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# A new three dimensional proton transfer compound including citric acid and 2,4,6-triamine-1,3,5-triazine: Synthesis, characterization and X-ray crystal structure

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ABSTRACT

A new three dimensional proton transfer compound, $(tataH)_2(citH).2H_2O$ (I) was synthesized from the reaction of citric acid ($citH_3$), and 2,4,6-triamino-1,3,5-triazine (tata). The characterization was performed using elemental analysis, IR spectroscopy, and single crystal X-ray structure determination. The crystal structure of the title compound consists of bis-2,4,6-triamino-1,3,5-triazin-1-ium cations, hydrogen citrate, and lattice water molecules. Intermolecular O–H•••O, N–H•••O, and N–H•••N hydrogen bonding interactions stabilize the crystal structure. The hydrogen bonds distances range from of 1.781 to 2.088 Å. The π–π stacking (centroid-centroid ranges 3.410-3.504 Å) between two aromatic rings of tata moieties can play an essential role in the creation and stabilization of the title crystalline network.

## 1. Introduction

There has been a previous report of a proton-transfer system using pyridine-2,6-dicarboxylic acid ($H_2pydc$) and 2,4,6-triamino-1,3,5-triazine, tata [1], along with some complexes containing proton transfer compounds [2-5]. In the title compound presented here, tata is mono-protonated, but it is also known to form $(tataH_2)^{2+}$ salts with trifluoroacetic acid [6], oxalic acid [7], and other strong acids. Tata has been widely studied for its potential in the formation of extended hydrogen-bonded solids. For example, crystal structure of tata with aromatic acids such as benzoic [8], phthalic [9], terephthalic [10-11], and mellitic acid [12] have been reported. Proton transfer compounds including tata and its derivatives can develop supramolecular structures *via* hydrogen bonding (for short H-bonding) through a self assembling process. The $(tataH)^+$ sulfate hydrate, $(C_3H_7N_6)_2SO_4.H_2O$, has been structurally investigated [13], and also presented the solid state structure of anhydrous $(tataH_2)^{2+}$ salt [14]. Due to the steadily increasing demand of $citH_3$ for industrial purposes, it is manufactured from cane or beet molasses, has proved to be of great importance to sugar industry. In this paper, we chose $citH_3$ and tata due to their suitable difference in $pK_a$ for better proton transferring as well as their diverse properties in industrial and other fields. In order to develop a new type of proton transfer compound with self-assembling capability and, further understanding of van der Waals interactive behavior of these two organic compounds in crystalline network, and in continuation of our research programs oriented to the preparation of supramolecular coordination compounds and proton transfer systems [15-28], we wish to report a new three dimensional proton transfer compound of $citH_3$ and tata, (**I**).

## 2. Experimental

### *2.1. Instrumentation*

All reagents and chemicals were purchased from commercial sources and used without further purification. IR spectra were recorded using Buck 500 Scientific spectrometer (KBr pellets, Nujol mulls, 4000-400 $cm^{-1}$). Elemental analysis was carried out with a Thermo Finnigan Flash-1112EA microanalyzer. A 0.121×0.08×0.04 mm crystal was selected and data were collected at 150(2) K using a STOE IPDS 2T diffractometer with a CCD detector. The weighted $R$-factor $wR$ and goodness of fit S were based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. Program(s) used to refine the structure was SHELXL97 (Sheldrick, 2008) [29]. Detailed data collection and refinement of the compound are summarized in Table 1.

### *2.2. Synthesis*

The title compound was synthesized by the reaction of $citH_3$ (0.01 g, 0.04 mmol) with tata (0.01 g, 0.01 mmol) in a water solution (5 mL). The solution was stirred at 338 K for five hrs. Colourless crystals of **I** were obtained and collected after five days through a slow evaporation of the solvent in an ambient condition for single crystal structure determination. Yield: 40% based on $citH_3$. M.p.: decomp. >300°. IR (KBr, $cm^{-1}$): 3352 (br), 1736 (s), 1632 (vs), 1650-1556 (br), 1445 (m), 1380

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(s). Anal. Calcd. for $C_{12}H_{24}N_{12}O_9$: C, 29.98; H, 4.99; N, 34.98. Found C, 29.27; H, 4.50; N, 34.85.

