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aghabozorg@saba.tmu.ac.ir**Key indicators**Single-crystal X-ray study  
 $T = 193\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.068  
 $wR$  factor = 0.138  
Data-to-parameter ratio = 13.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**A proton transfer compound: propane-  
1,3-diaminium–pyridine-2,6-dicarboxylate–  
pyridine-2,6-dicarboxylic acid–water (2/2/2/5)**

The title compound,  $\text{C}_3\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_7\text{H}_3\text{NO}_4^{2-} \cdot \text{C}_7\text{H}_5\text{NO}_4 \cdot 2.5\text{H}_2\text{O}$ , is a proton-transfer system obtained from pyridine-2,6-dicarboxylic acid and propane-1,3-diamine. Both neutral and dianionic forms of the diacid are observed in the crystal structure. The molecular structure contains also the diprotonated form of propane-1,3-diamine as well as water molecules. In the crystal structure, a wide range of hydrogen-bonding interactions connect the various fragments into a supramolecular structure.

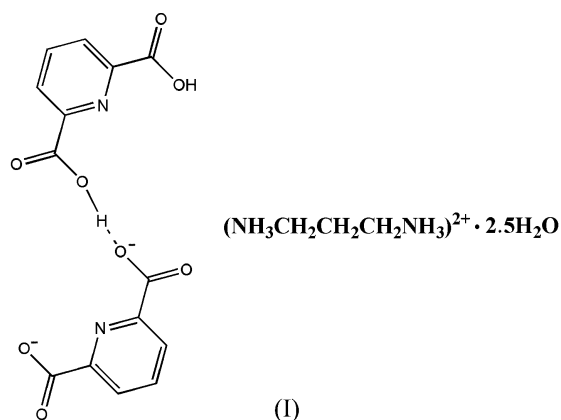
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**Comment**

Dicarboxylic acids possess a good potential to be used as proton donors in the synthesis of proton transfer compounds. Among these diacids, pyridine-2,6-dicarboxylic acid (pydcH<sub>2</sub>) has been used by our research group during recent years for the preparation of such compounds. For example, (pydaH)(pydcH), in which 2,6-pyridinediamine (pyda) was used as a proton acceptor (Aghabozorg, Akbari Saei & Ramezanipour, 2005). We have also used ethylenediguanidine (EDG) as an acceptor in the proton-transfer compound (EDGH<sub>2</sub>)(pydc)·3H<sub>2</sub>O (Moghimi, Aghabozorg, Sheshmani, Kickellbick & Soleimannejad, 2005). The crystal structure of (pyrimH){H(Hpydc)<sub>2</sub>} has also been reported. Here *N,N'*-diethyl-2-amino-6-methyl-4-pyrimidinol (pyrim) acted as a proton acceptor (Aghabozorg, Soleimannejad *et al.*, 2005). Creatinine (creat) is another acceptor, forming a proton transfer compound, (creatH)(pydcH)·H<sub>2</sub>O (Moghimi, Sharif *et al.*, 2005). We reported also on (phenH)<sub>2</sub>(pydc), synthesized using 1,10-phenanthroline (phen) (Moghimi, Sheshmani *et al.*, 2005). Compound (GH)<sub>2</sub>(pydc) was another product, prepared from guanidine (G) and pydcH<sub>2</sub> (Moghimi *et al.*, 2004). Additionally, we have worked on a derivative of pydcH<sub>2</sub>, that is, 4-hydroxy-pyridine-2,6-dicarboxylic acid (hypydcH<sub>2</sub>). Two distinct proton-transfer compounds were synthesized using hypydcH<sub>2</sub> as a donor and guanidine as an acceptor (Moghimi, Aghabozorg, Sheshmani & Soleimannejad, 2005; Moghimi, Aghabozorg, Soleimannejad & Ramezanipour, 2005). After synthesis of proton-transfer compounds, the next step has always been the use of these compounds to prepare metal complexes. Often, anionic fragments of these compounds act as ligands. The self-assembling characteristics of these complexes (Aghabozorg, Moghimi *et al.*, 2005; Moghimi, Sharif *et al.*, 2005; Moghimi, Sheshmani *et al.*, 2005; Moghimi, Sheshmani *et al.*, 2004) illustrate the suitability of using proton-transfer compounds in the preparation of supramolecular systems. We report here a new proton-transfer compound, (I), obtained from pydcH<sub>2</sub> as a donor and propane-1,3-diamine as an acceptor.

