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Segregated self-assembly and pillaring action of aliphatic dicarboxylic acids in the super structure of Cu–picolinate complexes

Chaitali Biswas [a,b], Atish Dipankar Jana [c], Michael G.B. Drew [d], Golam Mostafa [c,*], Ashutosh Ghosh [a,*]

[a] Department of Chemistry, University College of Science, University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India
[b] Sarojini Naidu College for Women, 30, Jessore Road, Kolkata 700 028, India
[c] Department of Physics, Jadavpur University, Kolkata 700 032, India
[d] School of Chemistry, The University of Reading, P.O. Box 224, Whiteknights, Reading RG6 6AD, UK

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ABSTRACT

Three new supramolecular assemblies of co-crystallized metal complexes and aliphatic dicarboxylic acids, $\{[Cu(pic)_2(H_2O)_2](H_2mal)\}_n$ (**1**), $\{[Cu(pic)_2(H_2O)_2](H_2mal)_2(H_2O)_2\}_n$ (**2**) and $\{[Cu(pic)_2(MeOH)](H_2succ)\}_n$ (**3**) {Hpic = 2-picolinic acid, H_2mal = malonic acid and H_2succ = succinic acid} have been synthesized and characterized by X-ray single-crystal structure determination. The crystal packings of the complexes reveal that supramolecular associations of the monomeric complex units lead to the formation of layers through hydrogen bonding. In all the complexes, the dicarboxylic acid units connect the 2-D layers to act as pillars. The interaction between water molecules and the dicarboxylic acid plays an important role in the overall supramolecular assembly.

1. Introduction

Self-assembly of molecular components give rise to composite molecular aggregates with specific structures and activities, and is at the heart of various biological processes which are very sophisticated and complex. The first step in understanding these complicated processes is to unravel the interplay of non-covalent interactions [1–3] (such as hydrogen bonding, π–π, C–H···π, C–H···O, metal–π interactions, etc.) that are responsible for crystal or solid formation.

The dicarboxylic acids [HOOC–$(CH_2)_n$–COOH] represent supramolecular connectors that can generate infinite high-dimensional networks through complementary hydrogen bonds involving a variety of basic building blocks such as amines, dipyridines and pyrazins, and their analogues have been documented recently [4–6]. However, there are only a very few examples where dicarboxylic acid molecules and metal complexes are used as supramolecular building blocks [7,8].

Cu–picolinate complexes are simple systems [9], but the reported self-assembled structures of this system are diverse [10–13], and the controlling factors pertaining to the robust features of the self-assembly can be only explored through a systematic study. In the present study we have adopted the principle of co-crystallization [14–16] by choosing aliphatic dicarboxylic acids in the Cu–picolinate system bearing a complementarity relationship. Co-crystallization is an emerging area of research, despite appearing in the literature for a considerable time under various guises, and has provided a venue for the practical application of crystal engineering. A co-crystal is a crystalline material made up of two or more components [17–20], usually in a stoichiometric ratio, each component being an atom, ionic compound or molecule. Numerous authors have investigated the co-crystallization of carboxylic acid-functionalized molecules with organic derivatives [21–26], but examples utilizing inorganic derivatives are scant [7,8]. Generally, these studies focus on the isolation of organic co-crystals, giving less emphasis to metal-containing co-crystal systems. Here, we are concerned with co-crystals of dicarboxylic acids with the [Cu(picolinate)$_2$(H_2O)$_2$] moiety to understand the role of non-covalent interactions occurring in the solid-state structure.

We are reporting in this paper three co-crystal supramolecular assemblies, $\{[Cu(pic)_2(H_2O)_2](H_2mal)\}_n$, $\{[Cu(pic)_2(H_2O)_2](H_2mal)_2(H_2O)_2\}_n$ and $\{[Cu(pic)_2(MeOH)](H_2succ)\}_n$, of Cu(pic)$_2$ (Hpic = 2-picolinic acid) with malonic acid (H_2mal) or succinic acid (H_2succ = succinic acid). The effect of the short malonic acid and relatively longer and flexible succinic acid in the self-assembled structures is investigated. We also report the effect of the increased concentration of dibasic acids and discuss the effect of the solvent on the self-assembly.

* Corresponding authors.
E-mail addresses: mostafa@phys.jdvu.ac.in (G. Mostafa), ghosh_59@yahoo.com (A. Ghosh).

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2. Experimental

2.1. Reagents

All chemicals were commercial products of reagent grade and were used without further purification.

2.2. Preparations

2.2.1. Synthesis of $\{[Cu(pic)_2(H_2O)_2](H_2mal)\}_n$ (**1**)

A methanol solution (30 ml) of copper(II) malonate (1.859 g, 5 mmol) was mixed with a methanol solution (10 ml) of 2-picolinic acid (0.615 g, 5 mmol) followed by the addition of a methanol solution (5 ml) of malonic acid (0.520 g, 5 mmol). The resultant mixture was refluxed for ca. 2 h and then allowed to cool to ambient temperature. The resulting solution was filtered to remove a small amount of $Cu(pic)_2$ that separated out immediately, and the filtrate was kept at room temperature. Blue colored single crystals suitable for X-ray analysis were obtained from the filtrate after several days.

Yield: 1.30 g (58%) based on Cu. *Anal.* Calc. for $C_{15}H_{16}CuN_2O_{10}$: C, 40.23; H, 3.60; N, 6.26. Found: C, 40.45; H, 3.47; N, 6.58%. μ_{eff} = 1.75 BM (per copper ion); IR (KBr, cm^{-1}): 3391 for υ(O–H), 2927 for υ(C–H), 1708 for υ(C–O of COOH), 1628 and 1601 for υ(C–O and C–C), 1568 for υ(C–N) and 1400 for υ(C–H). λ_{max} (solid, reflectance): 675 nm.

