of water molecules in **(1).**

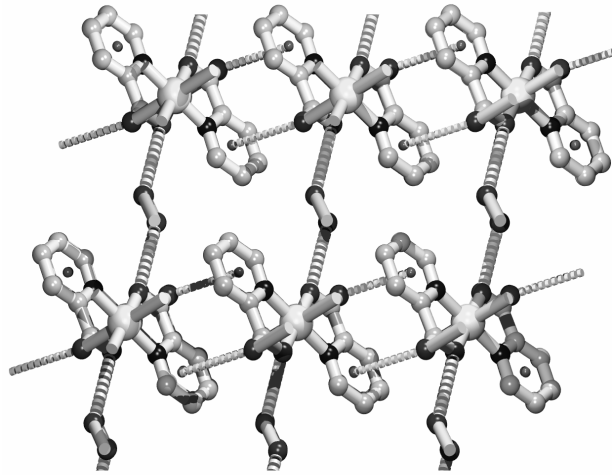

Fig. 3—The role of C=O… π interaction in the packing of successive water stitched supramolecular sheets in (1).

Table 2—Selected bond distances (Å) and bond angles (°) in $\{[Cu(pic)_2].2H_2O\}_n$ **(1)**

Bond distances (Å)			
Cu -O1	1.940(2)	Cu -O2_a	2.692(3)
Cu -N7	1.951(2)	Cu -O1_c	1.940(2)
Cu -N7_c	1.951(2)	Cu -O2_d	2.692(3)
Bond angles (°)			
O1 -Cu -N7	83.89(9)	O1 -Cu -O2_a	94.99(8)
O1 -Cu -O1_c	180.00	O1 -Cu -N7_c	96.11(9)
O1 -Cu -O2_d	85.01(8)	O2_a -Cu -N7	91.00(9)
O1_c -Cu -N7	96.11(9)	N7 -Cu -N7_c	180.00
O2_d -Cu -N7	89.00(9)	O1_c -Cu -O2_a	85.01(8)
O2_a -Cu -N7_c	89.00(9)	O2_a -Cu -O2_d	180.00
O1_c -Cu -N7_c	83.89(9)	O1_c -Cu -O2_d	94.99(8)
O2_d -Cu -N7_c	91.00(9)		

Translation of symmetry code to equiv positions: *a* = -1+*x, y, z*; *c* = 1-*x*, 1-*y*, 1-*z*; *d* = 2-*x*, 1-*y*, 1-*z*.

Table 3—Comparison of complexes **(1)**, **(2)** and **3** on the structural aspects

	$\{[Cu(pic)_2].2H_2O\}_n$(**1**)	$[Cu(pic)_2]$ (**2**)	$[Cu(pic)_2]$ (**3**)
Formula	$C_{12}H_8CuN_2O_4,2(H_2O)$	$C_{12}H_8N_2O_4Cu$	$C_{12}H_8N_2O_4Cu$
Formula wt.	343.79	307.74	307.74
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1 (No 2)	$P2_1/c$	$P2_1/c$
a, *b*, *c* (Å)	5.090(2), 7.480(4), 9.067(6)	3.697(7), 11.989(19), 11.888(19)	5.163(2), 24.658(6), 8.452(2)
α, β, γ (°)	75.89(5), 84.94(5), 71.96(4)	91.108(14)	92.22(3)
V (Å^3)	318.3(3)	526.92(15)	1075.2(6)
Z	1	2	4

sheets are stacked along the crystallographic *b* axis. In this stacking arrangement, successive step like sheets are interdigitated and glued to each other in a novel way, C=O…π interaction [O2…Cg3 = 3.59 Å], in which the carboxylate oxygen atom (O2) and the picoline pyridine ring interact (Fig. 3) forming a (O… π; π…O) closed synthon[15]. Though relatively scarce, C=O…π interaction has been seen to play an important role in the self-assembly of crystalline materials on several occasions[12], even though it is assumed to be much weaker than other non-covalent forces. It is interesting to note that though π...π interaction sites are available on picolinic acid moieties, no such interaction comes into play in the present complex. Instead, the sheets are stacked by C=O…π interaction. It is important to mention in this context that two identical complexes[8, 9], i.e., **(2)** and **3,** from the same building blocks have been reported recently that are found to be polymorphic to each other (Table 3). The present complex **(1)** is actually another analogous compound of the same system. Studies of polymorphic systems are of immense importance in crystal engineering because these systems provide valuable information regarding the various possible ways weak forces can cooperate to give different polymorphs. While carboxylato bridging of $[Cu(pic)_2]$ units give rises to polymeric chains in **(3)**, the $[Cu(pic)_2]$ units in **(2)** remains monomeric and interact with each other through weak C-H…O hydrogen bonding giving rise to 2D supramolecular sheets (Fig. 4) in the [-204] plane. These sheets are stacked on top of each other due to the cuprophilic interactions among the Cu centers on successive sheets. Cu…Cu separation between these sheets is 3.69Å due to this interaction. On the other hand, complex **(3)** like **(1)** is again a carboxylato bridged coordination polymer but in sharp contrast to **(2)**, π…π interaction[16] is responsible for the packing