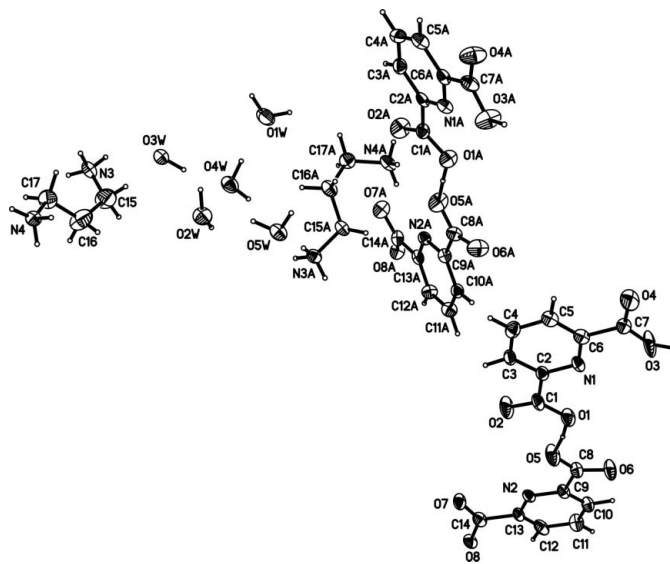


The asymmetric unit of the title compound, (I), is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The structure of (I) contains neutral pydcH<sub>2</sub> molecules, dianionic (pydc)<sup>2-</sup> species and water molecules. The negative charge of the anions is neutralized by dicationic propane-1,3-diaminium species. A double proton transfer has occurred from pydcH<sub>2</sub> to propane-1,3-diamine during the reaction. The use of propane-1,3-diamine as a proton acceptor has been reported in several publications, all of which show the formation of the diprotonated form of this diamine (Loiseau & Ferey, 2005, 2004; Kissick & Chippindale, 2002). On the other hand, propane-1,3-diamine has also been shown to act as a ligand in a number of metal complexes (Luo *et al.*, 2003; Kabak *et al.*, 1999; Tong *et al.*, 1999). Accordingly we can anticipate that (I) is an appropriate compound to be used for the synthesis of metal-organic systems, owing to the ability of both its cationic and its anionic fragments to form metal complexes, as mentioned above.

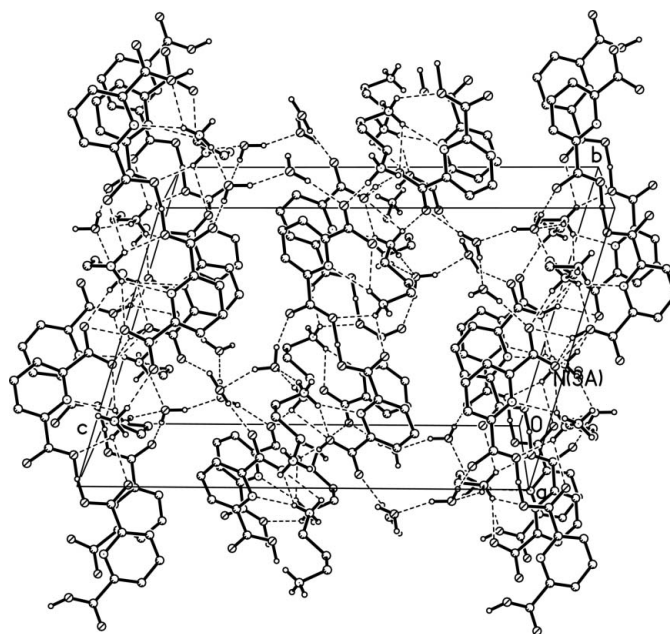
A remarkable feature in the crystal structure of compound (I) is the presence of a large number of N—H···O, N—H···N and O—H···O hydrogen bonds (Fig. 2 and Table 2). The shortest hydrogen bond is O3A—H30A···O7A(*x* + 1, *y* + 1, *z*) with *D*···*A* = 2.453 (4) Å, a very strong interaction. However, O—H···O interactions with *D*···*A* distances as long as 3.0802 (4) Å are also observed in the crystal structure (Table 2). The hydrogen bonds connect the different components, so forming infinite layers, which are finally linked together to form a hydrogen-bonded three-dimensional network (Fig. 2). Compound (I), consequently, can be considered as a supramolecular structure formed by non-covalent interactions.

## Experimental

The reaction of pyridine-2,6-dicarboxylic acid with propane-1,3-diamine in a 1:2 molar ratio in THF led to the formation of a white precipitate, which was filtered off and dried. The resulting powder was dissolved in water to give colorless crystals of compound (I) after four weeks.



