

Full Length Research Paper

# Structural study of pyridine-2,6-dicarbohydrazide nitrate salt

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Reaction between dimethyl-2,6-pyridinedicarboxylate and anhydrous hydrazine by microwave synthesis under solvent free conditions gave pyridine-2,6-dicarbohydrazide (pdch). This compound was recrystallized in methanol at low pH condition and gave the nitrate salt of pdch. In the crystal structure of this compound, protonated pdch cations and nitrate anions are linked via N-H...N<sub>nitrate</sub> and N-H...O<sub>nitrate</sub> hydrogen bonds into a three-dimensional network. The structure features extensive hydrogen bonding, with 13 distinct interactions. There are also weak intermolecular interactions including O... $\pi$ , O...O and N-H... $\pi$ .

**Key words:** Pyridine-2,6-dicarbohydrazide, spectral characterization, X-ray crystal structure.

## INTRODUCTION

Synthesis of compound based on 2,6-disubstituted pyridine has attracted a great deal of attention, with a broad array of both acyclic and macrocyclic ligands reported by Wilkinson et al. (1987). In particular, diamides incorporating a -NH-CO-pyridine-CO-NH- core based on pyridine-2,6-dicarboxylic acid (H<sub>2</sub>dipic) have been examined, with interest in these compounds extending to potential applications as diverse as azo dyes (Liu et al., 2002) and telomerase inhibitors (Bouchard and Hittinger, 2002). Our research interests lie in the study of multi N-donor compounds which can be coordinated to metals and in the past few years, we have published a series of paper in this field (Hakimi et al., 2011b, 2012b). In this paper, preparation of pyridine-2,6-dicarbohydrazide nitrate salt (L, Scheme 1) was described and elemental analysis, spectroscopic characteristic (IR), and crystal structure of this compound were determined.

## MATERIALS AND METHODS

### Instrumentation

All starting chemicals and solvents were reagent or analytical grade

and used as received. The infrared spectrum of a KBr pellet in the range of 4000 to 400 cm<sup>-1</sup> were recorded with a FT-IR 8400-Shimadzu spectrometer. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting point was determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

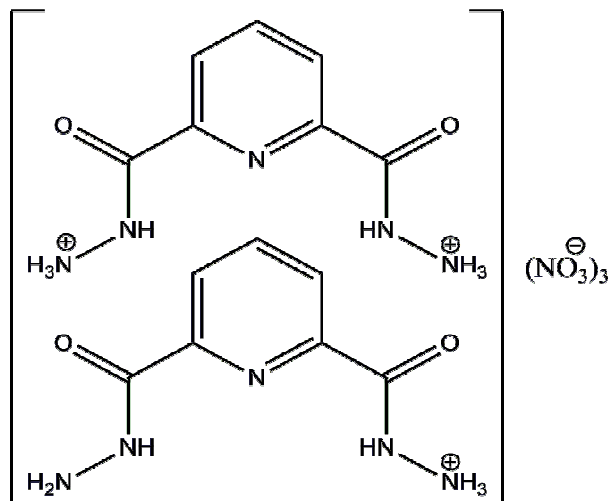
### Synthesis of L

1 cm<sup>3</sup> of hydrazine hydrate and 1.95 g (10 mmol) of dimethyl pyridine-2,6-dicarboxylate were irradiated using a microwave oven (MicroSYNTH, Milestone s.r.l) for 10 min with a power up to 1 kW. After microwave irradiation, the white crystalline solid was obtained and washed with dichloroethane. The residue was recrystallized from methanol in pH adjusted to 3 by addition of HNO<sub>3</sub>. After a day colorless crystals of L suitable for X-ray diffraction studies were obtained by slow evaporation of a solution and filtered. Yield 2.63 g (91%). m. p. 188°C. Elemental analysis: calculated for C<sub>14</sub>H<sub>21</sub>N<sub>13</sub>O<sub>13</sub>: C 29.02, H 3.65, N 31.43%; found: C 29.21, H 3.65, N 31.76%. IR (cm<sup>-1</sup>, KBr): 3340 and 3215 m ( $\nu$  NH<sub>3</sub><sup>+</sup>), 3160 m ( $\nu$  NH), 3078 m ( $\nu$  CH), 1682 s ( $\nu$  C=O), 1610 m ( $\delta$  NH<sub>2</sub>), 1527 s ( $\nu$  C=N and/or C=C), 1389 vs ( $\nu_4$  NO<sub>3</sub>), 1333 m ( $\nu_1$  NO<sub>3</sub>), 1203 m ( $\nu$  CN), 1011 m ( $\nu_2$  NO<sub>3</sub>), 856 w ( $\nu_6$  NO<sub>3</sub>).

