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PAPER

Conformation variation of tris(2-carboxyethyl)isocyanuric acid induced by cocrystallized *N*-heterocyclic organic molecules†

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Crystallizations of tris(2-carboxyethyl)isocyanuric acid (H₃tci) without or with *N*-heterocyclic organic molecules result in three distinct supramolecular complexes, [(H₃tci)] (1), organic salt [(Hma)⁺·(H₂tci)⁻] (2) and cocrystal [(H₃tci)·(bipy)_{1.5}] (3) (ma = melamine, bipy = 4,4'-bipyridine). In the absence of *N*-heterocyclic organic molecules, three 2-carboxyethyl arms of H₃tci show a *cis*^{anti}–*cis*^{anti}–*trans*^{anti} conformation. The H₃tci molecules are extended to a 2D 4⁴-sql net via O–H···O hydrogen bonds. However, in the presence of ma or bipy, the conformation of the 2-carboxyethyl arms of H₃tci in both 2 and 3 is transformed to *cis*^{anti}–*cis*^{anti}–*cis*^{gauche} induced by cocrystallized *N*-heterocyclic organic molecules. In 2, ma plays a crucial role in the formation of O–H···N, N–H···O and O–H···O hydrogen bonds which direct the binary species to form the 2D double-layer structure containing 24-membered supramolecular macrocycles. Complex 3 is a 1D chain based on a [(H₃tci)₂·(bipy)₂] 42-membered macrocycle incorporating the carboxyl–pyridyl H-bonding supramolecular synthons, which are extended by another bipy molecule to form the 1D chain. The 1D chains are further extended by means of a C–H···O non-classic hydrogen bond to form the resulting 2D layer containing three kinds of macrocycles. The 2D layers are packed into a 3D framework through π···π interaction between the triazinyl and pyridyl rings. Based on the structural analysis, we found that the conformation of H₃tci could be modulated by introduction of the cocrystallized *N*-heterocyclic organic molecules. Moreover, the thermal stabilities of 2 and 3 are discussed.

Introduction

The molecular design of supramolecular architectures and highly ordered networks with tailored physical and chemical properties in the solid state has attracted unparalleled attention in materials science and crystal engineering.¹ A reliable method for the design of supramolecular assemblies is to employ intermolecular interactions, notably, hydrogen bond,² halogen bond,³ cation···π,⁴ anion···π,⁵ lone-pair···π⁶ and π···π stacking,⁷ to guide the molecules into ordered structures. Among them, the hydrogen bond is one of the most important intermolecular interactions to consider for the design of crystal structures, owing to its directionality and energetic favorability.⁸ At the same time, hydrogen bonding heterosynthons² have been extensively studied in binary

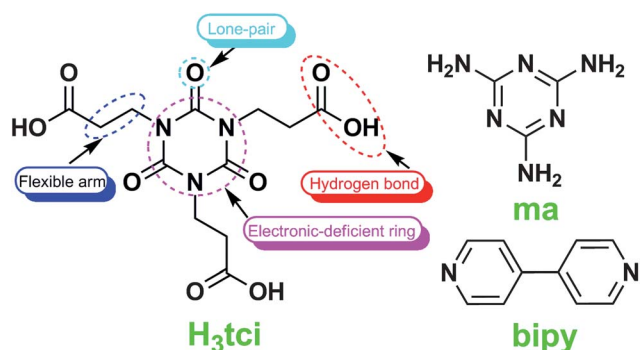
cocrystals or salts. As we know, when combinations of certain organic species are mixed together for crystallization, the crystals that are formed contain both the species in one structure which is quite different from those of the parent species in both structures and properties. The melamine (ma)^{1–5} and/or pyridine derivatives^{6–11} have also been widely utilized as excellent hydrogen donor and acceptor to create one-, two-, and three-dimensional (1D, 2D, and 3D) networks in crystalline solids.¹² For example, diverse 1D tapes, 2D sheets, 2D rectangular nets and organic–inorganic sandwich type 3D frameworks based on *N*-heterocyclic organic bases and carboxylic acid systems have been documented.¹³

