

Synthesis and crystal structures of 2,4,6-pyridine-tricarboxylic anions/guanidinium and tetraalkylammonium inclusion compounds

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Abstract Two different hydrogen-bonded inclusion compounds, $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3]_{0.5} \cdot [\text{C}(\text{NH}_2)_3^+]_{0.5} \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+] \cdot 2\text{H}_2\text{O}$ (**1**) and $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3] \cdot [\text{C}(\text{NH}_2)_3^+] \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+] \cdot [(\text{C}_3\text{H}_7)_4\text{N}^+] \cdot 6\text{H}_2\text{O}$ (**2**) are reported in this paper, in which 2,4,6-pyridine-tricarboxylic anions, guanidiniums and water molecules jointly construct host lattices while tetraalkylammonium cations are accommodated as guest species. Both two compounds formed sandwich-like hydrogen-bond inclusion compounds. In compound **1**, the dimers composed of 2,4,6-pyridine-tricarboxylic anions and guanidiniums form 2D hydrogen-bonded layers by connecting with water molecules. In compound **2**, 2,4,6-pyridine-tricarboxylic anions, guanidiniums and water molecules contribute to generate an undulate rosette hydrogen-bonded architecture. Interestingly, in compound **2**, there are two species of guest molecules, tetraethylammonium and tetrapropylammonium, which are alternately arranged between the neighboring layers. Mixed guest cations accommodated in hydrogen-bonded inclusion compounds are seldom seen.

Keywords Inclusion compound · Crystal structure · Hydrogen bond · 2,4,6-Pyridine-tricarboxylic acid · 1,3,5-Benzene-tricarboxylic acid

Abbreviations

TMA 1,3,5-Benzene-tricarboxylic acid (trimesic acid)
PTA 2,4,6-Pyridine-tricarboxylic acid

Introduction

The degree of similarity between crystal structures is of great importance in crystal engineering. Recently in crystal structure prediction [1, 2], Trimesic acid (1,3,5-benzene-tricarboxylic acid, **TMA**) is judiciously chosen as supramolecular synthon with a configuration of Y-shape in crystal engineering due to its formation of honeycomb-like hydrogen-bonded networks through assembling hydrogen bonds of its carboxyl groups by itself [3, 4]. Compared with the structure of **TMA**, 2,4,6-pyridine-tricarboxylic acid (**PTA**) has nitrogen atom replaced by aromatic C–H group of **TMA**, and it may induce isostructural structures described by Ashwini Nangia et al. [5]. As we know, there are various inclusion compounds composed of **TMA** and other assisting small molecules (e.g. water molecule) with template of tetraalkylammonium cations [6–9].

The sandwiched hydrogen-bonded inclusion compound $[1,3,5\text{-C}_6\text{H}_3(\text{COO}^-)_3] \cdot [\text{C}(\text{NH}_2)_3^+] \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+]_2 \cdot 6\text{H}_2\text{O}$ was once reported by Mak et al. in 2005 [8], where **TMA** anions and guanidinium, as shared host molecules, form a wonderful hydrogen-bond-mediated planar rosette-layer architecture, which is additionally consolidated by hydrogen-bonded water clusters inserted into rosettes. And tetraethylammonium cations are orderly arranged between layers as guest species. As a part of our ongoing investigation on synthesis of novel inclusion compounds based on multi-carboxylato aromatic rings, we tried to prepare new

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hydrogen-bonded inclusion compounds by replacing TMA by PTA in the exploration of isomorph, and finally obtained inclusion compound of $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3]_{0.5} \cdot [\text{C}(\text{NH}_2)_3^+]_{0.5} \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+] \cdot 2\text{H}_2\text{O}$ (**1**). During the experiments, we also got an interesting inclusion compound containing composite guest species, $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3] \cdot [\text{C}(\text{NH}_2)_3^+] \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+] \cdot [(\text{C}_3\text{H}_7)_4\text{N}^+] \cdot 6\text{H}_2\text{O}$ (**2**), where composites of host lattice are similar with compound **1**, but there are two kinds of guest cations, tetraethylammonium and tetrapropylammonium, between hydrogen-bonded layers. In this paper, synthesis and crystal structures of two hydrogen-bonded inclusion compounds **1** and **2** are reported.

