

The Effect of Hydrogen Bonding and π - π Stacking to Stabilization of 3D Networks of a New Proton Compound, (a-6-mpyH)(Hpyzd) H₂O

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ABSTRACT

A new proton transfer compound, formulated as (Hamp-6-pic)(Hpyzd) ·H₂O (**1**), has been synthesized from the reaction of pyrazine-2,3-dicarboxylic acid (H₂pyzd) and 2-amino-6-methyl pyridine (amp-6-pic), in 1:1 molar ratio. Extensive O-H...O, N-H...N and O-H...O hydrogen bonds involving (Hamp-6-pic)⁺ cation, (Hpyzd)⁻ anion and co-crystal water molecule, static electronic, and π ... π stacking interactions form a three-dimensional network.

Keywords: (Hamp-6-pic)(Hpyzd).H₂O, proton transfer, hydrogen bonds, π ... π stacking

INTRODUCTION

Several types of non-covalent forces, such as hydrogen bonding [1-4], π - π stacking [5] and electrostatic [6] interactions are of great interest in constructing extended supramolecular networks. Such non-covalent interactions play key roles in the construction of various architectures for molecular self assembly and aggregation [7-9]. In the past decade supramolecular species, containing amines and acids with novel structures and properties have been rapidly developed due to their fascinating molecular structure and potential applications as functional materials [10-12]. Aggregation of organic cations and anions can lead to formation of multi-dimensional networks which contain channels or cavities of various sizes and shapes. In recent years, there have been

several successful attempts at employing proton transfer compounds to aggregation of organic molecules and formation of multi-dimensional networks. Compounds containing oxygen or hybrid oxygen-nitrogen atoms, especially multicarboxylate compounds can act as hydrogen-bond donor or acceptor and aromatic systems such as those of 2,2'-bipyridine and 1,10-phenanthroline can be stabilized by stacking interactions involving the π systems. As is known, pyrazine-2,3-dicarboxylic acid is a bifunctional acid. Two carboxyl groups of acid may be completely or only partly deprotonated and 1:1 or 1:2 proton transfer compounds can be formed in the reaction of pyrazine-2,3-carboxylic acid with proton acceptors such as amines. In this

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paper the crystalline proton transfer self-associated 2-amino-6-methylpyridinume pyrazine-2,3-carboxylate ((Hamp-6-pic))(Hpyzd) H₂O is reported.

EXPERIMENTAL

Materials and Instrumentations

The starting materials pyridine-2,3-dicarboxylic acid and 2-amino-6-methylpyridine were all purchased from Merck, Germany. IR spectra were recorded using FT-IR Spectra Bruker Tensor 27 spectrometer (KBr pellets, 4000-400 cm⁻¹). Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer.

SYNTHESIS OF THE COMPOUND

A solution of pyrazine-2,3-dicarboxylic acid (0.168g, 1 mmol) and 2-amino-6-methyl pyridine (0.108g, 1 mmol) was refluxed in water (20 ml) for 3 h. The solid residue was filtered and the filtrate was kept at 4 °C. Colorless crystals of the title compound were obtained after a few days. IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3100-3500 (b), 2820 (s), 1716 (s), 1661 (s), 1603 (m), 1389 (s), 1250 (m), 1179 (m), 1094(s), 864 (s), 833 (m), 779 (s), 556 (w). Anal. For C₁₂H₁₄N₄O₅ (294.27): Calcd. C 48.93, H

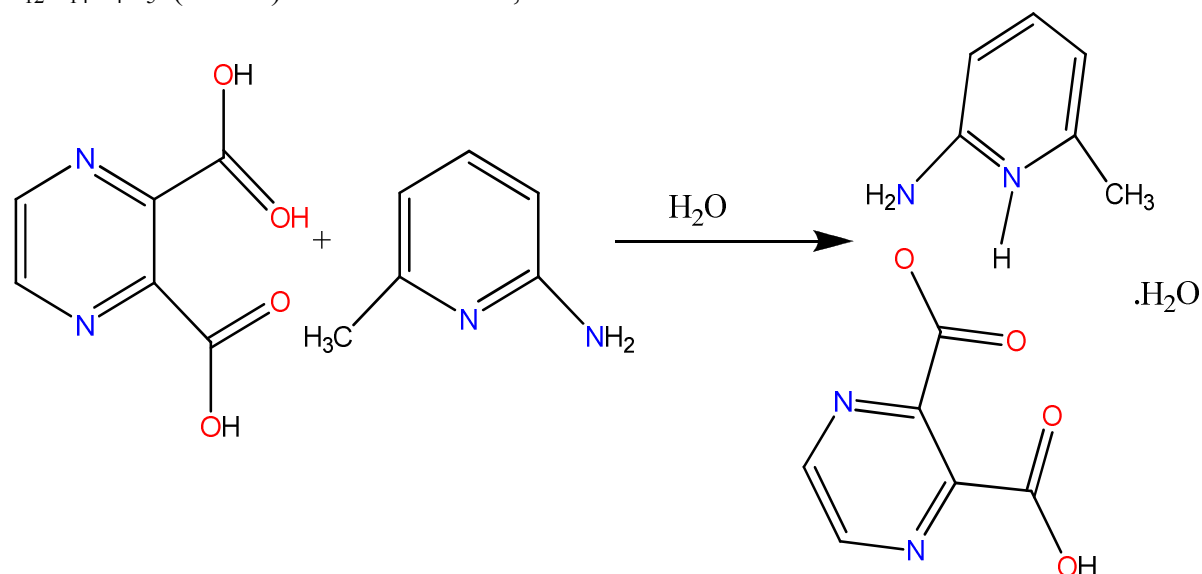
4.76, N 19.03; Found C 48.38, H 4.79, N 18.89.