To the best of our knowledge, the tris(2-carboxyethyl)isocyanuric acid (H₃tci) (Scheme 1) is a versatile supramolecular synthon due to its special structural features: (i) three carboxylate groups as both donors and acceptors of hydrogen bond; (ii) oxygen atoms of carbonyl groups as an auxiliary functional group can also serve as acceptors of hydrogen bonds as well as a lone-pair donor; (iii) three highly flexible arms (–CH₂–CH₂–) providing different relative positions of 2-carboxyethyl groups with respect to the C₃N₃ six-membered ring (*cis*–*cis*–*trans* and *cis*–*cis*–*cis*); (iv) the central electronic-deficient triazinyl ring can be utilized to construct π···π stacking, anion···π and lone-pair···π interactions; and (v) the 2-carboxyethyl group itself containing

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Scheme 1 Structures of H₃tci, ma and bipy.

a chain of three carbon atoms also has potential to change the conformations such as *anti* and *gauche* according to the torsion angles formed by successive C–C–N atoms. Until now, only limited coordination polymers constructed from H₃tci have been reported by Kitagawa and co-workers,¹⁴ however, hydrogen bond assembly of H₃tci without or with other cocrystallized organic species has not been observed yet.

As part of our extensive crystal engineering investigations with multidentate carboxylic acid ligands,¹⁵ herein, we focused our attention on supramolecular assembly of flexible H₃tci with melamine (ma) and 4,4'-bipyridine (bipy), and found that the variable conformations of H₃tci as we anticipated intensively depend on cocrystallized *N*-heterocyclic organic molecules. We hydrothermally prepared three supramolecular complexes, namely [H₃tci] (1), organic salt [(Hma)⁺·(H₂tci)⁻] (2) and cocrystal [(H₃tci)·(bipy)_{1.5}] (3). In the absence of *N*-heterocyclic organic molecule, the 2-carboxyethyl group of H₃tci adopts *cis*^{anti}–*cis*^{anti}–*trans*^{anti} conformation in 1. However, in the presence of ma or bipy, the conformation of the 2-carboxyethyl arms of H₃tci in both 2 and 3 is transformed to *cis*^{anti}–*cis*^{anti}–*cis*^{gauche} induced by cocrystallized *N*-heterocyclic organic molecules.

Experimental section

Materials and general methods

All chemicals were as purchased and used without purification. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 10 °C min⁻¹, nitrogen stream).

[(H₃tci)] (1)

A mixture of H₃tci (10 mg, 0.028 mmol), Zn(NO₃)₂·6H₂O (10 mg, 0.034 mmol) and pyridine (0.05 mL) was suspended in 15 mL solvents of CH₃CN, and heated in a Teflon-lined steel bomb at 90 °C for 3 days. The colorless block crystals formed were collected, washed with CH₃CN, and dried in the air (yield: 37%).

[(Hma)⁺·(H₂tci)⁻] (2)

A mixture of H₃tci (10 mg, 0.028 mmol), and ma (10 mg, 0.079 mmol) was suspended in 15 mL solvents of EtOH, and heated in a Teflon-lined steel bomb at 90 °C for 3 days. The colorless stick crystals formed were collected, washed with ethanol, and dried in the air (yield: 48%).

[(H₃tci)·(bipy)_{1.5}] (3)

The complex was prepared with the similar procedure as for complex 2 except that bipy (10 mg, 0.064 mmol) was used instead of ma. The colorless prism crystals formed were collected, washed with ethanol, and dried in air (yield: 55%).

X-Ray crystallography

Single crystals of the complexes 1–3 with appropriate dimensions were mounted on a glass fiber and used for data collection. Data were collected on a Bruker SMART APEXII CCD Detector single-crystal X-ray diffractometer with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) source at 25 °C. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.¹⁶ All structures were solved by direct methods using SHELXS-97¹⁷ and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.¹⁸ Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C or N atoms. All structures were examined using the Addsym subroutine of PLATON¹⁹ to assure that no additional symmetry could be applied to the models. Crystal data as well as details of the data collection and refinements for 1–3 are summarized in Table 1. The hydrogen bond metrics for 1–3 are shown in Table 2.