2.2.2. Synthesis of $\{[Cu(pic)_2(H_2O)_2](H_2mal)_2(H_2O)_2\}_n$ (**2**)

Complex **2** was obtained by following a similar procedure to that of **1**, but 10 mmol of malonic acid were added in place of 5 mmol. Dark blue colored single crystals suitable for X-ray analysis were obtained from the filtrate after two weeks.

Yield: 1.62 g (55%) based on Cu. *Anal.* Calc. for $C_{18}H_{24}CuN_2O_{16}$: C, 36.77; H, 4.11; N, 4.76. Found: C, 36.96; H, 4.23; N, 4.59%. μ_{eff} = 1.77 BM (per copper ion); IR (KBr, cm^{-1}): 3385 for υ(O–H), 2960 for υ(C–H), 1714 for υ(C–O of COOH), 1628 and 1603 for υ(C–O and C–C), 1571 for υ(C–N), 1477 for υ(C–H). λ_{max} (solid, reflectance): 680 nm.

2.2.3. Synthesis of $\{[Cu(pic)_2(MeOH)](H_2succ)\}_n$ (**3**)

This was synthesized by following a similar procedure to that adopted for **1**, but using a methanol solution of succinic acid (5 mmol, 0.590 g) instead of a methanol solution of malonic acid. Overnight, light-blue single crystals of **3**, suitable for X-ray diffraction, were obtained.

Yield: 1.24 g (54%) based on Cu. *Anal.* Calc. for $C_{17}H_{18}CuN_2O_9$: C, 44.59; H, 3.96; N, 6.12. Found: C, 44.45; H, 3.07; N, 6.15%. μ_{eff} = 1.71 BM (per copper ion); IR (KBr, cm^{-1}): 3441 for υ(O–H), 2931 for υ(C–H), 1699 for υ(C–O of COOH), 1642 and 1600 for υ (C–O and C–C), 1475 for υ(C–H). λ_{max} (solid, reflectance): 688 nm.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240 C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurements were done with an EG&PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants. Thermal analyses (TG-DTA) were carried out on a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate = 30 cm^3 min^{-1}). The samples were heated in an alumina crucible at a rate of 10 °C min^{-1}.

2.4. X-ray crystallography

Data were measured with Mo Kα radiation at 150 K using an X-Calibur CCD diffractometer from Oxford Instruments. The crystals were positioned at 50 mm from the CCD and 330 frames were measured with a counting time of 10 s. Data analysis was carried out with the Crysalis program [27] to provide 2626, 6071 and 5048 independent reflections, respectively. The structures were solved using direct methods with the SHELX97 program [28]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. All the hydrogen atoms bonded to oxygen were located in difference Fourier maps and refined with distance constraints. The structures were refined on F^2 using SHELX97 [28]. Crystal data for the three crystals are given in Table 1.

3. Results and discussion

3.1. Synthesis of the complexes

To construct the hydrogen-bonded molecular self-assemblies of $Cu(pic)_2$ with aliphatic dicarboxylic acids we dissolved the individual components, copper salts (malonate or succinate), picolinic acid and the corresponding dicarboxylic acid (H_2mal or H_2succ) in methanol in 1:2:1 ratios. The complex compound $Cu(pic)_2$, which is formed immediately by the reaction of the Cu(II) salts and picolinic acid, remains in solution in the acidic pH of the resulting solution and the desired supramolecular H-bonded assemblies **1** and **3** were separated out on slow evaporation of methanol. In order to investigate the possibility to obtain any other assembly, we increased the proportion of the respective dicarboxylic acid in solution and got crystals of compound **2** when the H_2mal:$Cu(pic)_2$ ratio was 2:1 or higher. For H_2succ we did not get any compound other than **3**, even on increasing the H_2succ:-$Cu(pic)_2$ ratio up to 5:1.

3.2. Crystal structures of complexes

X-ray crystallographic analysis reveals that all three structures consist of a copper complex containing two bidentate 2-picolinate ligands in an equatorial plane, together with 1 or 2 solvent molecules weakly bound in axial positions. In addition, in each case a dicarboxylic acid co-crystallises with the complex but is not bonded to the metal, instead it forms a hydrogen-bonded network

Table 1
Summary of crystallographic data for the complexes.

	1	**2**	**3**
Formula	$C_{15}H_{16}CuN_2O_{10}$	$C_{18}H_{24}CuN_2O_{16}$	$C_{17}H_{18}CuN_2O_9$
Formula weight	447.84	587.93	457.87
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.1202(9)	7.3145(9)	6.822(6)
b (Å)	12.941(2)	11.0404(14)	10.7410(10)
c (Å)	22.727(4)	15.5565(19)	14.0073(14)
α (°)	90	87.772(10)	69.877(9)
β (°)	90.76(1)	82.276(10)	78.855(8)
γ (°)	90	72.054(11)	72.183(9)
V (Å^3)	1799.9(5)	1184.3(3)	918.43
Z	4	2	2
D_{calc} (g cm^{-3})	1.653	1.649	1.656
μ (mm^{-1})	1.273	1.007	1.245
R [$I > 2\sigma(I)$]	0.0480	0.0643	0.0432
Temperature (K)	150	150	150

Table 2
Selected bond lengths (Å) and angles (°) for the complexes.