Experimental

Synthesis of compounds (**1**) and (**2**)

PTA was synthesized with 2,4,6-trimethyl pyridine (99%, A. R.), which is commercially afforded by the Alfa Aesar company, following the procedures in the literature [10], and guanidine hydrochloride (98.5%, A. R.) was bought from Tianjin Guangfu Fine Chemical Research Institute. Samples of PTA (0.25 mmol) and guanidine hydrochloride were separately dissolved in water-ethanol (50/100 v/v) according to a 1:3 molar ratio. Tetraethylammonium hydroxide (30% solution, C. R.) was carefully added to obtain the solution with a 1:3 molar ratio of acid to hydroxide. The mixture was stirred for about 2 h and set aside to crystallize, finally yielding colorless block-shaped crystals of **1** suitable for single crystal X-ray diffraction after 7 days. But during the recrystallizing process of a parallel experiment with same methods, the tetraethylammonium hydroxide was replaced by tetrapropylammonium hydroxide to drop in the solution accidentally, and finally the colorless block-shaped crystals of **2** were separated after standing in the air about 15 days.

X-ray data collection and structure determination

Crystals of **1** and **2** were mounted on glass fibers for geometry and intensity data collection with a Bruker SMART Apex II CCD area detector [11] under different temperatures. The data were collected at room temperature for **1** and at 150 K for **2**. The structures were solved with the direct methods and refined by full matrix least square methods based on F^2 , using the structure determination and graphics package SHELXTL [12] based on SHELX97 [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms bonded to carbon were introduced in idealized positions. The hydrogen atoms bonded to oxygen and nitrogen were

located in the difference map with the fixed distances of 0.86 and 0.93 Å. In compound **2**, there exists twinning and the refinement was done with TWIN and BASF instructions. The final reliability indices together with crystal data of the refinement calculations are given in Table 1 and the selected geometric parameters of two crystal structures are listed in Table 2.

Results and discussion

Crystal structure analysis of inclusion compounds (**1**) and (**2**)

Crystal structure of inclusion compound (**1**)

Asymmetric unit of compound **1** (*Pbcn* space group, $Z = 4$) is composed of half a PTA anion arranged at about twofold axis, half a guanidinium lying on the same symmetry element, one tetraethylammonium cation and two independent water molecules. The crystal structure shows carboxyl groups of PTA turn to anion by losing three protons, where the distances of C–O (1.238–1.246 Å) significantly tend to be averaged. One of the protons is accepted by nitrogen atom of C = N group of the neutral guanidine to be guanidinium.

Table 1 Crystallographic data

Compound	(1)	(2)
CCDC No.	762562	762563
Formula	$\text{C}_{25}\text{H}_{56}\text{N}_6\text{O}_{10}$	$\text{C}_{29}\text{H}_{68}\text{N}_6\text{O}_{12}$
Formula weight	600.76	692.89
Crystal color	Colorless	Colorless
Crystal shape	Block	Block
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2₁/n</i>
Crystal size (mm)	$0.22 \times 0.19 \times 0.16$	$0.31 \times 0.22 \times 0.15$
<i>a</i> (Å)	14.8115(8)	11.842(2)
<i>b</i> (Å)	15.1328(7)	16.292(3)
<i>c</i> (Å)	14.7208(7)	20.599(4)
β (°)	90	90.459(3)
<i>V</i> (Å ³)	3299.5(3)	3973.9(14)
<i>Z</i>	4	4
<i>D_c</i> (mg cm ⁻³)	1.209	1.158
μ (mm ⁻¹)	0.093	0.089
θ range for data collection	1.92–27.59	2.13–25.01
Reflection number	13504	14957
Independent reflections	3817	6843
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0442, 0.1084	0.0542, 0.1391
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0855, 0.1297	0.0809, 0.1576
<i>S</i>	1.025	1.025

Table 2 Selected geometric parameters (°, Å)