Result and discussion

Structure description [H₃tci] (1)

As indicated by X-ray single crystal diffraction, complex 1 crystallized in the monoclinic $P2_1/n$ space group. The asymmetric

Table 1 Crystal data for 1 and 2^a

Complex	1	2	3
Formula	C ₁₂ H ₁₅ N ₃ O ₉	C ₁₅ H ₂₁ N ₉ O ₉	C ₂₇ H ₂₇ N ₆ O ₉
M_r	345.27	471.41	579.55
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$Pbca$	$P\bar{1}$
$a/\text{Å}$	8.6775(7)	14.348(12)	8.375(4)
$b/\text{Å}$	15.7719(12)	8.033(7)	11.257(5)
$c/\text{Å}$	10.9612(8)	35.93(3)	15.807(6)
$\alpha/^\circ$	90.00	90.00	69.947(7)
$\beta/^\circ$	96.0660(10)	90.00	75.476(7)
$\gamma/^\circ$	90.00	90.00	84.278(7)
$V/\text{Å}^3$	1491.8(2)	4141(6)	1354.9(10)
Z	4	8	2
$D_{\text{calc}}/\text{g cm}^{-3}$	1.537	1.512	1.421
$F(000)$	720	1968	606
μ/mm^{-1}	0.134	0.126	0.109
Ref. unique	2621	2969	4688
GOF	1.060	1.002	1.028
$R_1, wR_2 [I > 2\sigma(I)]$	0.0393, 0.1062	0.0720, 0.1182	0.0637, 0.1807
R_1, wR_2 (all data)	0.0466, 0.1121	0.1666, 0.1513	0.0886, 0.2101

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2 The hydrogen bond metrics for **1–3**

D–H···A	D–H	H···A	D···A	D–H···A
Complex 1^a				
O5–H5C···O8 ⁱ	0.82	1.84	2.6577(18)	174.2
O6–H6A···O3 ⁱⁱ	0.82	1.91	2.639(17)	148.0
O9–H9A···O4 ⁱⁱⁱ	0.82	1.85	2.6701(18)	175.6
Complex 2^b				
O5–H5C···O8 ⁱ	0.82	1.74	2.556(5)	172.8
O6–H6A···N6 ⁱⁱ	0.82	1.82	2.625(6)	168.7
N4–H4C···O8 ⁱ	0.86	1.90	2.720(6)	160.2
N7–H7C···O9 ⁱⁱⁱ	0.86	1.97	2.827(6)	174.8
N7–H7D···O4	0.86	2.22	3.002(6)	151.1
N8–H8C···O7 ^{iv}	0.86	2.10	2.952(6)	169.3
N8–H8D···O2 ^v	0.86	2.30	3.057(6)	147.0
N9–H9A···O7 ^v	0.86	2.06	2.905(6)	167.2
N9–H9B···O9 ⁱ	0.86	1.92	2.784(6)	177.2
Complex 3^c				
O5–H5C···N4 ⁱ	0.82	1.92	2.703(3)	160.3
O7–H7C···N5 ⁱⁱ	0.82	1.87	2.671(3)	167.2
O8–H8C···N6 ⁱⁱⁱ	0.82	1.82	2.633(3)	172.1

^a Symmetry codes: (i) $-x + 3/2, y - 1/2, -z + 5/2$; (ii) $x, y, z - 1$; (iii) $-x + 3/2, y + 1/2, -z + 5/2$. ^b Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + 3/2, z + 1/2$; (iii) $-x + 1, -y, -z + 1$; (iv) $x, -y + 1/2, z - 1/2$; (v) $x, -y + 3/2, z - 1/2$. ^c Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y + 2, -z + 1$; (iii) $x - 1, y - 1, z$.