	1	2	3
Cu(1)–O(100)	2.497(2)	2.538(2)	2.312(9)
Cu(1)–N(11)	1.987(2)	1.966(3)	1.969(10)
Cu(1)–O(18)	1.944(2)	1.943(2)	1.953(8)
Cu(1)–O(200)	–	2.574(2)	–
Cu(1)–N(21)	–	1.955(3)	1.968(10)
Cu(1)–O(28)	–	1.963(2)	1.948(8)
O(18)–Cu(1)–N(11)	83.6(1)	83.6(1)	83.4(4)
O(18)–Cu(1)–O(100)	91.3(1)	92.1(1)	98.9(4)
O(18)–Cu(1)–O(28)	–	177.3(1)	169.5(4)
O(18)–Cu(1)–N(21)	–	94.2(1)	95.8(4)
O(18)–Cu(1)–O(200)	–	88.7(1)	–
N(11)–Cu(1)–O(100)	90.1(1)	89.0(1)	91.9(4)
N(11)–Cu(1)–O(28)	–	98.9(1)	97.0(4)
N(11)–Cu(1)–N(21)	–	177.7(1)	177.2(4)
N(11)–Cu(1)–O(200)	–	92.2(1)	–
O(100)–Cu(1)–O(28)	–	89.1(1)	91.6(4)
O(100)–Cu(1)–N(21)	–	90.3(1)	90.9(4)
O(100)–Cu(1)–O(200)	–	178.6(1)	–
O(28)–Cu(1)–N(21)	–	83.3(1)	83.3(4)
O(28)–Cu(1)–O(200)	–	90.1(1)	–
N(21)–Cu(1)–O(200)	–	88.5(1)	–

Table 3
Hydrogen bonding interactions (Å, °) for complexes **1**–**3**.

Complex	D–H···A	D–H	H···A	D···A	<D–H···A
1	O100–H1···O19[a]	0.89	1.82	2.702(3)	173(3)
	O100–H2···O19[b]	0.86	1.90	2.709(3)	158(3)
	O91–H91···O100	0.84	1.73	2.567(3)	172(2)
2	O100–H1···O19[c]	0.85	1.93	2.741(3)	160(3)
	O100–H2···O18[d]	0.85	2.49	3.253(3)	151(3)
	O100–H2···O19[d]	0.85	2.01	2.771(3)	150(3)
	O200–H3···O29[e]	0.84	1.92	2.756(3)	176(3)
	O200–H4···O28[f]	0.86	1.93	2.787(3)	176(3)
	O300–H5···O59[d]	0.85	2.05	2.824(5)	153(4)
	O300–H6···O44	0.86	1.91	2.756(4)	168(3)
	O400–H8···O54	0.85	1.91	2.739(4)	165(3)
	O43–H43···O200	0.86	1.73	2.576(4)	165(4)
	O48–H48···O300[g]	0.72	1.89	2.589(4)	162(6)
	O53–H53···O100	0.85	1.75	2.592(4)	172(5)
	O58–H58···O400[h]	0.72	1.91	2.611(4)	166(5)
3	O73–H73···O29	0.83	1.77	2.585(2)	166(3)
	O78–H78···O77[i]	0.84	1.84	2.678(3)	180(6)
	O81–H81···O19[j]	0.82	1.88	2.682(2)	165(3)
	C15–H15···O29[k]	0.93	2.49	3.345(5)	153
	C25–H25···O19[l]	0.93	2.44	3.314(3)	157

Symmetry elements: [a] = 1 + *x*, *y*, *z*; [b] = 1 − x, −*y*, 2 − *z*; [c] = 1 + *x*, *y*, *z*; [d] = 1 − *x*, 2 − *y*, 1 − *z*; [e] = −1 + *x*, *y*, *z*; [f] = 2 − *x*, 1 − *y*, 1 − *z*; [g] = 1 − *x*, 1−*y*, 2 − *z*; [h] = 2 − *x*, 2 − *y*, −*z*; [i] = 1 − *x*, 1 − *y*, −1 − *y*; [j] = 1 − *x*, 1 − *y*, −*z*; [k] = *x*, 1 + *y*, *z*; and [l] = *x*, −1 + *y*, *z*.

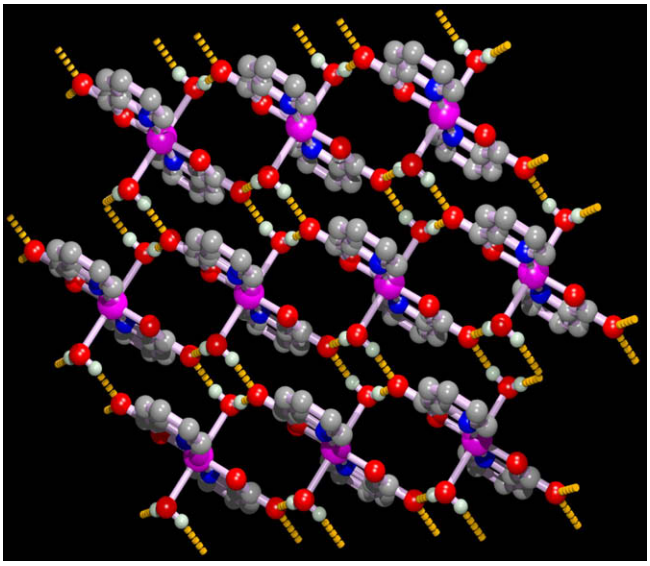

Fig. 2. The supramolecular layer of $[CuL_2(H_2O)_2]$ units through the formation of $R_4^2(8)$ synthons.

with the complex. Dimensions in the metal coordination spheres are given in Table 2, with details of the hydrogen bond networks in Table 3.