(1)			
O(1)–C(4)	1.2456(18)	C(2)–C(3)	1.3826(16)
C(1)–N(1)	1.3385(16)	C(3)–C(5)	1.524(3)
C(1)–C(2)	1.3904(19)	O(3)–C(5)	1.2375(14)
C(1)–C(4)	1.525(2)	N(3)–C(6)	1.3276(17)
O(2)–C(4)	1.2349(18)	N(2)–C(6)	1.313(3)
N(1)–C(1)–C(2)	122.44(13)	O(2)–C(4)–O(1)	126.03(14)
N(1)–C(1)–C(4)	117.62(12)	O(2)–C(4)–C(1)	116.94(13)
C(2)–C(1)–C(4)	119.91(13)	O(1)–C(4)–C(1)	117.02(13)
C(3)–C(2)–C(1)	119.58(13)	O(3)–C(5)–C(3)	117.07(10)
C(2)–C(3)–C(5)	121.07(9)	N(2)–C(6)–N(3)	120.51(10)
(2)			
C(1)–N(1)	1.346(3)	O(3)–C(7)	1.252(3)
C(1)–C(2)	1.390(4)	C(4)–C(5)	1.391(4)
C(1)–C(6)	1.510(4)	O(4)–C(7)	1.239(3)
N(1)–C(5)	1.338(3)	C(5)–C(8)	1.527(4)
O(1)–C(6)	1.246(3)	O(5)–C(8)	1.250(3)
C(2)–C(3)	1.379(4)	O(6)–C(8)	1.241(3)
O(2)–C(6)	1.250(3)	N(2)–C(9)	1.310(4)
C(3)–C(4)	1.391(4)	C(9)–N(3)	1.327(3)
C(3)–C(7)	1.520(3)	C(9)–N(4)	1.333(4)
N(1)–C(1)–C(2)	123.0(2)	O(1)–C(6)–O(2)	125.3(3)
N(1)–C(1)–C(6)	117.2(2)	O(1)–C(6)–C(1)	117.6(2)
C(2)–C(1)–C(6)	119.8(2)	O(2)–C(6)–C(1)	117.2(2)
C(5)–N(1)–C(1)	117.48(19)	O(4)–C(7)–O(3)	125.7(2)
C(3)–C(2)–C(1)	119.3(2)	O(4)–C(7)–C(3)	117.1(3)
C(2)–C(3)–C(4)	117.9(2)	O(3)–C(7)–C(3)	117.2(3)
C(2)–C(3)–C(7)	120.7(2)	O(6)–C(8)–O(5)	125.2(3)
C(4)–C(3)–C(7)	121.3(3)	O(6)–C(8)–C(5)	117.9(2)
C(5)–C(4)–C(3)	119.5(2)	O(5)–C(8)–C(5)	116.9(2)
N(1)–C(5)–C(4)	122.6(2)	N(2)–C(9)–N(3)	120.0(3)
N(1)–C(5)–C(8)	116.8(2)	N(2)–C(9)–N(4)	119.6(2)
C(4)–C(5)–C(8)	120.5(2)	N(3)–C(9)–N(4)	120.4(3)

Seen from block diagram (Fig. 1), with the help of water molecules, **PTA** anions and guanidiniums form a waving hydrogen-bonded layer architecture along a direction (001), which are arranged at about $c = 1/4$ and $c = 3/4$. And tetraethylammonium cations arranged at about $c = 0$ and $c = 1/2$ are regularly accommodated between layers and form a typical sandwiched hydrogen-bonded inclusion complex, where a distance is maintained within layers, $c/2 = 7.36$ Å.

Figure 2 shows two oxygen atoms in different carboxyl groups in **PTA** anion **N1** [**PTA** anion carrying **N1** is represented by **N1** and so on] form a pair of symmetrical O through interaction with nitrogen atom **N2** of guanidinium **C6** and generate **PTA**[−] guanidinium dimer with H–N acceptor hydrogen bonds; hydrogen-bond pattern can be written as $A = R_2^2(8)$. Additionally, two water molecules

related to twofold axis connect with neighboring dimers to form hydrogen-bonded ring B ($B = R_4^4(12)$). The latter turns into hydrogen-bond ribbon stretching along b axis by connecting with linked dimers. In succession, between bordering ribbons arranged along a axis, water molecule **O1W** acts as donor for an O–H···O contact (separation of O···O is 2.7728 Å and the angle 165°) on **N1C** anion, whereas another water molecule **O2W** can be used as donor for two anions of **N1B** and **N1C** and as an acceptor for **C6C** cation (Table 3), thus introducing a series of hydrogen-bonded clusters between bordering ribbons shown in Fig. 2, $C = R_4^3(10)$, $D = R_3^2(8)$, $E = R_4^4(14)$. These hydrogen bonds turn to a 2-dimensional hydrogen-bonded layer structure along the plane (001) by connecting with **PTA**[−] guanidinium ribbons.

Noticeably, calculating the interplanar angles between carboxyl groups and pyridine ring in **PTA** anion, it can be easily found that the pyridine ring is coplanar (the mean deviation from the plane is 0.0037 Å) and the carboxyl group of O1 distorts 8.4° and another one of O3 twists 10.7°. Deducing from general principles, the ortho-carboxyl group near to N atom in **PTA** anion should distorts more than the para-carboxyl group due to the repulsion of unshared electron pairs of N atom. But the fact is opposite in compound **1**. The reason may be explained with different linking modes of hydrogen-bonded rings of A and B (Fig. 2), in which A is composed of the carboxyl group of O1 that distorts a smaller angle to form hydrogen bonds with guanidinium directly and B is constructed with the carboxyl group of O3 that twists a larger angle to adapt to the bridged water molecule of O1W to contact with the same guanidinium.

