Electronic Supplementary Material for CrystEngComm


## Electronic Supplementary Information‡

All starting materials were obtained from commercial suppliers in good purity and used as such for reactions and crystallizations. *N*-3-Pyridyl-*N*′-4-pyridyl urea was synthesized as given below.

**$H_3CTA\cdot(3H\text{-}pyr)_2$**
1,3*cis*,5*cis*-Cyclohexanetricarboxylic acid and 4(3H)-pyrimidinone were co-crystallized in a 1:3 ratio from MeOH at room temperature. Diffraction quality crystals of 1:2 composition were obtained in two days.
M.p. 169-172°C.

***N*-3-Pyridyl-*N*′-4-pyridyl urea**
Isonicotinic acid hydrazide (0.68 g, 5 mmol) was dissolved in 10 mL 25% HCl aq. solution in an RB flask and cooled below 5 ºC. An ice cold solution of $NaNO_2$ (0.52 g, 7.5 mmol) in 5 mL water was added to it with stirring. Stirring was continued for 1 h keeping the temperature below 5 ºC. The mixture was neutralized with solid $NaHCO_3$ and the compound was extracted in benzene. The organic layer was dried over $Na_2SO_4$ and filtered. 3-Aminopyridine (0.47 g, 5 mmol) was added to the benzene solution and the mixture was refluxed for 8 h. The precipitate was filtered and dried to obtain the title pyridyl urea.
Yield: 0.94 g (88%).
M.p. The compound decomposes on heating. Melting point could not be determined.
IR (KBr, $cm^{-1}$): 3028, 1730, 1587, 1554, 1473, 1332, 1271, 904.
$^1$H NMR (MeOH-d4, δ, ppm): 8.63 (1 H, s), 8.33 (2 H, br s), 8.21 (1 H, d, J = 4 Hz), 8.04 (1 H, d, J = 8 Hz), 7.54 (2 H, d, J = 4 Hz), 7.39 (1 H, dd, J = 8, 4 Hz).

**Single crystal X-ray diffraction**
X-ray reflections were collected on Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-Kα fine focus sealed tube (λ = 0.71073 Å). Data integration was done using SAINT.[1] Intensities for absorption were corrected using SADABS.[2] Structure solution and refinement were carried out using Bruker SHELX-TL.[3] Hydrogen atoms were refined isotropically and heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from difference electron density maps and C-H hydrogens were fixed using HFIX command in SHELX-TL. Reflection intensities of 3,4-PyrU hydrate crystal were found to be twinned and twinned reflections were removed using RLATT.[4] The Friedel reflections in this all-light-atoms crystal structure were merged. ORTEP diagrams are shown in Fig. S1.

1 SAINT, version 6.45 /8/6/03, Bruker AXS, 2003.
2 G. M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997.
3 G. M. Sheldrick, *SHELXS-97* and *SHELXL-97*, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
4 RLATT, Reciprocal Lattice Viewer, version 3.0, Bruker AXS, 2000.

| Compound | $H_3CTA\cdot(3H\text{-}pyr)_2$ | PyrU hydrate |
|---|---|---|
| Chemical formula | $(C_4H_4N_2O)_2\cdot(C_9H_{12}O_6)$ | $C_{11}H_{12}N_4O_2$ |
| Formula weight | 408.37 | 232.25 |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | $P2_12_12_1$ |
| T/K | 298 | 100(2) |
| a / Å | 13.3218(14) | 7.0712(14) |
| b / Å | 5.7554(6) | 10.343(2) |
| c / Å | 24.093(3) | 15.516(3) |
| $\alpha$ / ° | 90 | 90 |
| $\beta$ / ° | 90.508(2) | 90 |
| $\gamma$ / ° | 90 | 90 |
| Z | 4 | 4 |
| V / Å$^3$ | 1847.2(4) | 1126.1(4) |
| $\rho_{cal}$ / g cm$^{-3}$ | 1.468 | 1.370 |
| $\mu$ / mm$^{-1}$ | 0.118 | 0.099 |
| $F_{000}$ | 856 | 488 |
| $2\theta$ range | 3.0 – 52.0 | 4.7 – 50.0 |
| Reflns. collected | 9509 | 6456 |
| Unique reflns. | 3603 | 1317 |
| Observed reflns | 2305 | 1198 |
| $R_1[I > 2\sigma(I)]$ | 0.0533 | 0.0639 |
| $wR_2$ [all] | 0.1394 | 0.1207 |
| Diffractometer | SMART-APEX CCD | SMART-APEX CCD |

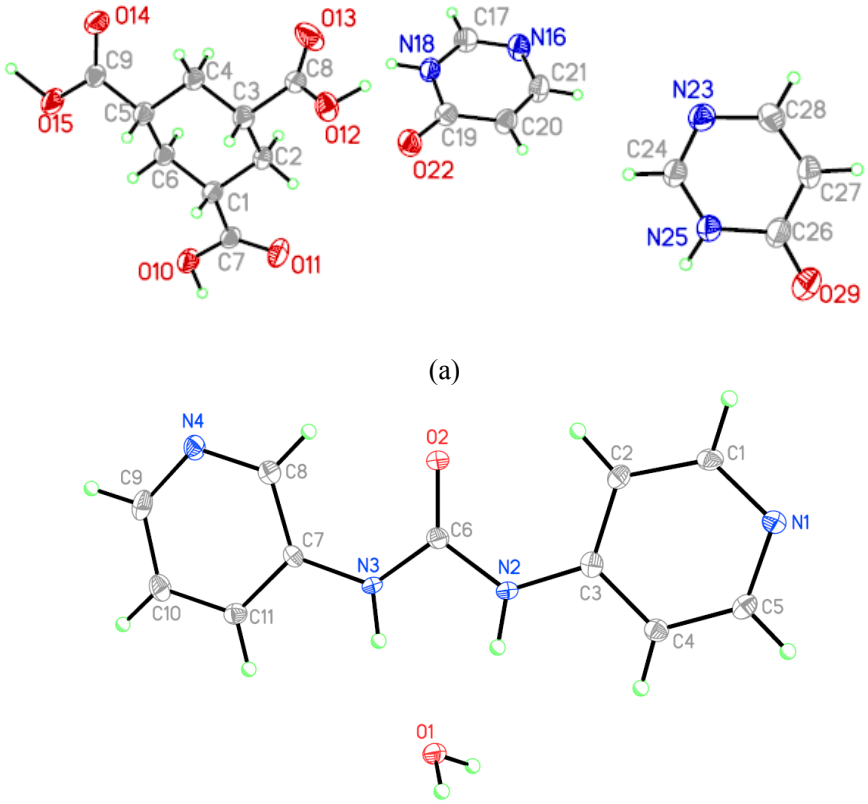


**Fig. S1** ORTEP at 35% probability of thermal ellipsoids for heavy atoms. (a) $H_3CTA \cdot (3H\text{-}pyr)_2$. (b) 3,4-PyrU hydrate.