**Figure 1**  
The asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.



**Figure 2**  
A view down the *a* axis of the crystal packing of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

## Crystal data

$C_3H_{12}N_2^{2+} \cdot C_7H_3NO_4^{2-} \cdot C_7H_5NO_4 \cdot 2.5H_2O$	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 453.41	<i>D<sub>x</sub></i> = 1.474 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.8724 (16) Å	Cell parameters from 24 reflections
<i>b</i> = 13.534 (3) Å	<i>θ</i> = 9–12°
<i>c</i> = 20.986 (4) Å	<i>μ</i> = 0.12 mm <sup>-1</sup>
<i>α</i> = 106.64 (3)°	<i>T</i> = 193 (2) K
<i>β</i> = 90.54 (3)°	Prism, colorless
<i>γ</i> = 106.54 (3)°	0.30 × 0.25 × 0.20 mm
<i>V</i> = 2043.5 (7) Å <sup>3</sup>	

## Data collection

Rebuilt Syntex P2<sub>1</sub>/Siemens P3  
four-circle diffractometer  
 $\omega/2\theta$  scans  
Absorption correction: none  
8323 measured reflections  
7768 independent reflections  
3755 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.074$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.138$   
 $S = 1.02$   
7768 reflections  
572 parameters  
H-atom parameters constrained

$\theta_{\text{max}} = 26.0^\circ$   
 $h = 0 \rightarrow 9$   
 $k = -16 \rightarrow 16$   
 $l = -25 \rightarrow 25$   
2 standard reflections  
every 98 reflections  
intensity decay: 1.5%

$w = 1/[\sigma^2(F_o^2) + (0.0007P)^2 + 1.66P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N3—C15	1.465 (6)	O3A—C7A	1.269 (5)
N4—C17	1.470 (5)	O4A—C7A	1.222 (5)
O1—C1	1.273 (5)	O5A—C8A	1.258 (5)
O2—C1	1.233 (4)	O5A—H1OA	1.4247
O3—C7	1.243 (5)	O6A—C8A	1.226 (5)
O4—C7	1.232 (5)	O7A—C14A	1.286 (5)
C1—C2	1.514 (5)	O8A—C14A	1.236 (4)
C6—C7	1.522 (5)	C1A—C2A	1.518 (5)
N3A—C15A	1.478 (4)	C6A—C7A	1.505 (5)
N4A—C17A	1.478 (5)	C8A—C9A	1.525 (5)
O1A—C1A	1.296 (5)	C13A—C14A	1.511 (5)
O2A—C1A	1.222 (4)		
O2—C1—O1	125.7 (4)	O2A—C1A—O1A	125.0 (4)
O2—C1—C2	118.6 (4)	O2A—C1A—C2A	118.9 (4)
O1—C1—C2	115.8 (3)	O1A—C1A—C2A	116.0 (3)
O4—C7—O3	125.7 (4)	O4A—C7A—O3A	124.5 (4)
O4—C7—C6	118.8 (4)	O4A—C7A—C6A	120.6 (4)
O3—C7—C6	115.5 (3)	O3A—C7A—C6A	114.9 (3)
O6—C8—O5	126.4 (4)	O6A—C8A—O5A	125.8 (4)
O6—C8—C9	116.9 (4)	O6A—C8A—C9A	117.0 (4)
O5—C8—C9	116.6 (3)	O5A—C8A—C9A	117.2 (3)
O8—C14—O7	125.2 (4)	O8A—C14A—O7A	124.6 (4)
O8—C14—C13	117.6 (4)	O8A—C14A—C13A	119.0 (4)
O7—C14—C13	117.2 (3)	O7A—C14A—C13A	116.4 (3)
C16—C15—N3	119.2 (4)	N3A—C15A—C16A	112.1 (3)
N4—C17—C16	114.1 (4)	N4A—C17A—C16A	112.2 (3)
O2—C1—C2—N1	-173.0 (4)	O2A—C1A—C2A—N1A	170.7 (3)
O1—C1—C2—N1	6.1 (5)	O1A—C1A—C2A—N1A	-9.4 (5)
N1—C6—C7—O4	179.7 (4)	N1A—C6A—C7A—O4A	174.4 (4)
N1—C6—C7—O3	0.6 (5)	N1A—C6A—C7A—O3A	-5.5 (5)
O6—C8—C9—N2	171.3 (3)	O6A—C8A—C9A—N2A	-170.2 (3)
O5—C8—C9—N2	-6.1 (5)	O5A—C8A—C9A—N2A	8.2 (5)
N2—C13—C14—O8	-166.1 (3)	N2A—C13A—C14A—O8A	165.6 (3)
N2—C13—C14—O7	11.6 (5)	N2A—C13A—C14A—O7A	-15.0 (5)
N3—C15—C16—C17	-39.1 (8)	N3A—C15A—C16A—C17A	-153.7 (3)
C15—C16—C17—N4	-155.5 (5)	C15A—C16A—C17A—N4A	-53.4 (4)