Crystal structure of inclusion compound (2)

Compared with compound **1**, there are one **PTA** anion, one guanidinium cation, one tetraethylammonium cation, one tetrapropylammonium cation and six independent water molecules in asymmetric unit of compound **2** ($P2_1/n$ space group, $Z = 4$). Similarly, protons of **PTA** are all eliminated and nitrogen atom does not accept proton. In **PTA** anion, the bond lengths of C–O (1.239–1.252 Å) of carboxyl groups is mean length. With respect to pyridine ring (the mean deviation from plane is 0.0160 Å), two ortho-carboxyl groups rotate 26.1° and 22.5° and the para-carboxyl group distorts 6.2°, which is consistent with the repulsion of unshared electron pairs of N atom in **PTA** anion.

As illustrated in Fig. 3, **PTA** anions, guanidiniums and water molecules jointly construct undulate hydrogen-bonded layers parallel to the direction (010), which are arranged at about $b = 1/4$ and $b = 3/4$. It can be seen that tetraethylammonium cations are located between relatively flat layers and the interlayer distance is approximate 6.89

Table 3 Hydrogen bond parameters ($^{\circ}$, Å)

Hydrogen bond	D...A	D–H...A	Hydrogen bond	D...A	D–H...A
(1)					
O2WD–H...O1	2.6880	167	N2–H...O1	2.8488	173
O2WD–H...O3C	2.8110	167	N3–H...O1W	2.8227	166
O1W–H...O3AB	2.7953	171	N3–H...O2WD	3.0238	174
O1W–H...O2AC	2.7728	165			
(2)					
O2W–H...O3W	2.7216	175	O1W–H...O2W	2.7602	168
O2W–H...O6A	2.7588	173	O6W–H...O2B	2.7746	166
O3W–H...O1A	2.7640	177	O6W–H...O1W	2.7654	173
O3W–H...O4W	2.7330	161	N4–H...O1A	2.7993	173
O4W–H...O4	2.7359	145	N2B–H...O6A	2.8284	172
O4W–H...O5W	2.7595	176	N2B–H...O3B	2.8771	177
O5W–H...O5	2.7803	175	N3C–H...O2B	2.8453	177
O5W–H...O6W	2.7957	171	N3C–H...O5	2.8893	178
O1W–H...O3B	2.7656	177	N4–H...O4	2.8700	168

$0.283x + 15.539y - 6.174z = 7.7658$ and mean deviation is 0.0162 \AA and departure distances are 0.2264 and 0.8015 \AA . The water cluster is enmeshed in the center of $(\text{PTA})_3(\text{guanidium})_3$ rosette by six $\text{O–H}\cdots\text{O}$ hydrogen bonds yielded by inner water molecules and outer **PTA** anions to form a dish-like hydrogen-bonded cluster, the water circle being as the ‘bottom’ of ‘dish’ and the rosette as the ‘top’, and the depth between the ‘top’ and the ‘bottom’ is 1.93 \AA (Fig. 4d). Finally, the ‘dishes’ are arranged in face-to-back way to form fluctuant hydrogen-bonded layer structures.

Structural characteristics of inclusion compounds **(1)** and **(2)**

In sandwiched crystal structure of compound **3**, $[1,3,5\text{-C}_6\text{H}_3(\text{COO}^-)_3]\cdot[\text{C}(\text{NH}_2)_3]^+\cdot[(\text{C}_2\text{H}_5)_4\text{N}^+]_2\cdot 6\text{H}_2\text{O}$ (*Pbcn* space group, $Z = 4$), reported by Mak and coworkers [8], the asymmetric unit includes half a **TMA** anion and half a guanidinium which are both arranged at twofold axis, one tetraethylammonium and three independent water molecules. The guanidinium and **TMA** anions form a wonderful planar rosette hydrogen-bonded architecture together and