X-RAY CRYSTALLOGRAPHY

Data were collected on a Bruker Kappa APEX-DUO diffractometer using a Copper ImuS (microsource) tube with multi-layer optics and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX2 and SAINT (Bruker, 2007). Absorption corrections were carried out using SADABS [13]. The structure was solved and refined using SHELXTL [14] for full-matrix least-squares refinement that was based on F². All H atoms bonded to C atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom. H atoms bonded to O and N atoms were refined independently with isotropic displacement parameters. Details of the crystal structure analysis are shown in Table 1.

RESULTS AND DISCUSSION

Compound 1 was prepared according to Scheme 1.



Scheme 1. Preparation of compound 1.

Crystal Structure

Figure 1 illustrates the principle structural features of **1**. In the compound, just one of the carboxyl groups of pyrazine-2,3-dicarboxylic acid is deprotonated and one H atom being transferred to the endocyclic nitrogen atom of 2-amino-6-methylpyridine (Fig. 1). The H atom of carboxylate group (H10) acts as bridging agent by forming a strong hydrogen bonding (O4–H10 1.10(2) Å, H10⋯O1 1.36(2), O4–H10⋯O1: 2.4574 (12) Å and \angle O4–H10⋯O1 175(2) °) between two 3-carboxypyrazine-2-carboxylato ions. Therefore, it is responsible for dimerization of two ions (Fig. 2). The dimers are also linked to cations and co-crystalline water molecule via O–H⋯O, N–H⋯N and N–H⋯O hydrogen bonds

(Table. 2) and form an interesting 2D-Network of cations, anions and water molecules in (010) plane (Fig. 3).

There are also stacking interactions between pyridine and pyrazine (*cg1-cg2*) or pyrazine (*cg2-cg2*) rings in **1** defined by N3/C7/C8/C9/C10/C11 and N1/C2/C5/N2/C4/C3 [symmetry code 1-X,1-Y,1-Z; centroid–centroid distance 3.6936(7) Å; the angle between the planes is 0.0°; the perpendicular distance between the planes is 3.390 Å; the slippage is 1.337 Å]. Two dimensional networks are further assembled into a supramolecular network *via* other non-covalent interactions such as crystal field forces, static electronic, and π ⋯ π stacking interactions.