*3.2.1. Structure of {[Cu(pic)$_2$(H$_2$O)$_2$](H$_2$mal)}$_n$ (**1**)*

The ORTEP diagram (Fig. 1) reveals that the asymmetric unit of **1** consists of a half of a Cu atom, a 2-picolinate molecule and half of the malonic acid molecule. The metal complex $[Cu(pic)_2(H_2O)_2]$ is situated on a centre of symmetry. The two bidentate 2-picolinate ligands occupy the equatorial plane, coordinated by the pyridine N atoms (N11) and the carboxylate O atoms (O18) with Cu–N and Cu–O bond lengths as expected, being 1.987(2) and 1.944(2) Å, respectively. There are water molecules (O100) in axial positions at 2.497(2) Å. One of the carboxylate oxygen atoms (O19) remains uncoordinated and acts as hydrogen bond acceptor site for the uncoordinated malonic acid donor molecule, which has a crystallographic twofold axis through the central carbon atom.

The supramolecular association of the monomeric units through hydrogen bonding leads to layers (*ab* plane) of $[Cu(pic)_2(H_2O)_2]$ monomeric units, in which the adjacent monomers are united through coordinated water mediated hydrogen bonding. Water molecules in association with the uncoordinated picolinate carboxylate oxygen atoms (O19) form a $R_4^2(8)$ hydrogen bonding synthon [29–32]. Diagonally opposite corners of this rectangular

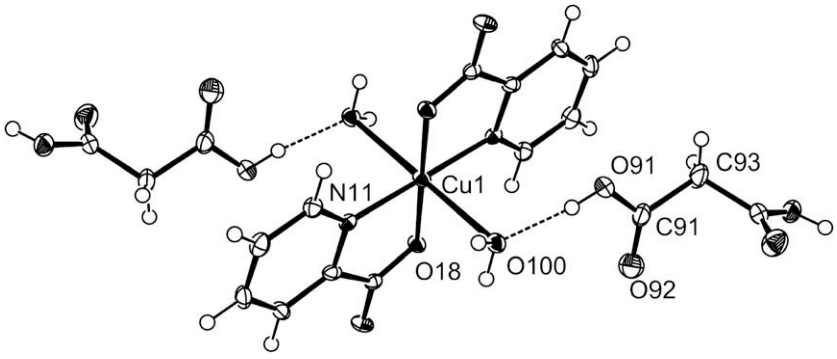

Fig. 1. The structure of **1** with ellipsoids at 50% probability. Hydrogen bonds shown as dotted lines.

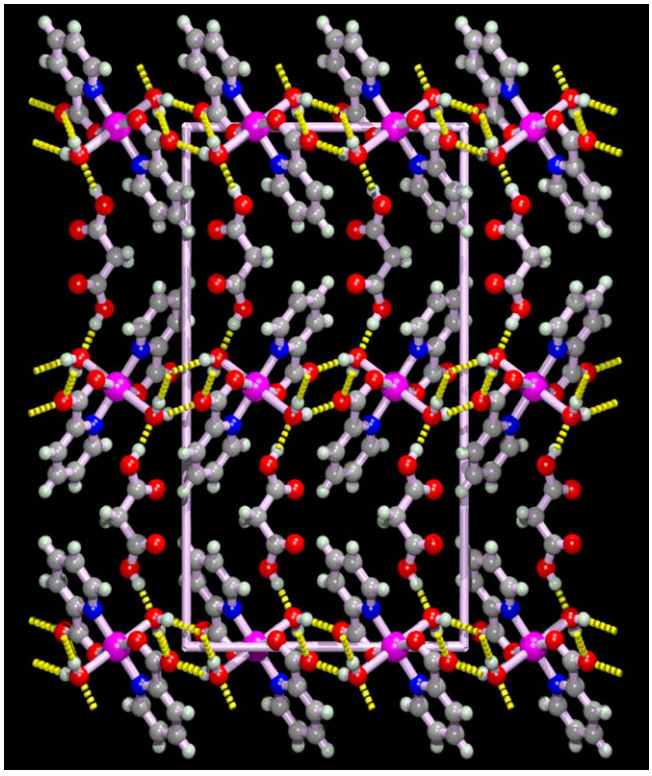

Fig. 3. Pacing of successive $[CuL_2(H_2O)_2]_n$ layers. Malonic acid molecules act as pillars separating the layers.

motif are occupied by water molecules (O100) and picolinate carboxylate O19 atoms, respectively (Table 3), and these form an infinite two-dimensional four-connected sublayer 4^4-net along the [1 1 0] direction (Fig. 2). The copper–copper distances within this 4^4-net are 11.23 and 6.12 Å. In this supramolecular assembly the malonic acid molecule is attached directly to the coordinated water molecule O(1 0 0) of the Cu–picolinate moiety, through an O–H···O H-bond, exhibiting the recognition phenomenon of the dicarboxylic acid by the neutral coordination complex.

Successive $[Cu(pic)_2(H_2O)_2]_n$ layers are stacked (along the *c*-axis) in such a way that malonic acid units connect them in a one to one fashion by acting as hydrogen bond donors to coordinated water molecules on adjacent layers. The malonic acid molecules thus act as pillars between the layers (Fig. 3, Table 3). A characteristic of this structure is that all the available hydrogen bond donors and acceptors are engaged in a fully supramolecular assembly.