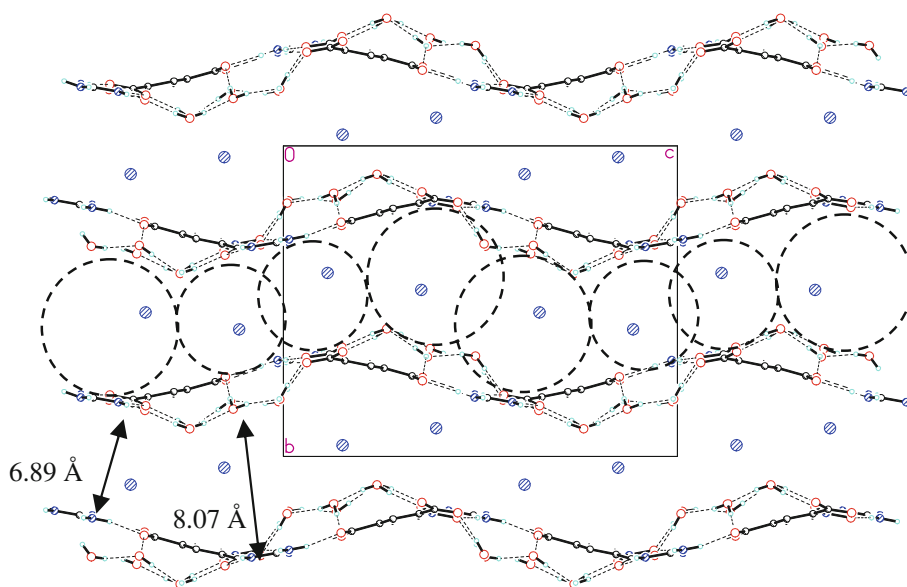


Fig. 3 Packing diagram of $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3]\cdot[\text{C}(\text{NH}_2)_3]^+\cdot[(\text{C}_2\text{H}_5)_4\text{N}^+]\cdot[(\text{C}_3\text{H}_7)_4\text{N}^+]\cdot 6\text{H}_2\text{O}$ (**2**) (for the sake of clarity, the hydrogen atoms bonded to carbon and the carbon atoms of guest

cations are all omitted; the nitrogen atoms of guests are represented with the *hatching circles*; the *bigger dashed circles* represent tetrapropylammoniums and the *smaller ones* tetrethyammoniums)