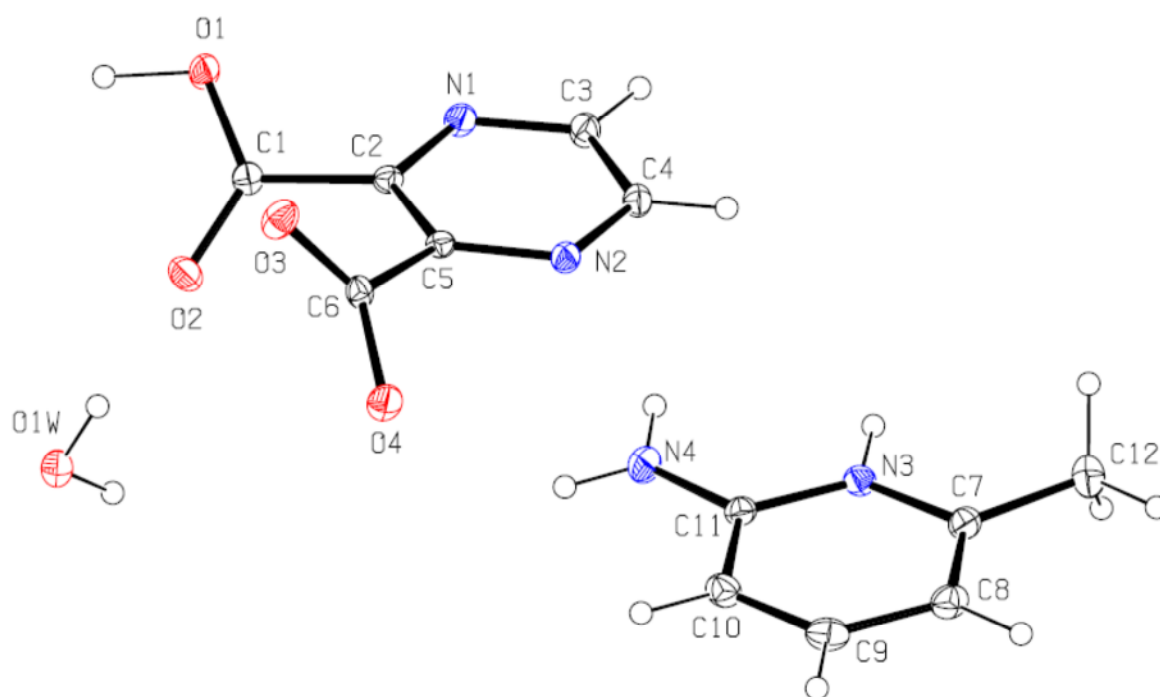


Fig. 1. The molecular structure of (Hamp-6-pic)(Hpyzd) · H₂O with 30% displacement ellipsoids for non-hydrogen atoms.

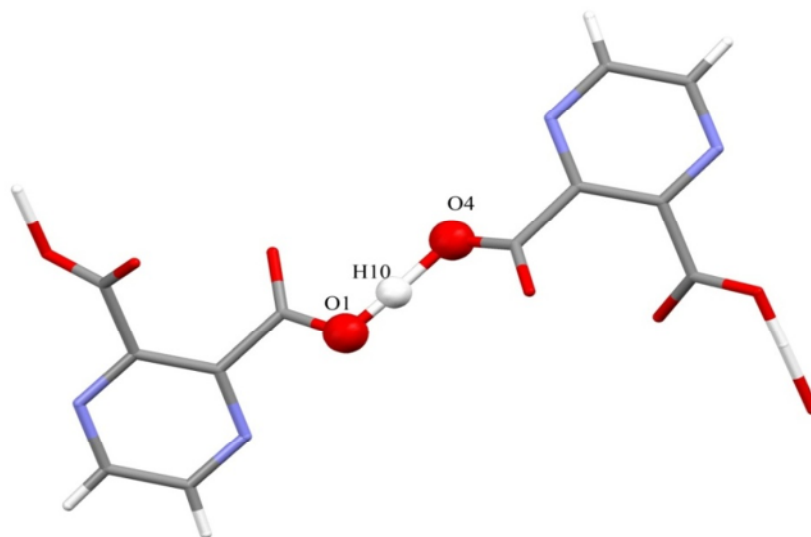


Fig. 2. Dimerization of two 3-carboxypyrazine-2-carboxylate ions *via* strong Hydrogen bonds.

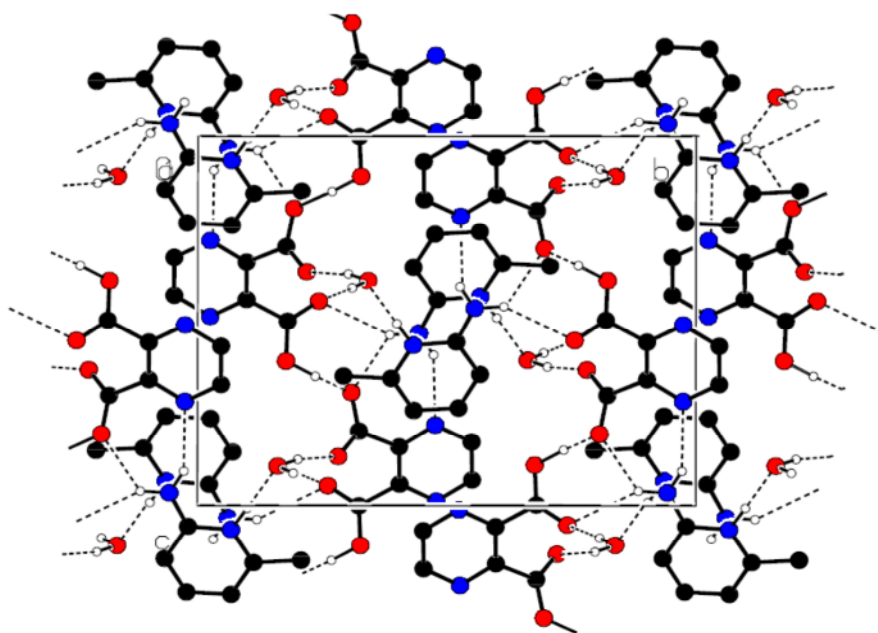


Fig. 3. A view of the crystal structure of **1**. The Hamp-6-pic⁺ cations, (Hpyzd)⁻ anions and solvated water molecule are connected into an infinite 2D chain, extending along the [101] direction, by the O–H···O, N–H···N and N–H···O hydrogen bonds (shown by the dotted lines).