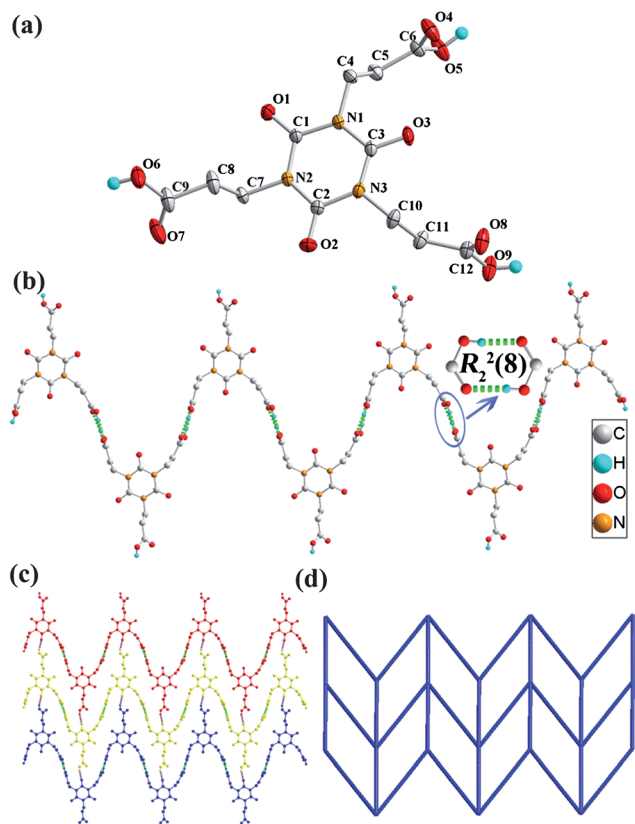


Fig. 1 (a) Drawing of a crystal structure of H₃tci with the thermal ellipsoids at 30% probability level. (b) Presentation of a 1D supramolecular zigzag chain incorporating an $R_2^2(8)$ ring motif. (c) View of the 2D hydrogen-bonded layer in **1** along the bc plane. (d) The simplified 4^4 -sql supramolecular net.

unit of **1** contains one H₃tci molecule (Fig. 1a). The C6–O5, C9–O6, and C12–O9 distances (1.301(2), 1.308(15) and 1.297(2) Å) are much longer than the C6–O4, C9–O7, and C12–O8 distances (1.225(2), 1.220(4) and 1.223(2) Å) which assists us to distinguish the C–O single and double bonds of the carboxyl group. Normally, the C–O distance parameter is restated as $\Delta d < 0.03$ Å for the deprotonated carboxyl group and $\Delta d > 0.08$ Å for neutral COOH.

The conformation of H₃tci interests us due to three flexible 2-carboxyethyl (–CH₂–CH₂–COOH) groups. Considering the relative positions of 2-carboxyethyl groups with respect to the C₃N₃ six-membered ring, the conformations of H₃tci have two kinds, *cis–cis–trans* and *cis–cis–cis*. At the same time, the 2-carboxyethyl group itself containing a chain of three carbon atoms also has two potential conformations, *anti* and *gauche*, according to the torsion angles formed by successive C–C–C–N atoms.²⁰ In **1**, H₃tci has two 2-carboxyethyl groups above the C₃N₃ six-membered ring and the other one below it, giving a *cis–cis–trans* conformation. Three 2-carboxyethyl groups bonded to the C₃N₃ six-membered ring give three torsion angles (τ) of 127, 177, and 151°, respectively, all of which fit well with an *anti* conformation according to the stereochemistry terminology. The combination of two kinds of conformations of H₃tci shows a total conformation of *cis^{anti}–cis^{anti}–trans^{anti}* in **1**. Three dihedral angles (ϕ) determined by the plane of a carboxyl group and a C₃N₃ six-membered ring are 84.6, 58.9 and 83.3°, respectively. Two *cis* 2-carboxyethyl groups are hydrogen-bonded with its two adjacent H₃tci molecules to form a 1D supramolecular zigzag chain (Fig. 1b) along the b axis (O9–H9A···O4ⁱⁱⁱ = 2.6701(18) and O5–H5C···O8ⁱ = 2.6577(18) Å) incorporating the homosynthon $R_2^2(8)$ ring motif,²¹ which is one of the 24 most frequently encountered bimolecular cyclic hydrogen-bonded motifs in organic crystal structures.²² The *trans* 2-carboxyethyl group and carbonyl group between the *cis* 2-carboxyethyl groups form another hydrogen bond (O6–H6A···O3ⁱⁱ = 2.639(17) Å) which further connects the 1D zigzag chains to the 2D layer (Fig. 1c) consisting of 40-membered supramolecular macrocycles (Fig. S1†). (Symmetry codes: (i) $-x + 3/2, y - 1/2, -z + 5/2$; (ii) $x, y, z - 1$; (iii) $-x + 3/2, y + 1/2, -z + 5/2$.)