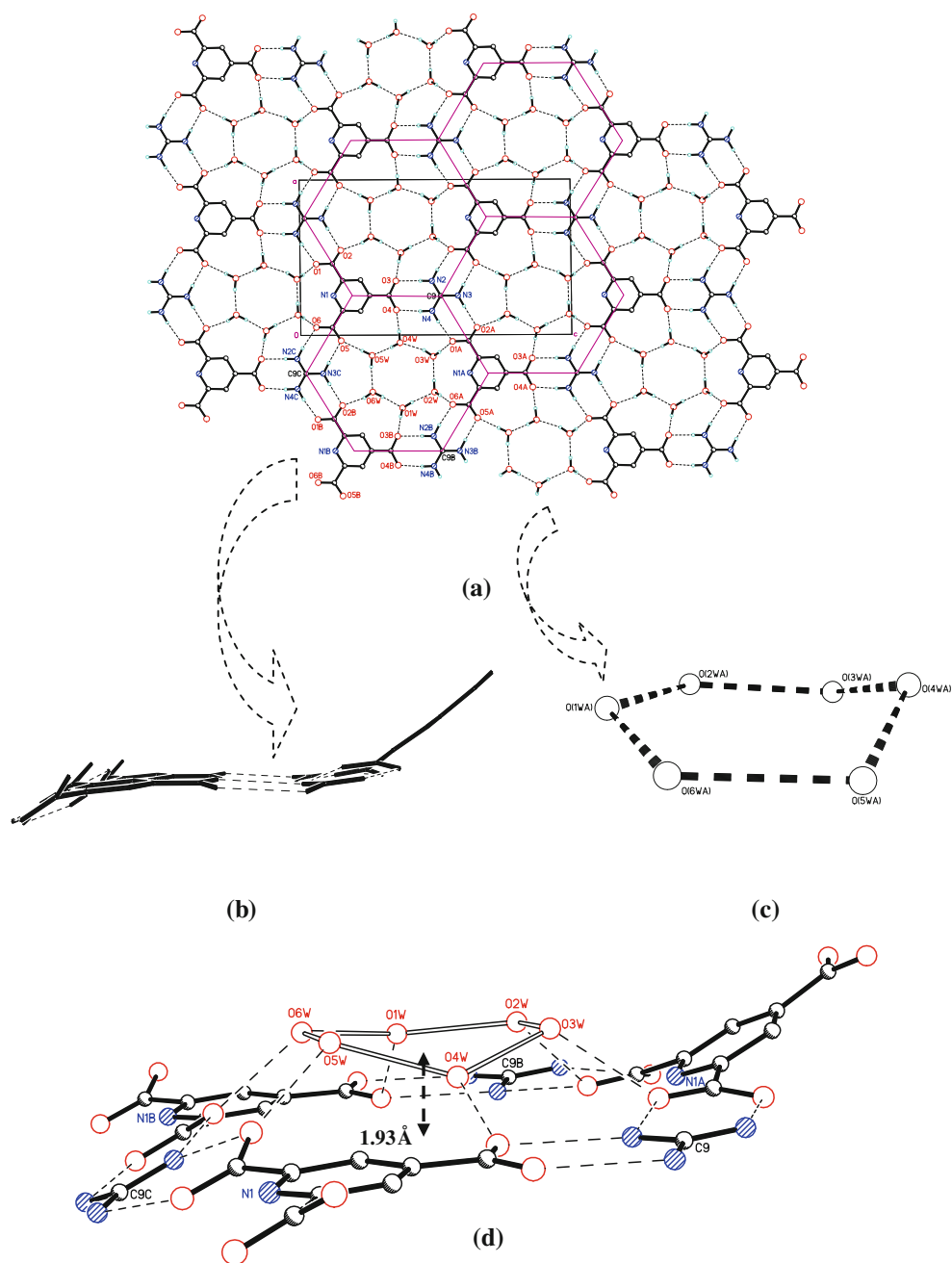


Fig. 4 **a** Hydrogen-bond layer projection along *b* axis in $[2,4,6\text{-C}_5\text{H}_2\text{N}(\text{COO}^-)_3]\cdot[\text{C}(\text{NH}_2)_3]^+ \cdot [(\text{C}_2\text{H}_5)_4\text{N}^+] \cdot [(\text{C}_3\text{H}_7)_4\text{N}^+] \cdot 6\text{H}_2\text{O}$ (**2**) (the hydrogen atoms bonded to carbon are all omitted for clarity and the purple hexagon represents the rosette hydrogen-bond

architecture); **b** the chair-configuration of rosette structure; **c** the asymmetrical boat-like hexagon water cluster; **d** the dish-like architecture composed of the rosette and water cluster [*A*: $-1/2 + x, 3/2 - y, 1/2 + z$; *B*: $-1 + x, y, z$; *C*: $-1/2 + x, 3/2 - y, -1/2 + z$]

three pairs of 2-related water molecules constitute a water cyclic cluster with a flattened-chair configuration inlaid in the rosette structure in an out-of-plane orientation.

Clearly, compound **1** has the same sandwiched layer structure with an interlayer distance of 7.36 Å as the structure of compound **3** with the corresponding value of 7.5 Å, and the two complexes also crystallize in the same space group of *Pbcn*. But the host hydrogen-bond layers in

compound **1** and **3** are very different. As calculated, it is found the mean deviation from the plane of the benzene of **TMA** anion in compound **3** is 0.0051 Å and the dihedral angles between carboxyl groups and benzene are 0.5° and 4.8° separately, whereas the relevant deviation in compound **1** is 0.0037 Å and the angles are 8.4° and 10.7°. It is obviously seen the hexagon rings of **1** and **3** are both coplanar, but the torsion angles between the carboxyl

groups and the related rings are very distinct. Through searching CSD database [14], we got 45 organic crystal structures comprising **TMA** or its anions: The dihedral angles of carboxyl groups and benzenes range from 0° to 29.4° . Meanwhile, we also found 59 crystal structures containing **PTA** or its anions, in which 57 crystal structures are metal organic compounds, with the torsion angles between carboxyl groups and pyridine rings ranging from 0.9° to 72.0° . Analyzing two series of compounds, the distribution percent of dihedral angles involving **TMA** between 0° and 10° is 73%; the percentage whose angles is greater than 20° just accounts for about 4%, whereas the corresponding percents in **PTA** compounds are 57 and 19% separately (Fig. 5). That is to say, the torsion angles between carboxyl groups and pyridine rings in **PTA** complexes are greater than those in **TMA** compounds. This may be influenced by unshared electron pairs of the nitrogen atom of **PTA**. The torsion angles of **PTA** in compound **1** is larger and different amounts of water molecules in two host lattices contribute to accelerate the final undulate hydrogen-bonded layer structure in compound **1**, differing from host layer of compound **3**.

Interestingly, compound **2** crystallizes in different space group from compounds **1** and **3**, but **PTA** anion and guanidinium of compound **2** generate a similar rosette architecture compared with **3**, and six independent water molecules in compound **2** also form the same hexagon water cyclic cluster inlaid in center of the rosette structure as that in **3**. What is obvious, the rosette of compound **2** showing a chair-like hexagon configuration and the water cluster in the middle of rosette with an asymmetric boat-like shape ultimately form a ‘dish’ structure in compound **2**. In compound **3**, the rosette displays a hexagon flattened-chair configuration (Fig. 6), in which **TMA** anions of **O1B** and **O1C** are coplanar and the dihedral angle of **O1** related to the plane is 6.6° , and the guanidiniums of **C1** and **C1E** are also coplanar and the interplanar angle between **C1D** and the plane is 8.0° . It is noted the plane of **O1B** and **O1C** only deviates by 0.7° from planes of **C1** and **C1E**.