Infrared spectra

IR (KBr) $\tilde{\nu}$ (cm⁻¹): 3100-3500 (b), 2820 (s), 1716 (s), 1661 (s), 1603 (m), 1385 (m), 1380 (m), 1250 (m), 1179 (m), 1094(s), 864 (s), 833 (m), 779 (s), 556 (w). Anal. For C₁₂H₁₄N₄O₅ (294.27): Calcd. C 48.93, H 4.76, N 19.03; Found C 48.38, H 4.79, N 18.89.

The IR spectra of compound show two sets of vibrations due to the water molecules and dipicolinate ligands. In the IR spectra of compound, the band associated to the antisymmetric stretching vibrational modes, $\nu_{as}(\text{COO})$, appear at 16716 and 1661 cm⁻¹, indicating the presence of two different COO groups

(COOH and COO⁻) in the compound which is in agreement with its crystal structures. The $\nu_s(\text{COO})$ bands appear at 1385 cm⁻¹ and 1380 cm⁻¹. The IR spectra of the compounds shows broad, strong bands at the region of 3400–3100 cm⁻¹, which could be related to the existence of O–H...O hydrogen bonding, including water molecules. These bands have been coupled by the other indicative peaks such as N–H and O–H stretching frequencies and the stretching frequencies due to the aromatic rings which originally fall within

this region [15, 16].

Supplementary material

CCDC 902701 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk]. Structure factor table is available from the authors.

Table 1. Crystal data and details of the structure determination for 1.

Compound	1
Formula	C ₁₂ H ₁₄ N ₄ O ₅
M_r	294.27
Colour and habit	colorless, plate
Crystal system, space group	monoclinic, $P21/n$
Crystal dimensions / mm ³	0.13 × 0.12 × 0.04
a / Å	7.0564(3)
b / Å	15.5368(7)
c / Å	12.0844(5)
α / °	90
β / °	99.723(2)
γ / °	90
V / Å ³	1305.83(10)
Z	4
D_{calc} / g cm ⁻³	1.497
μ / mm ⁻¹	1.011
$F(000)$	616
Temperature / K	147(2)
θ range for data collection / °	4.68–66.45
h, k, l range	-8:8, -18:17, -9:14
Scan type	ω, φ
No. measured reflections	8633
No. independent reflections (R_{int})	2256/0.0250
No. observed reflections, $I \geq 2\sigma(I)$	2135
No. refined parameters	215
R^a , wR^b [$I \geq 2\sigma(I)$]	0.0309, 0.0780
R , wR [all data]	0.0326, 0.0794
Goodness of fit on F^2 , S^c	1.053
Max., min. electron density / e Å ⁻³	0.182, -0.231

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = \left[\frac{\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

$$^c S = \left[\frac{\sum [w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]}{N_{\text{obs}} - N_{\text{param}}} \right]^{1/2}$$

Table 2. Hydrogen bond geometry for 1.

D-H...A	$d(\text{D-H})/\text{\AA}$	$d(\text{H...A})/\text{\AA}$	$d(\text{D...A})/\text{\AA}$	$\angle(\text{D-H...A})^\circ$	Symmetry code on A
O1-H10-O4	1.10(2)	1.36(2)	2.4573(12)	175(2)	-1/2+x,3/2-y,-1/2+z
N3-H3N-O1W	0.933(18)	1.804(18)	2.7372(13)	178.9(15)	1/2-x,-1/2+y,1/2-z
N4-H4B-O4	0.911(19)	2.290(18)	2.9054(14)	124.6(14)	
N4-H4B-O2	0.911(19)	2.471(19)	3.2912(15)	149.9(14)	1/2+x,3/2-y,1/2+z
N4-H4C-N2	0.867(17)	2.363(17)	3.1413(15)	149.5(14)	
O1W-H1WA-O2	0.88(2)	1.95(2)	2.8315(13)	175.9(18)	
O1W-H1WB-O3	0.90(2)	1.81(2)	2.7055(12)	169.0(18)	-1+x,y,z

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