Considering the hydrogen bonds as linear linkers and the H₃tci as 4-connected nodes, the 2D supramolecular layer of complex **1** can be simplified as a 4^4 -sql net²³ incorporating rhombic windows with the dimension of 10.96×13.29 Å. The 2D layers adopt ABAB stacking arrangement to give rise to a 3D supramolecular architecture (Fig. S2†) with an inter-layer distance of *ca.* 4.33 Å by weak C–H···O interactions (C4–H4A···O3^v = 3.417(2), \angle C4–H4A···O3^v = 156° and C8–H8A···O9^{vi} = 3.445(2) Å, \angle C8–H8A···O9^{vi} = 148°) and no aromatic stacking is found between them. (Symmetry codes: (v) $-x + 2, -y, -z + 2$; (vi) $x + 1/2, -y + 1/2, z - 1/2$.)

Organic salt [(Hma)⁺·(H₂tci)[–]] (**2**)

In the presence of ma, H₃tci cocrystallized with ma to form an organic salt by transferring one proton from a carboxyl group to an aromatic N atom of ma. The complex **2** crystallized in the orthorhombic *Pbca* space group and its asymmetric unit consists of one H₂tci[–] and one Hma⁺ (Fig. 2a). Differently, three 2-carboxyethyl groups are located at the same side of the C₃N₃

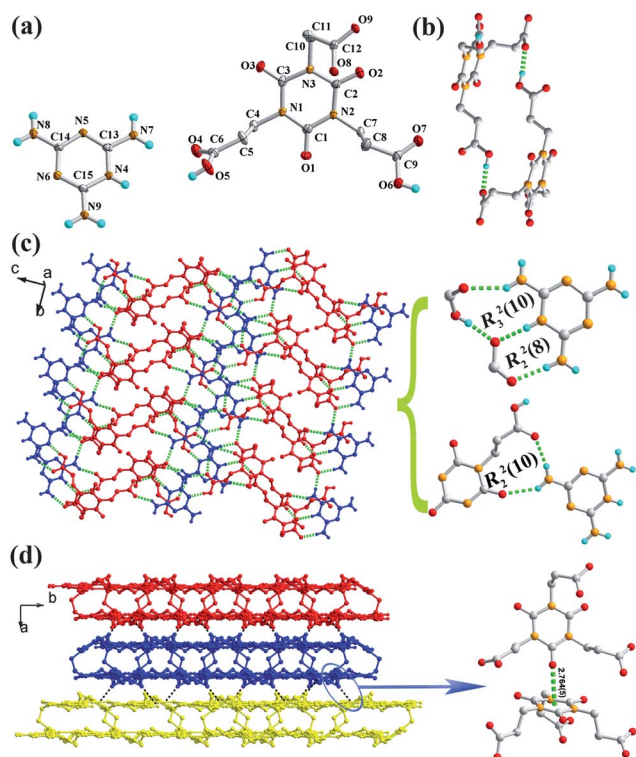


Fig. 2 (a) Drawing of a crystal structure of **2** with the thermal ellipsoids at the 30% probability level. (b) Presentation of a 24-membered supramolecular macrocycle. (c) View of the 2D hydrogen-bonded double layer comprised of $R_2^2(8)$, $R_2^2(10)$ and $R_3^2(10)$ heterosynths in **2** (blue for Hma⁺, red for H₂tci⁻). (d) 3D supramolecular framework built from packing of 2D double layers through lone-pair $\cdots\pi$ interaction.