**Table1**. Crystallographic data of compound **I**.

| | |
|---|---|
| Formula | $C_6H_6O_7$•2($C_3H_7N_6$)•2($H_2O$) |
| Formula weight | 480.24 |
| Crystal system | Triclinic |
| Space group | *P* |
| Unit cell dimensions | *a* = 6.5042 (6) Å |
| | *b* = 12.2080 (12) Å |
| | *c* = 13.3652 (13) Å |
| | *α* = 75.771(8)° |
| | *β* = 80.923 (8)° |
| | *γ* = 74.921 (8)° |
| Unit cell volume (Å$^3$) | 988.26 (16) Å$^3$ |
| *Z*, Calculated density (Mg m$^{-3}$) | 2, 1.614 |
| Temperature (K) | 150(2) |
| Wavelength | 0.71073 Å |
| Absorption coefficient (mm$^{-1}$) | 0.14 |
| *F*(000) | 504 |
| Crystal size (mm) | 0.12 × 0.08 × 0.04 |
| θ range for data collection | 4.2-63.9° |
| Limiting indices | $-7 \le h \le 7$ |
| | $-13 \le k \le 13$ |
| | $0 \le l \le 5$ |
| Reflections collected/unique | 3062/895 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3062/0/221 |
| Final *R* indices [I > 2sigma(I)] | *R*1 = 0.048, *wR*2 = 0.108 |
| *R* indices (all data) | *R*1 = 0.1913, *wR*2 =0.1082 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.19 and –0.24 |

## 3. Results and Discussion

In compound **I**, citH$_3$ is doubly deprotonated while two tata are mono-protonated. In the crystal structure of **I**, non-covalent interactions cause the structure to form a self-assembled supramolecular system (Figure 1). According to the packing diagram of compound **I** (Figure 2), one may conclude that citrate ions create many layers consisting of empty spaces as suitable vacancies for entering tata moieties. Some selected bond lengths and angles of the title compound are shown in Table 2. Table 3 lists hydrogen bonding data for compound **I**. Three obvious factors causing the formation of such three dimensional self assembled supramolecular system are: *i*) intermolecular H-bonding between ion pairs, *ii*) electrostatic attractions between opposite ions and *iii*) π-π interactions between the components of two neighbouring sheets. As is obvious from Table 2, all bond lengths and angles are in normal ranges. It should be pointed out that the bond lengths and angles related to two tata moieties are nearly the same. This verifies that both tata moieties are equally engaged in van der Waals interactions. Indeed, van der Waals interactions and in particular H-bondings, connect the anionic and cationic moieties to each other in created spaces. Also, anionic and cationic moieties linked with the help of water molecules *via* H-bondings as good connectors as well as ion pairing interactions. By further considerations of this crystal structure, one may found that excess H-bonding interactions presence between layers cause to produce three dimensional supramolecular architecture. By considering Table 3 and Figure 1, two adjacent tata cations are hydrogen bonded to each other with a cyclic $R_2^2(8)$ pattern [30]. Also, by considering the crystal structure of compound **I,** as it is seen in Figure 3, there are also π-π stacking interactions between the aromatic rings of the tata moieties with distances 3.410-3.504 Å.

The IR spectrum of compound **I** show absorbance in 1650 and 1380 cm$^{-1}$ due to the carboxylate group of ligand [31]. The C=O stretching frequency of carboxylate group in our synthesized compound is about 1736 cm$^{-1}$. Losing of a broad band at 2500-3300 cm$^{-1}$ due to carboxyl O–H stretching frequency shows that acids moiety deprotonated, completely. The feature located at 1632 cm$^{-1}$ is belonging to bending H–O–H frequency, as well as the broad band at 3352 cm$^{-1}$ may be assigned to stretching frequencies of H$_2$O. In summary, the results and discussion presented here indicating that the reaction between citH$_3$ and tata in water results in an intermolecular proton transfer from carboxylic acid protons of citH$_3$ to an endocyclic nitrogen atom of tata molecules.

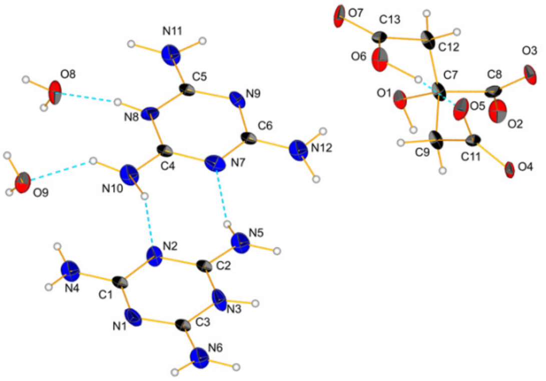

**Figure 1.** The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

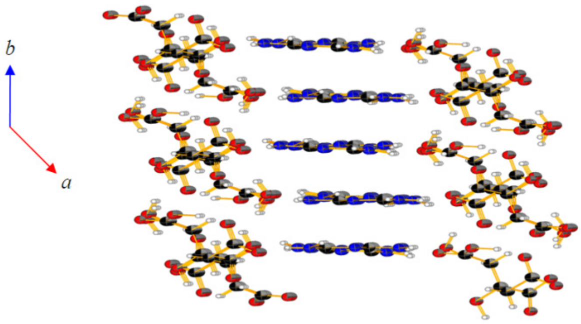

**Figure 2.** The packing diagram of the title compound along *c*-axis. The (tataH)$^+$ are located between layers created by (citH)$^{2-}$.