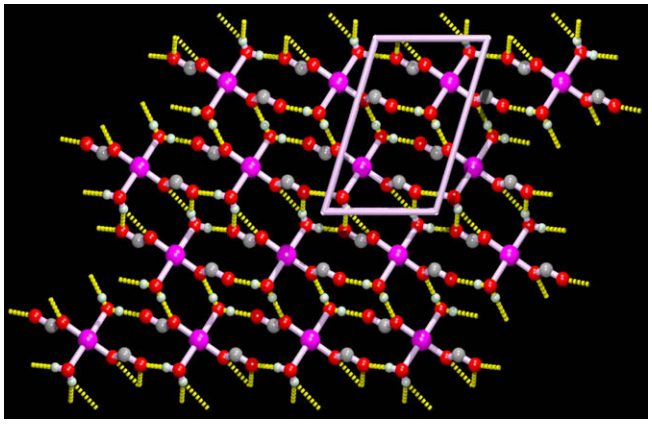

Fig. 5. The supramolecular layer of $[CuL_2(H_2O)_2]$ units in **2** (picolinate pyridine rings have been omitted for clarity).

3.2.2. Structure of $\{[Cu(pic)_2(H_2O)_2](H_2mal)_2(H_2O)_2\}_n$ (**2**)

The crystal structure determinations reveal that complex **2** is a pseudo-polymorph of complex **1**. The ORTEP diagram (Fig. 4) reveals that the asymmetric unit of **2** consists of a Cu atom, two 2-picolinate ligands, two malonic acid molecules and four water molecules (two coordinated and two lattice). Analyses of crystal packing of **2** shows that the $[Cu(pic)_2(H_2O)_2]$ complex is in a general position, although the structure is equivalent to that found in **1**. There are two acid groups per complex, unlike **1** where the ratio is 1 to 1. The bond lengths to the pyridine nitrogen atoms (N11 and N21) are 1.955(3) and 1.966(3) Å, to the acid oxygen atoms (O18 and O28) 1.943(2) and 1.963(2) Å and the bonds to the water molecules (O100 and O200) in the axial positions 2.538(2) and 2.574(2) Å. Two lattice water molecules (O300 and O400) and two malonic acid molecules remain as independent units and take part only in hydrogen bonding.

The supramolecular assembly of the monomeric units of **2** is also in the form of hydrogen-bonded layers of $[Cu(pic)_2(H_2O)_2]$ (Fig. 5). The layers are the (1 1 0) planes. The mode of hydrogen bonding association in this layer is slightly different from that in **1**. While the similar $R_4^2(8)$ hydrogen-bonded rectangular motifs be-

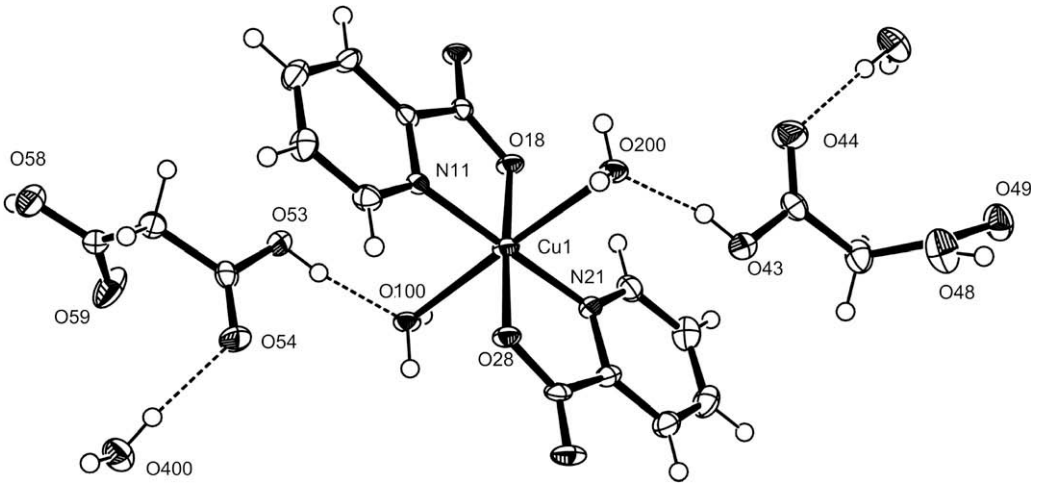

Fig. 4. The structure of **2** with ellipsoids at 50% probability. Hydrogen bonds shown as dotted lines.

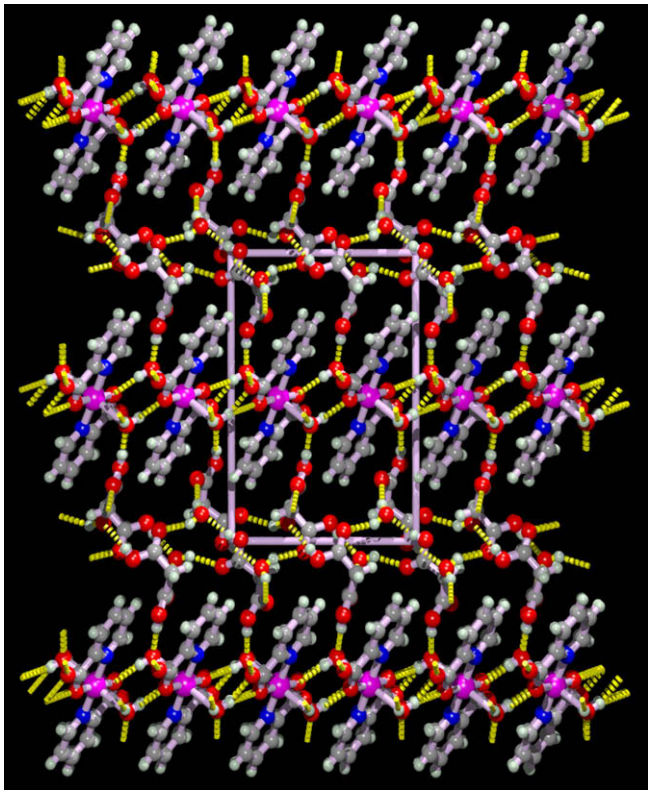

Fig. 6. Packing of successive layers in **2**.