six-membered ring of H₂tci⁻, generating a *cis-cis-cis* conformation. Three 2-carboxyethyl groups bonded to the C₃N₃ six-membered ring give three torsion angles of 179, 166, and 70°, respectively. So the total conformation of H₂tci⁻ in **2** can be best represented as *cis^{anti}-cis^{anti}-cis^{gauche}*. As indicated by CSD (Cambridge Structure Database) survey with the help of ConQuest version 1.3,²⁴ there are only 9 H₃tci-containing complexes and all of them are metal-involved.^{14,25} A conformational analysis of the 9 crystal structures containing the H₃tci fragment revealed that out of 13 non-equivalent H₃tci, 7 exhibit the *cis^{anti}-cis^{anti}-trans^{anti}* conformation, 2 the *cis^{gauche}-cis^{gauche}-cis^{gauche}* conformation, 2 the *cis^{anti}-cis^{anti}-cis^{gauche}* conformation, 1 the *cis^{anti}-cis^{gauche}-trans^{gauche}* conformation and 1 the *cis^{anti}-cis^{anti}-cis^{anti}* conformation (Table S1†). Based on the above analysis, the *cis^{anti}-cis^{anti}-trans^{anti}* conformation in **1** tends to be favored in coordination polymers, while *cis^{anti}-cis^{anti}-cis^{gauche}* conformation in **2** may be not the lowest energy one for H₃tci and relatively hard to be observed. Three dihedral angles (φ) are 73.4, 27.2 and 32.8°, respectively.

Four 2-carboxyethyl arms from two symmetry-related H₂tci⁻ anions interact with each other through two strong O5–H5C \cdots O8 (2.556(5) Å) hydrogen bonds to form centrosymmetric 24-membered supramolecular macrocycles (Fig. 2b), which are further extended by Hma⁺ cations to form the 2D double sheet (Fig. 2c) through N–H \cdots O_{carboxyl} (2.720(6)–3.002(6) Å), N–H \cdots O_{carbonyl} (N8–H8D \cdots O2^{iv} = 3.057(6) Å) and O_{carboxyl}–H \cdots N (O6–H6A \cdots N6ⁱⁱ = 2.625(6) Å) hydrogen bonds incorporating

$R_2^2(8)$, $R_2^2(10)$ and $R_3^2(10)$ heterosynths. (Symmetry codes: (ii) $x, -y + 3/2, z + 1/2$; (iv) $x, -y + 1/2, z - 1/2$.)

The 2D double sheets were packed into a 3D framework governed by significant lone-pair $\cdots\pi$ interaction (Fig. 2d), which belongs to a new type of noncovalent supramolecular interaction involving a lone pair and an electron-deficient aromatic ring.²⁶ In **2**, the C₃N₃ six-membered ring is involved in strong lone-pair $\cdots\pi$ association, and contact is observed between the carbonyl oxygen atoms O1 and the centroid of a C₃N₃ six-membered ring. The distance between them is 2.764(5) Å, obviously shorter than the sums of van der Waals radii (C + O) and (N + O). The average C \cdots O and N \cdots O contacts related to this lone-pair $\cdots\pi$ interaction are 3.097(6) and 3.214(6) Å, respectively. Such short lone-pair $\cdots\pi$ interaction in **2** has very little precedence in the literature. As an example, Domasevitch and co-workers previously used a typical electron deficient heterocycle ligand pyridazino[4,5-*d*]pyridazine to construct a Cu(II) 3D metal-organic framework containing *N*-basic sulfamate anions, which shows coexistent short lone-pair(N) $\cdots\pi$ (3.101(2) Å) and anion $\cdots\pi$ (3.140(2) Å) interactions.^{5g} The angle α (which corresponds to the angle between the O, the ring centroid and the aromatic plane) is 86°, indicating the carbonyl group has a head-on orientation toward the ring centroid that will indicate the existence of a significant lone-pair $\cdots\pi$ interaction between the two entities.²⁷ Another important geometry parameter for lone-pair $\cdots\pi$ interaction is the dihedral angle (ω) between the planes defined by the N₂C=O and C₃N₃ six-membered ring, that is 59.8°, indicating that the C=O \cdots centroid short contact is not due to the $\pi\cdots\pi$ interaction involving the π electrons of the C=O double bond and the aromatic ring. Although searches of the protein database for lone-pair(carbonyl) $\cdots\pi$ interactions indicated that over 250 protein structures from the databank were found where carbonyl oxygen atoms are below 3.5 Å of the centroid of aromatic rings,²⁸ amazingly, only limited examples of lone-pair $\cdots\pi$ interactions in synthetic complexes have been reported so far in the literature.²⁹ Notably, the C=O \cdots centroid contact found in **2** is very short, even below the distance criterion (2.8–3.8 Å) defined by Egli and co-workers.^{6a}