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

D—H...A	D—H	H...A	D...A	D—H...A
N3—H1N3...O5 <sup>i</sup>	0.91	2.11	2.841 (4)	136
N3—H1N3...O2 <sup>i</sup>	0.91	2.29	2.997 (4)	135
N3—H2N3...O3W	0.91	2.03	2.859 (4)	150
N3—H3N3...O7 <sup>v</sup>	0.91	2.23	2.982 (4)	140
N3—H3N3...N2 <sup>i</sup>	0.91	2.28	3.077 (4)	146

D—H...A	D—H	H...A	D...A	D—H...A
N4—H1N4...N1 <sup>ii</sup>	0.91	2.12	3.003 (4)	162
N4—H2N4...O8 <sup>iii</sup>	0.91	2.09	2.938 (4)	155
N4—H3N4...O3W <sup>iv</sup>	0.91	1.92	2.823 (4)	174
O3—H3O...O7 <sup>v</sup>	0.94	1.61	2.457 (4)	147
O3—H3O...O7 <sup>v</sup>	0.94	1.61	2.457 (4)	147
O3—H3O...O8 <sup>v</sup>	0.94	2.30	3.078 (4)	140
O5—H1O1...O1	1.20	1.28	2.471 (4)	170
N3A—H1NA...N1A <sup>vi</sup>	0.91	2.09	2.963 (4)	161
N3A—H1NA...O3A <sup>vi</sup>	0.91	2.29	2.737 (4)	110
N3A—H2NA...O8A <sup>vii</sup>	0.91	2.11	2.919 (4)	147
N3A—H3NA...O5W	0.91	1.89	2.791 (4)	173
N4A—H1NB...N2A	0.91	2.29	3.116 (4)	152
N4A—H1NB...O7A	0.91	2.35	3.074 (4)	137
N4A—H2NB...O2A	0.91	2.15	2.895 (4)	139
N4A—H2NB...O5A	0.91	2.18	2.847 (4)	130
N4A—H3NB...O5W <sup>viii</sup>	0.91	2.03	2.836 (4)	147
O1A—H1OA...O5A	1.07	1.43	2.475 (4)	167
O3A—H3OA...O7A <sup>ix</sup>	0.95	1.52	2.453 (4)	167
O1W—H1W1...O8 <sup>x</sup>	0.95	1.91	2.861 (4)	174
O1W—H2W1...O2W <sup>xiii</sup>	0.95	2.08	2.876 (4)	140
O2W—H1W2...O4 <sup>vi</sup>	0.95	2.02	2.820 (4)	141
O2W—H2W2...O4A <sup>xi</sup>	0.95	1.90	2.705 (4)	142
O3W—H1W3...O4W	0.95	1.90	2.814 (4)	161
O3W—H2W3...O6 <sup>xii</sup>	0.95	1.74	2.684 (4)	175
O4W—H1W4...O1W	0.95	1.83	2.781 (4)	175
O4W—H2W4...O8A <sup>vii</sup>	0.95	2.01	2.934 (4)	166
O5W—H1W5...O2W	0.95	1.94	2.821 (4)	154
O5W—H2W5...O6A <sup>vi</sup>	0.95	1.73	2.656 (4)	163

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $x + 1, y, z + 1$ ; (iii)  $x + 1, y + 1, z + 1$ ; (iv)  $x + 1, y, z$ ; (v)  $x, y + 1, z$ ; (vi)  $-x + 1, -y + 1, -z + 1$ ; (vii)  $-x, -y, -z + 1$ ; (viii)  $x - 1, y, z$ ; (ix)  $x + 1, y + 1, z$ ; (x)  $x, y + 1, z + 1$ ; (xi)  $x, y - 1, z$ ; (xii)  $x, y, z + 1$ .

The H atoms of the carboxyl and  $\text{NH}_3$  groups, and of the water molecules, were located in difference Fourier syntheses and refined as riding atoms with distances constraints of  $\text{N—H} = 0.91 \text{ \AA}$ ,  $\text{O}_{\text{water}}\text{—H} = 0.95 \text{ \AA}$  and  $\text{O}_{\text{carboxyl}}\text{—H} = 0.94\text{--}1.42 \text{ \AA}$  [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$ ]. There are some long O—H bonds, for example,  $\text{O1—H1O1} = 1.28 \text{ \AA}$  and  $\text{O5A—H1OA} = 1.42 \text{ \AA}$ . We believe that this is connected with the possible superposition of two different tautomers, which can lead to pseudosymmetric hydrogen bonds or long O—H distances. The remainder of the H atoms were included in calculated positions and refined as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{methine}})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{methylene}})$ , and  $\text{C—H} = 0.95\text{--}0.99 \text{ \AA}$ .

Data collection: *P3/PC* (Siemens, 1989); cell refinement: *P3/PC*; data reduction: *P3/PC*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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