Additionally, the water cluster of compound **3** also shows a flattened-chair configuration, in which **O4**, **O6**, **O4A** and **O6A** are also coplanar (The equation of plane is $7.824x + 0.000y - 11.133z = 12.2621$, and the mean deviation from the plane is 0.0216 \AA) and the distances of **O5** and **O5A** deviating from the plane are -0.5021 and 0.5021 \AA respectively. As shown in Fig. 6, there is a flat water cluster inlaid in the center of the rosette structure in an out-of-plane orientation, with the dihedral angle between the plane of **O4**, **O6**, **O4A**, **O6A** and the **C1** plane being 36.3° .

Obviously, the puckering host layers of compound **2** yield varying interlayer distances which simultaneously contains tetraethylammonium and greater tetrapropylammonium. The interlayer distance accommodating tetraethylammonium is about $0.5\text{--}0.6 \text{ \AA}$ smaller than compound **1** and **3**, and the separation containing tetrapropylammonium is almost $0.6\text{--}0.7 \text{ \AA}$ greater than compound **1** and **3**, compared with interlayer values ($7.6\text{--}8.6 \text{ \AA}$) of those sandwich-like hydrogen-bonded structures only accommodating tetrapropylammonium [15, 16]. The calculating results show that the mean deviation from plane of pyridine ring in compound **2** is 0.0160 \AA and the dihedral angles between carboxyl groups and pyridine ring are 26.1° , 22.5° and 6.2° respectively, greater than compound **3**. Due to greater torsion angles of compound **2**, it causes rosette layer not as planar as that in compound **3**. However, the formation of rosette architecture of compound **2** is not affected.

It is interesting to find the appearance of mixed guest species in complex **2**. There are only several papers related to mixed solvent guest species published to explore competition of guest molecules in inclusion compounds [17–22]. Until now, it has not been found the crystal structures containing mixed guest tetraalkylammonium cations. In this research, various inclusion compounds containing different tetraalkylammonium cations are prepared and investigated, but mixed guest cations in one inclusion compound are never showed. In the crystal structure of compound **2**, two kinds of guest cations,

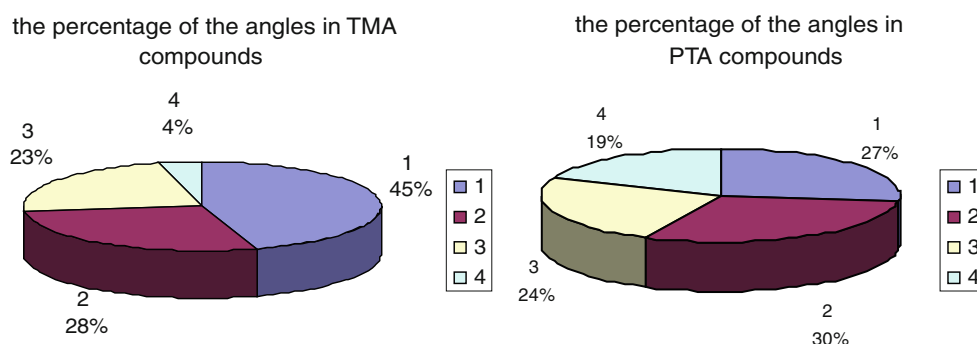


Fig. 5 **a** The distribution of interplanar angles between carboxyl groups and benzene ring in **TMA** compounds; **b** the distribution of interplanar angles between carboxyl groups and pyridine ring in **PTA** compounds (1: $0\text{--}5^\circ$; 2: $5\text{--}10^\circ$; 3: $10\text{--}20^\circ$; 4: $>20^\circ$)