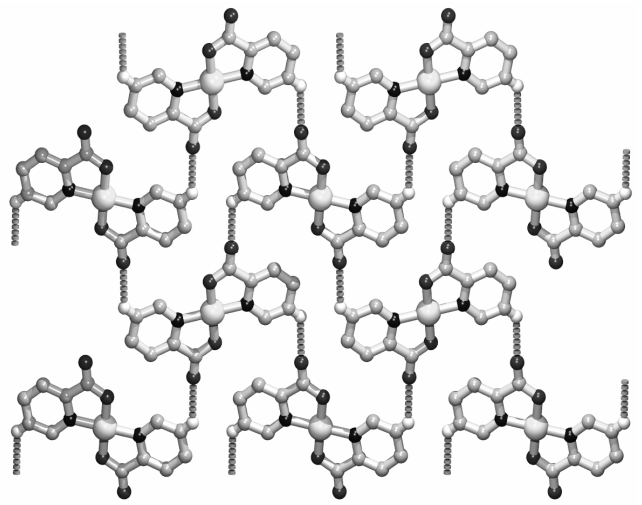

Fig. 4—C-H…O hydrogen bonded 2D sheet of **(2).**

of the polymeric chains now. In both **(3)** and **(1)** the picolinate ligand bridges successive Cu(II) units leading to coordination polymers, with the axial Cu-O bond distance being appreciably longer than the equatorial Cu-O distances. Flexibility of the Cu(II) coordination environment has led to polymeric chains in **(3)** and **(1)**, as against monomeric units of **(3)**, which have a square planar Cu(II) coordination environment. In this sense, the present system of three complexes is an interesting example which shows, not only the variation of weak forces but also a subtle interplay of coordinative and weak forces which may sometimes be responsible for the appearance of polymorphism. While complexes **(2)** and **(3)** were synthesized from non-aqueous solvent, **(1)** was deliberately synthesized from aqueous medium with an intention to study the effect of water molecules on the self-assembly. Complex **(1)** interestingly reveals that water has tremendous effect on the self-assembly

of the molecular components. Instead of weak C-H…O hydrogen bonding as in **(2)**, water molecules act as strong hydrogen bond donor for strong carboxylate acceptor in **(1)**. The polymeric chains are glued by a unique zig-zag 1D water chain and the assembly of the water chain has been templated by the coordination polymer itself. The resulting 2D sheets are stacked by a novel C=O…π interaction in **(1)**, as compared to Cu…Cu and π…π interactions in **(2)** and **(3)** respectively.

In summary, studies of the present system originating from simplest building blocks reveal how finely balanced the self-assembly process is due to subtle interplay of not only multiple non-covalent interactions but also interaction between non-covalent and coordinative forces. Our study also shows how water molecules can decisively influence the molecular self-assembly and the possibility of screening out a particular complex through the choice of proper solvent. Studies of one-dimensional water chains have recently drawn great attention due to their possible use as model for various biological processes such as in proton wires, transport of water molecules through cell walls. In this respect, studies of **(1)** provide us with important clues towards the ordered environment required for the formation of such water chains in an artificial system.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, Cb2 1EZ, UK. (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk) and are available on request by quoting the deposition number CCDC 656610.

Acknowledgement

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16 Cg(4)…Cg(4)* distance is 4232(7)Å [*=X,1/2-Y,-1/2+Z], dihedral angle is 6.24° and Cg(4)…Cg(4)** distance is 4.231(7)Å [**=X,1/2-Y,1/2+Z], and dihedral angle is 6.24°.