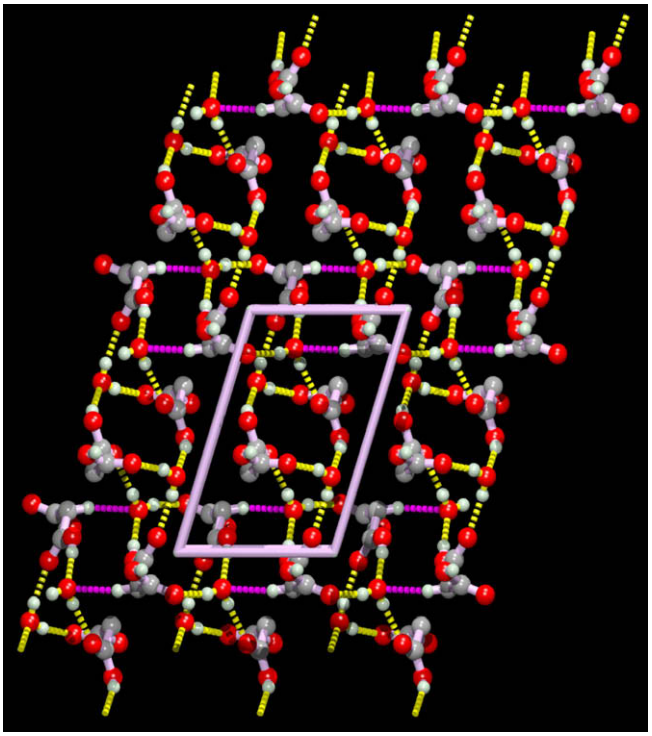

Fig. 7. The malonic acid water hydrogen-bonded supramolecular layer in **2**. Dotted lines represent H–bond.

tween the coordinated O100 water molecules and the uncoordinated carboxylate O19 atoms of picolinate still persists in **2**, due to perturbation another elongated ring motif $R_4^4(12)$ arises which is the result of hydrogen bonding between coordinated water molecules (O200) and both coordinated (O28) and uncoordinated (O29) carboxylate oxygen atoms of the 2-picolinate moiety (Table 3). These two ring motifs co-exist and the $R_4^2(8)$ motif slightly adjusts itself so that in this motif the hydrogen bond is bifurcated and the water oxygen atom (O100) donate its proton (H2) simultaneously to both the coordinated (O18) and uncoordinated carboxylate (O19) atoms of picolinate.

Successive $[Cu(pic)_2(H_2O)_2]_n$ layers are stacked along the *c*-axis (Fig. 6), but unlike **1**, the single malonic acid molecules do not act as pillars in **2**. Two sets of malonic acid molecules and lattice water molecules O300 and O400 self-assemble into hydrogen-bonded (Table 3) centro-symmetric layers (Fig. 7) in **2**, on both sides of which carboxylate terminals of malonic acid molecules protrude out and act as hydrogen bond donors for the coordinated water molecules that are part of the $[Cu(pic)_2(H_2O)_2]_n$ layers on either side. The O300 water molecule forms two donor hydrogen bonds to malonic acid carboxylate O59 atoms at 2.824(5) Å and with O44 atoms at 2.756(4) Å, and also acts as an acceptor of a hydrogen

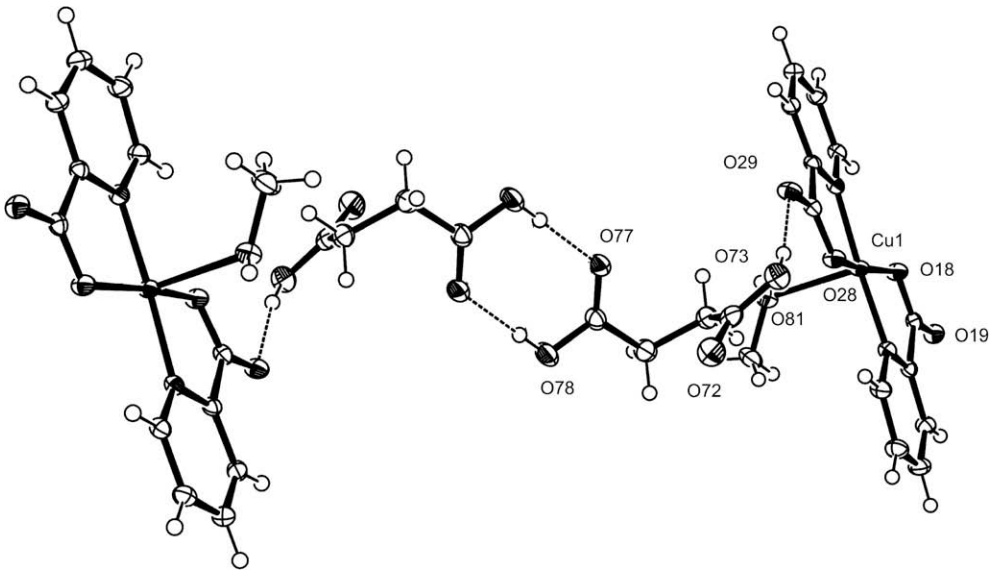

Fig. 8. The structure of **3** with ellipsoids at 50% probability. Hydrogen bonds shown as dotted lines.