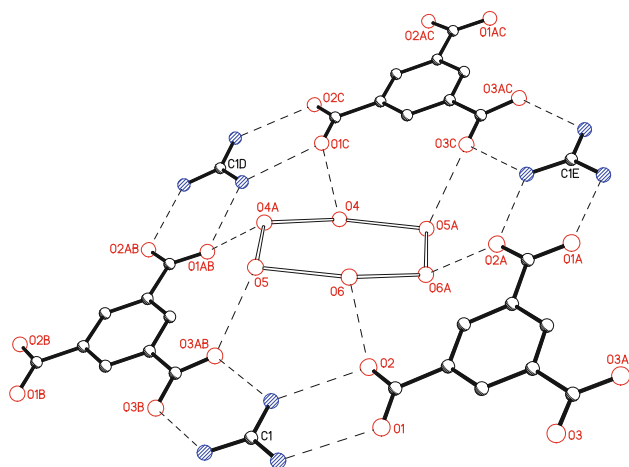


Fig. 6 TMA-guanidinium rosette structure with the water cluster inlaid in the rosette in $[1,3,5\text{-C}_6\text{H}_3(\text{COO}^-)_3]\cdot[\text{C}(\text{NH}_2)_3]^+\cdot[(\text{C}_2\text{H}_5)_4\text{N}^+]_2\cdot 6\text{H}_2\text{O}$ (**3**) (for clarity, all the hydrogen atoms are omitted and the hydrogen bonds formed among the water molecules are represented by the *open bonds*) [A: $1 - x, y, 3/2 - z$; B: $-1/2 + x, 1/2 + y, 3/2 - z$; C: $1/2 + x, 1/2 + y, 3/2 - z$; D: $1/2 + x, 1/2 + y, z$; E: $1 + x, y, z$]

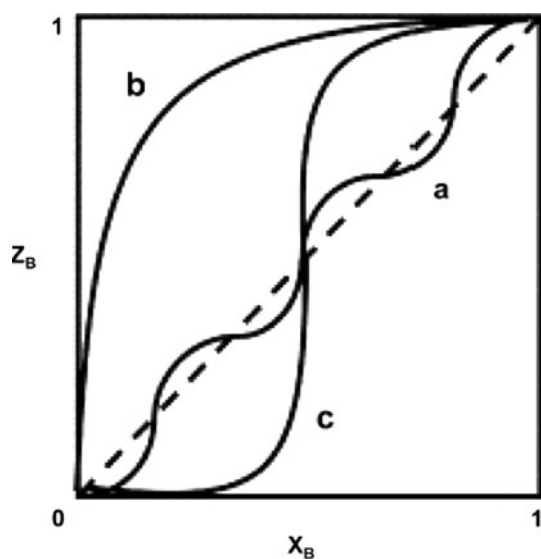


Fig. 7 Typical selectivity curves obtained from competition experiments

tetraethylammonium and tetrapropylammonium, both act as the ‘stuffing’ of the ‘sandwich’ to form the stable crystal structure. In general, three kinds of selectivity curves can be obtained (Fig. 7) by extensively studying several organic host compounds and their selectivity *via* competition experiments between similar guests [20].

X_B is the mole fraction of guest B in the liquid mixture and Z_B that of guest B which has been enclathrated in the host–guest crystal. The broken diagonal line represents zero selectivity. Curve *a* represents poor selectivity and is

likely to arise when the pure compounds H·An and H·Bn are isostructural with respect to the host structure and the guests A and B are located in similar positions of the host lattice. Curve *b* occurs when guest B is strongly selected over guest A for the whole concentration range. Curve *c* occurs when the selectivity is concentration dependent.

In this paper, **PTA** can form a stable mixed inclusion compound with tetraethylammonium and tetrapropylammonium, and with one of the guests, tetraethylammonium. Additionally, we have prepared the crystal of inclusion compound of **PTA** with another guest of tetrapropylammonium, in which the crystal structure is very different from compounds **1** and **2** (relative paper is now in preparation). It can be concluded that the selectivity curve of **PTA** with mixed guests of tetraethylammonium and tetrapropylammonium may follow curve *a* or curve *c*. We are attempting to prepare samples of **PTA** containing different mole fractions of tetraethylammonium and tetrapropylammonium to validate its selectivity curve.

In addition, from the crystal structures published before, it can be illustrated that the volumes of tetrapropylammonium and tetraethylammonium are 221 and 127 \AA^3 [15], and the distinction between them is less than 100 \AA^3 , so what will happen if we mix tetraethylammonium and tetrapropylammonium (287 \AA^3) [15] into one system? Which selectivity curve it will follow? For curiosity in such questions, we are attempting to validate hypothesis by preparing inclusion compounds with different guest species and various sizes. This work is ongoing.

Conclusion

The field of inclusion compounds with mixed guests is an important one in which systematic studies may yet establish what aspects are important in the selection of different guests. These include steric factors, polarity, guest symmetry and solubility [20]. In this regard, it is noteworthy that **PTA** can form a stable mixed inclusion compound with tetraethylammonium and tetrapropylammonium, and even with either of the guests alone.

In addition, the occurrence of N atom in **PTA**, which provides unshared electron pairs, makes three carboxyl groups distort more than that in **TMA**. The distortion may lead to various host lattices compared with coplanar **TMA**. Thus, **PTA** can be regarded as a potential supramolecular synthon with a similar configuration of Y-shape to build novel crystal structures with different guest templates in crystal engineering.

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