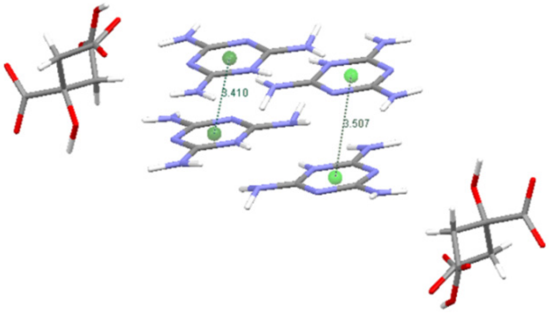

**Figure 3.** Intermolecular π-π stacking between two aromatic rings of tata moieties.

**Table 2**. Selected bond lengths (Å) and angles (°) of compound **I**.

| **Bond lengths** | | **Bond angles** | |
|---|---|---|---|
| N1-C3 | 1.318(8) | C2-N2-C1 | 115.7(5) |
| N1-C1 | 1.349(8) | C3-N3-C2 | 119.6(5) |
| N2-C2 | 1.322(8) | N1-C1-N2 | 125.8(6) |
| N2-C1 | 1.368(8) | N1-C3-N3 | 122.2(6) |
| N4-C1 | 1.334(8) | C4-N7-C6 | 116.4(5) |
| N3-C3 | 1.352(8) | C4-N8-C5 | 119.0(5) |
| N3-C2 | 1.373(8) | N7-C6-N9 | 126.5(6) |
| N5-C2 | 1.322(8) | N9-C5-N8 | 123.1(6) |
| N6-C3 | 1.329(6) | O4-C11-O5 | 124.4(5) |
| O1-C7 | 1.439(7) | O7-C13-O6 | 118.1(6) |
| O3-C8 | 1.273(7) | O2-C8-O3 | 126.0(6) |
| O5-C11 | 1.274(8) | | |
| O6-C13 | 1.320(7) | | |
| O4-C11 | 1.232(8) | | |
| O2-C8 | 1.246(8) | | |
| O7-C13 | 1.221(7) | | |

**Table 3**. Hydrogen bonds of compound **I**.

| **D–H···A** | **d(D–H)** | **d(H···A)** | **d(D···A)** | **<(DHA)** |
|---|---|---|---|---|
| O1-H1···O6$^{i}$ | 1.05 | 2.05 | 3.046(7) | 158 |
| O6-H106···O5 | 1.18 | 1.34 | 2.491(6) | 161 |
| N3-H3···O3$^{ii}$ | 0.93 | 1.73 | 2.659(7) | 175 |
| N4-H4A···O9 | 1.00 | 2.23 | 3.213(7) | 170 |
| N4-H4B···O7$^{i}$ | 0.91 | 2.03 | 2.913(7) | 162 |
| N5-H5A···O4$^{ii}$ | 0.98 | 2.09 | 2.809(6) | 129 |
| N5-H5A···O3$^{ii}$ | 0.98 | 2.29 | 3.058(7) | 135 |
| N5-H5B···N7$^{iii}$ | 1.10 | 1.93 | 2.944(7) | 151 |
| N6-H6A···O1$^{iv}$ | 0.98 | 2.06 | 2.905(6) | 143 |
| N6-H6B···N9$^{iv}$ | 0.87 | 2.09 | 2.954(7) | 171 |
| N8-H8···O8 | 0.89 | 1.77 | 2.633(7) | 162 |
| N10-H10A···O9$^{iii}$ | 1.01 | 1.98 | 2.836(7) | 141 |
| N11-H11A···N1$^{iv}$ | 1.07 | 1.92 | 2.975(7) | 167 |
| N11-H11B···O7$^{v}$ | 1.07 | 2.09 | 2.763(6) | 118 |
| N11-H11B···O8 | 1.07 | 2.45 | 3.257(7) | 131 |
| N12-H12A···O4$^{vi}$ | 0.95 | 2.05 | 2.877(6) | 145 |
| N12-H12B···O1 | 0.93 | 2.39 | 3.295(7) | 166 |
| O8-H108···O2$^{vii}$ | 0.94 | 1.78 | 2.721(7) | 175 |
| O8-H208···O3$^{ii}$ | 0.87 | 2.03 | 2.880(6) | 167 |
| O9-H109···O4$^{viii}$ | 0.92 | 2.09 | 2.967(7) | 158 |
| O9-H209···O5$^{vi}$ | 0.85 | 2.04 | 2.842(6) | 157 |

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y, z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+2, -y, -z+1$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z$; (vii) $x-1, y, z+1$; (viii) $-x+2, -y+1, -z$.

## Supplementary material

CCDC-756796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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