Cocrystal [(H₃tci)·(bipy)_{1.5}] (**3**)

X-Ray single crystal diffraction analysis revealed that complex **3** formed a crystal structure in the triclinic $\bar{P}1$ space group. The asymmetric unit consists of one H₃tci, and one and a half of bipy (Fig. 3a). The H₃tci shows the similar *cis^{anti}-cis^{anti}-cis^{gauche}* conformation to that in **2** with three torsion angles (τ) of 170, 171 and 61°, respectively. Three dihedral angles (φ) are 38.5, 11.2, and 42.0°, respectively. Two of the three carboxyl groups of H₃tci have the same orientation and take part in the formation of centrosymmetric 42-membered supramolecular macrocycles incorporating two linear bipy molecules through two kinds of O–H \cdots N (2.703(3) and 2.671(3) Å) hydrogen bonds. Another crystallographic independent bipy molecule lying on the inversion center is nearly perpendicular to the 42-membered supramolecular macrocycle and connects the macrocycle to a 1D zigzag supramolecular chain through another O–H \cdots N (2.633(3) Å) (Fig. 3b).

The O2 atoms in the carbonyl groups of H₃tci also play an important role in extending the 1D zigzag chains into a 2D layer

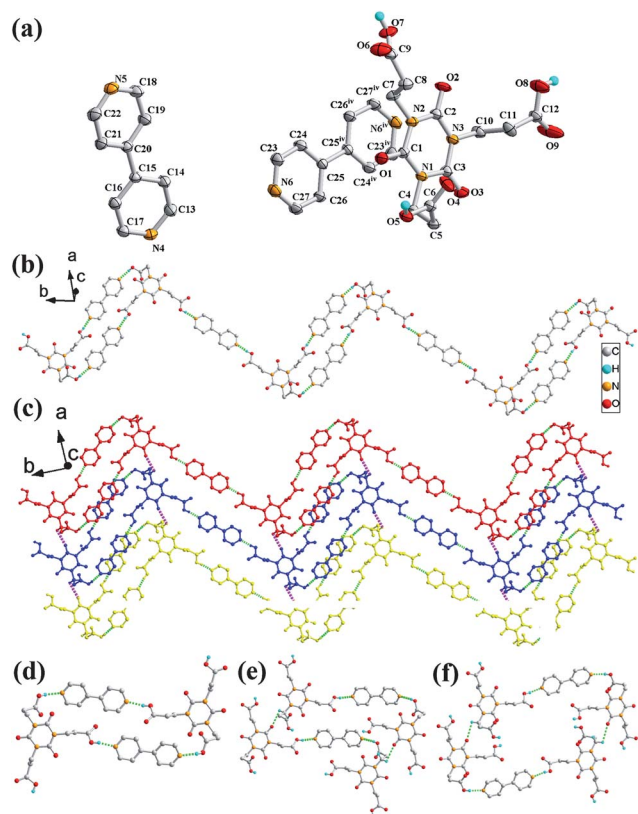


Fig. 3 (a) Drawing of a crystal structure of **3** with the thermal ellipsoids at 30% probability level. (b) Presentation of a 1D zigzag chain incorporating O–H...N hydrogen bonds (green dashed lines). (c) View of the 2D hydrogen-bonded layer built from the combination of O–H...N (green dashed lines) and C–H...O hydrogen bonds (pink dashed lines). (d) 42-membered, (e) 50-membered and (f) 56-membered supramolecular macrocycles in **3**.

(Fig. 3c) through the C–H...O hydrogen bond (C4^{vi}–H4B...O2 = 3.023(4) Å, ∠C4^{vi}–H4B...O2 = 101°). In the 2D layer, there are three types of supramolecular macrocycles (Fig. 3d–f): (I) 42-membered macrocycle (2H₃tci and 2 bipy); (II) 50-membered macrocycle (4H₃tci and 2 bipy); and (III) 56-membered macrocycle (4H₃tci and 2 bipy). The above three types of macrocycles interconnected to form the 2D layer. There exists a face-to-face π ... π interaction involving the C₃N₃ six-membered ring of H₃tci and pyridyl ring of bipy with an inter-centroid distance of 3.459 (2) Å and interplane angle of nearly zero (2.2°) between neighboring layers (Fig. S3†) which contributes to the stability of the resulting 3D framework. (Symmetry code: (vi) $x - 1, y, z$.)

Conformation variation of H₃tci

