Crystal Structure of a Co-crystalline Compound from of 2-Aminopyrimidine and Pyridine-2,6-dicarboxylic acid

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Abstract

The addition of 2-aminopyrimidine (amp) and pyridine-2,6-dicarboxylic acid (pydcH2) in water solution led to co-crystalline compound (amp)(pydcH2). The compound crystallized in a Orthorhombic system, space group Pmn21 with cell parameters at -173 C°: a = 11.550(2), b = 12.324(3), c = 3.6057(7), V= 513.25(18)Å3, Z = 1. The R [I ≥ 2s(I)] and wR2 values are 0.0365 and 0.0856, respectively, for all 612 independent reflections. Crystal structure of (amp)(pydcH2) was stabilized by hydrogen bonds, π-π stacking between aromatic rings and van der Waals interactions.

Keywords: co-crystalline compound, 2-aminopyrimidine, pyridine - 2,6dicarboxylic acid, Crystal structure.

Introduction

Co-crystals, referred to multi-component crystals, include two or more different compounds which are bound to each other by non-covalent bonds. Hydrogen bonds play an important role in adducting neutral molecules [1]. Bronsted acids can be used as proton-donors in hydrogen-bonded systems for preparing co-crystals, without the transfer of hydrogen ions to form salts. A large number of co-crystals have been prepared using various organic substances and given various names, such as molecular complexes, addition compounds and heteromolecular co-crystals [2]. di- or tri-carboxylic acids act as proton-donors in hydrogen-bonded systems and as linkers in supramolecular crystals [3, 4]. Pyridine-2,6-dicarboxylic acid (pydcH2) a very important carboxylate derivative, has attracted much interest to prepare the proton transfer compounds and supramolecular structures [5]. As a part of our study on the coordination chemistry of pridine-2,6-dicarboxylic acid in the presence of heterocyclic amines [6-11], here we report crystal structure of a co-crystal compound resulted from the 2-aminopyrimidine and pyridine-2,6-dicarboxylic acid, (amp)(pydcH2).

Experimental

Synthesis. A solution of pyridine-2,6-dicarboxylic acid (0.334g, 2mmol) and 2-aminopyrimidine (0.190 g, 2 mol) was refluxed in water (30 ml) for 2 h (Scheme1). The resulted solution was kept at 293 K. Colourless crystals the title compound suitable for x-ray
analysis was obtained after a one month.

X-ray diffraction data were collected on a Bruker APEX2 using a graphite monochromated Mo Ka (\(\lambda = 0.71073 \text{ Å}\)) radiation. The crystal parameters, data collection and refinement results for compound are summarized in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F2 with SHELXL97 [12]. H atoms treated by a mixture of independent and constrained refinement. SHELXS97 [13] program(s) used to refine structure

**Results and discussion**

The molecular structure of the title compound is shown in figure1. However, there are acid and amine in solution, but the reaction was not accorded between these two compounds and two compounds were crystalized as co-crystalline compound. There are intermolecular and intramolecular N–H···O and O–H···N hydrogen bonds (table 2) linking 2-aminopyrimidine and pyridine-2,6-dicarboxylic acid molecules into one-dimensional networks parallel to the [100] axis (Fig. 2). There are also some \(\pi\)-\(\pi\) stacking interactions between pyridine rings N1/C2/C3/C4/C3a/C2a [symmetry code X,Y,-1+Z; centroid–centroid distance 3.606(3) Å; the angle between the planes is 0º; the perpendicular distance between the planes is 3.3028(16) Å; the slippage is 1.447 Å] and pyrimidine rings N5/C5/C5b/C6b/C7/C6 and C22i/C23i/C24i/C25i/C26i/C27i [symmetry code -1- X,Y,-1+Z; centroid–centroid distance 3.606(3) Å; the angle between the planes is 0º; the perpendicular distance between the planes is 3.2613(16) Å; the slippage is 1.538 Å (Fig. 3). Crystal structure of co-crystal was stabilized by \(\pi\) - \(\pi\) stacking between aromatic rings and van der Waals interactions.

**Table 1. Crystallographic data for 1.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C(<em>{22})H(</em>{20})N(_8)O(_8)</td>
</tr>
<tr>
<td>(M_t)</td>
<td>524.46</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.34x 0.10 x 0.08</td>
</tr>
<tr>
<td>Crystal syste, space group</td>
<td>Orthorhombic, Pmn2(_1)</td>
</tr>
<tr>
<td>a[Å]</td>
<td>11.550(2)</td>
</tr>
<tr>
<td>b[Å]</td>
<td>12.324(3)</td>
</tr>
<tr>
<td>c[Å]</td>
<td>3.6057(7)</td>
</tr>
<tr>
<td>(\alpha^\circ)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta^\circ)</td>
<td>90</td>
</tr>
</tbody>
</table>
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$\gamma[^{\circ}]$

Volume[$\text{Å}^3.103$] 513.25(18)

$Z$

$D_{\text{calcd}}$ (g.cm$^{-3}$) 1.697

Absorption correction analytical

F(000) 272

T [k] 100(2)

$\theta$ range for data collection (°) 2.38-25.61

h,K,l range 0→14, 0→15, 0→4

No. independent reflections / Rint 612/0.0590

No. refined parameters 102

$R_1$ $wR$ [I $\geq$ 2$\sigma$(I)] 0.0365, 0.0856

$wR_2$ (all data) 0.0935

Max., min. Electron density, e $\text{Å}^{-3}$ 0.215, -0.287

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2 --H2...N5</td>
<td>1.01(4)</td>
<td>1.63(4)</td>
</tr>
<tr>
<td>N4 --H4N...O1</td>
<td>0.91(3)</td>
<td>2.00(3)</td>
</tr>
<tr>
<td>C6 --H6...O2</td>
<td>0.95</td>
<td>2.52</td>
</tr>
</tbody>
</table>

Conclusions

Figure 1. The molecular structure of co-crystal, (amp)(pydcH$_2$) with 50% probability ellipsoids.
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Figure 2. A view of the crystal structure of co-crystal. The Amine and acid molecules are linked by hydrogen bonds of the (represented by dotted lines) into a 1-D chain along [1 0 0] direction.

Figure 3. \(\pi-\pi\) stacking between aromatic rings.

Acknowledgements
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References


[8] Tabatabaee, M., Kukovec, B. M. and Kazeroonizadeh, M.," A unique example of a co-crystal of [Ag( atr)2][Cr( dipic)2] ( dipic= dipicolinate; atr=3-amino-1H-1,2,4-triazole) and dinuclear [Cr(H2O)( dipic)( μ-OH)2, with different coordination environment of Cr(III) ions", Polyhedron., 30, 1114 (2011).