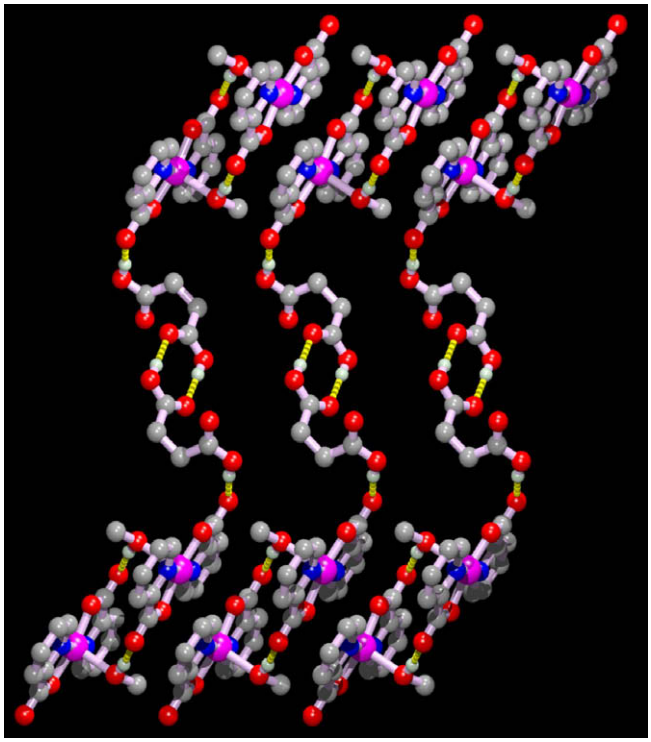

Fig. 9. The mode of binding of dimeric succinic acid pillars in complex **3**.

bond to O48 at 2.589(4) Å. On the other hand, the lattice water O400 molecule forms only one donor hydrogen bond with O54 at 2.739(4) Å and one accepter hydrogen bond with O58 at 2.611(4) Å, (Table 3), which leads to one dimensional hydrogen-bonded ribbons of malonic acid and water molecules along the [0 1 0] direction (Fig. 7). The supramolecular entity of two malonic acid molecules and two lattice water molecules here act as pillars between $[Cu(pic)_2(H_2O)_2]_n$ layers, and this entity is part of the water–malonic acid supramolecular layer.

3.2.3. Structure of $\{[Cu(pic)_2(MeOH)](H_2succ)\}_n$ (**3**)

The ORTEP diagram (Fig. 8) reveals that the asymmetric unit of **3** consists of a Cu atom, two 2-picolinate ligands, one succinic acid molecule and one coordinated methanol molecule. The crystal packing analyses of **3** shows that the copper complex $[Cu(pic)_2(MeOH)]$ is five coordinate with a square pyramidal environment in which the methanol occupies an axial position with a Cu–O(81) distance of 2.312(9) Å. In the equatorial plane, the Cu–O distances are 1.953(8) and 1.948(8) Å, and the Cu–N distances are 1.968(10) and 1.969(10) Å. This complex is unique in that the dicarboxylic acid forms a hydrogen bond to O(29) of the 2-picolinate ligand rather than to the solvent methanol.

Like the previous complexes, the $[Cu(pic)_2(MeOH)]$ units in **3** are also self-assembled into supramolecular layers which are pillared by dimeric units of succinic acid molecules (Fig. 9). The $[Cu(pic)_2(MeOH)]_n$ supramolecular layers have been depicted in Fig. 10. The basic supramolecular unit in this layer is the centrosymmetric dimer of $[Cu(pic)_2(MeOH)]$ monomers, which is the result of hydrogen bonding between coordinated methanol (O81) and the uncoordinated picolinate carboxylate oxygen O19 atoms of complementary monomers (Table 3). These dimeric units are arranged in the form of a 1D supramolecular chain as a result of C–H···O hydrogen bonding, shown in Fig. 10 (Table 3). These 1D chains are aligned side by side due to π···π interactions (Table 4) between the pyridine rings of adjacent chains, resulting in the supramolecular layer which is the (0 0 1) plane. Two succinic acid molecules form an end to end dimeric unit through the formation a $R_2^2(8)$ hydrogen bonding synthon (Table 3) and through the other terminals form hydrogen bond with the picolinate carboxylate O29 oxygen atoms (Fig. 9), and thus act as pillars between the layers.

3.3. Discussion

To facilitate an easy comparison, the structural features have been summarized in Table 5. Pseudo-polymorphs **1** and **2** have identical building blocks, but whereas for **1** $Z = 4$, for **2** $Z = 2$. Complex **1** possesses higher symmetry than **2**. The environmental parameter that is responsible for this is the increased concentration of malonic acid in **2**. The structural features discussed in the previous section reveals that the robust feature of the self-assembly in all three complexes is that the 2-picolinate ligands and the Cu(II) ions form monomeric complexes which are self-organized into distinct layers and the organic acid molecules also organize themselves in a separate region in between the Cu–picolinate layers and act as pillars for these layers. In the self-organization of the metal picolinate layers, in the case of complexes **1** and **2** coordinated water molecules play a very important role to steer successive monomeric units through the formation of a $R_4^2(8)$ hydrogen-