It has been demonstrated that the conformational diversities of the **1–3** are undoubtedly related to the cocrystallized heterocyclic organic molecules. Different hydrogen bond acceptor and donor as well as different orientations of hydrogen bonds are key points to influence the hydrogen-bonded networks. That is to say, H₃tci has the ability to adjust itself to satisfy the hydrogen bonding preference and the lower energetic arrangement in the assembly process. In complexes **1–3**, H₃tci shows diverse conformations. Without any cocrystallized species, the H₃tci in **1** exhibits the

Table 3 Conformational parameters for H₃tci in **1–3**

Complex	1	2	3
τ^a/\circ	127, 177, 151	179, 166, 70	170, 171, 61
ϕ^b/\circ	84.6, 58.9, 83.3	73.4, 27.2, 32.8	38.5, 11.2, 42.0

^a τ is the torsion angle formed by successive C–C–C–N atoms of 2-carboxyethyl groups and N atom on a C₃N₃ six-membered ring. ^b ϕ is the dihedral angle defined by the plane of a carboxyl group and a C₃N₃ six-membered ring.

widely reported *cis^{anti}–cis^{anti}–trans^{anti}* conformation. However, in the presence of cocrystallized species, the H₃tci in **2** and **3** shows a rare *cis^{anti}–cis^{anti}–cis^{gauche}* conformation. The detailed conformational parameters are listed in Table 3.

TG analysis

Thermogravimetric analyses (TGA) were performed to determine the thermal stability of **2** and **3** (Fig. S4†). For complex **2**, there is no weight loss from 50 to 250 °C, and after that, it starts to decompose. For complex **3**, the first weight loss was 39.34% in the temperature range 50–290 °C, which compares well to the calculated values of 40.4%, corresponding to the loss of bipy molecules. At higher temperatures, the supramolecular framework of the complex **3** starts to decompose.

Conclusions

In summary, we synthesized and characterized three supramolecular complexes without or with *N*-heterocyclic organic molecules, which exhibit interesting hydrogen bonding patterns and 2D supramolecular layers. The flexible H₃tci adopts the *cis^{anti}–cis^{anti}–trans^{anti}* conformation in **1** and *cis^{anti}–cis^{anti}–cis^{gauche}* conformation in **2** and **3**. The different conformations of H₃tci are induced by the cocrystallized *N*-heterocyclic organic molecules with different hydrogen bond acceptor and donor as well as different orientations of hydrogen bonds.

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