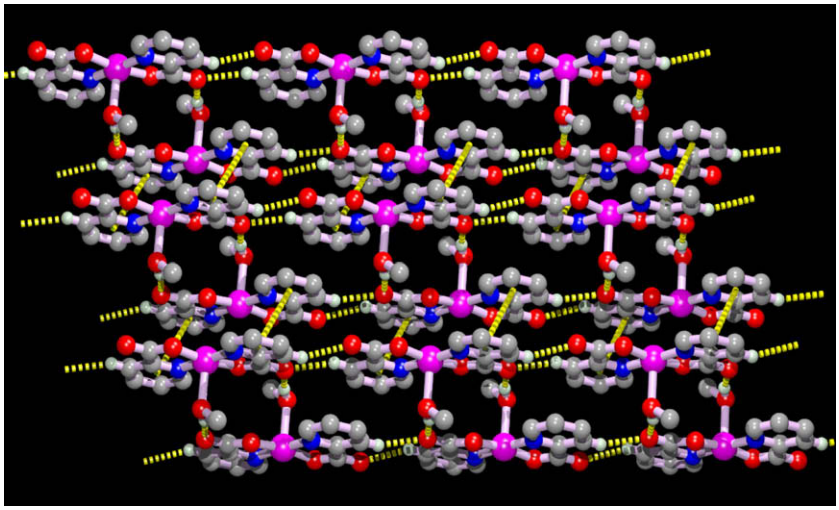

Fig. 10. Formation of $[CuL_2(MeOH)]_n$ supramolecular layers through hydrogen bonding and π–π interactions.

Table 4
Data for the π–π interactions in complex **3**.

Ring(i) → ring(j)	Dihedral angle (i,j) (°)	Slip angle (i,j) (°)	Distance of centroid (i) from ring (j) (Å)	Distance between the (i,j) ringcentroids (Å)
R(3) → R(4)[i]	6.33	31.66	3.389	3.8455
R(4) → R(4)[ii]	0.00	31.09	3.377	3.9440

Symmetry elements: [i] = $-x$, $1-y$, $-z$, [ii] = $1-x$, $-y$, $-z$.

Table 5
Comparison of salient features of complexes **1**–**3**.

	1	**2**	**3**
Coligand	malonic acid	malonic acid	succinic acid
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
Asymmetric unit	Cu(II) at the symmetry position	Cu(II) not at the symmetry position	One Cu(II) center
Coordination environment	octahedral	octahedral	square pyramidal
Axial sites occupied by	water molecules	water molecules	methanol
Supramolecular architecture	pillared layered	pillared layer	pillared bilayer
Supramolecular interaction	H-bonding $R_4^2(8)$ synthon, water tetramer analogue and only O–H···O	H-bonding $R_4^4(8)$ and $R_2^2(12)$ synthon, water tetramer analogue and both O–H···O and C–H···O	H-bonding $R_2^2(8)$ synthon and π–π

bonded synthon [29,31,32] with the uncoordinated carboxylate oxygen atom of picolinate. In **2** the organization has accommodated an additional synthon $R_4^4(12)$ and as a result the original synthon is distorted. This indicates the labile but robust nature of the $R_4^2(8)$ synthon, and it should be noted that this kind of organization has been observed in many other cases. This motif can be assumed to be the analogous motif of the planar water tetramer in which two water molecules have been replaced by picolinate oxygen atoms. In complex **2**, in between the Cu–picolinate layers malonic acid water supramolecular layers position themselves, but the basic pillaring action of malonic acid remains unchanged. In complex **3** though, instead of water, a methanol molecule is coordinated to Cu which has a square pyramidal coordination environment, yet the same Cu–picolinate layer structure is achieved through the formation of supramolecular dimeric complexes that organize themselves through hydrogen bonding and π···π interactions. The succinic acid molecules in this case act as pillars between the layers; in this process it forms a dimeric unit.

3.4. Thermal studies

To examine the thermal stabilities of the co-crystalline complexes, thermal gravimetric (TG) analyses were carried out in air on powdered samples of **1**–**3**. In **1**, the first endothermic weight loss of 7.92%, corresponding to the departure of two water molecules (Calc. 8.04%), was observed between 50 and 100 °C, the second endothermic weight loss of 22.92% was observed between 120 and 200 °C due to the removal of one malonic acid molecule (Calc. 22.99%). On further heating the $Cu(pic)_2$ complex start to decompose endothermally at 240 °C. Similarly the TG curve of **2** exhibits three endothermic weight loss in the temperature ranges 50–100 °C, 130–190 °C and 290–340 °C, corresponding to the release of four water molecules (Found 12.3%, Calc. 12.25%), two malonic acid molecules (Found 34.5%, Calc. 35.03%) and decomposition of $Cu(pic)_2$, respectively. Complex **3** also shows weight loss stages in the temperature ranges 80–120 °C, 130–190 °C and 270–360 °C corresponding to the release of one methanol molecule (Found 6.83%, Calc. 6.99%), one succinic acid molecule (Found 27.5%, Calc. 25.55%) and decomposition of $Cu(pic)_2$, respectively.

4. Conclusions

The viability of a crystal engineering approach to the identification of stable co-crystals has been demonstrated through the rational synthesis of metal-containing co-crystals of picolinate with malonic and succinic acids. In all three cases the organic acid was found to interact through hydrogen bonds act as a pillar to the $R_4^2(8)$ synthon assisted Cu–picoinate layer. Research with other neutral carboxylic acids is in progress to explore the metal-containing co-crystals.

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Appendix A. Supplementary data

CCDC 695481, 695482 and 695483 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.061.

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