### Single crystal structure determination

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo K $\alpha$  radiation (50 kV, 30 mA) using the APEX 2 (Bruker, 2005a) data collection software. The collection method involved  $\omega$ -scans of width 0.5° and 512 × 512 bit data frames. Data reduction was

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**Scheme 1.** Structure of the L.

**Table 1.** Crystal data and structure refinement for L.

|   |   |
|---|---|
| Empirical formula                                   | C <sub>14</sub> H <sub>21</sub> N <sub>13</sub> O <sub>13</sub> |
| Formula weight (g mol <sup>-1</sup> )               | 579.44  |
| Temperature (K)                                     | 173(2)  |
| Crystal system                                      | Monoclinic  |
| Space group   | C2/c  |
| Unit cell dimensions (Å, °)                         |   |
| <i>a</i>  | 13.0563(5)  |
| <i>b</i>  | 5.5522(2)   |
| <i>c</i>  | 31.3941(12)   |
| $\beta$   | 91.658(2)   |
| Volume (Å <sup>3</sup> ), <i>Z</i>                  | 2274.84(15), 4  |
| Calculated density (mg m <sup>-3</sup> )            | 1.692   |
| Absorption coefficient (mm <sup>-1</sup> )          | 0.150   |
| <i>F</i> (000)                                      | 1200  |
| Crystal size (mm <sup>3</sup> )                     | 0.30 × 0.18 × 0.10  |
| $\theta$ range for data collection (°)              | 1.30–27.98  |
| <i>h</i> , <i>k</i> , <i>l</i> ranges               | –17:17, –7:7, –41:41  |
| Reflections collected                               | 8853  |
| Independent reflections                             | 2749  |
| <i>R</i> <sub>int</sub>                             | 0.0504  |
| Data / restraints / parameters                      | 2749 / 1 / 191  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>            | 0.878   |
| Final <i>R</i> indexes [ <i>I</i> > 2σ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0417, <i>wR</i> <sub>2</sub> = 0.0889 |
| <i>R</i> indexes (all data)                         | <i>R</i> <sub>1</sub> = 0.0780, <i>wR</i> <sub>2</sub> = 0.0993 |
| Largest diff. peak and hole (e.Å <sup>-3</sup> )    | 0.732 and –0.206  |

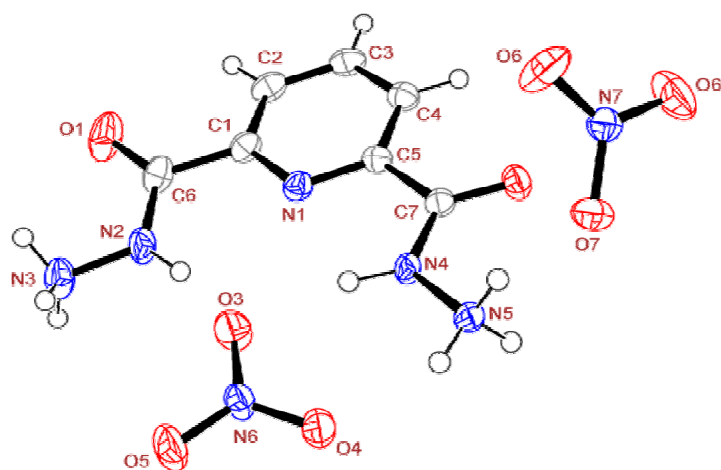
carried out using the program *SAINTE* (Bruker, 2005b).

The crystal structure was solved by direct methods using *SHELXTL* (Bruker, 1999). Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on *F*<sup>2</sup> using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned

geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using *SHELXTL*, *PLATON* (Spek, 2003), *ORTEP-3* (Farrugia, 1997), and *Mercury* (Macrae et al., 2008). Crystallographic data and details of the data collection and structure refinement are listed in Table 1. Bond lengths (Å) and angles (°) are reported in Table 2.

**Table 2.** Selected bond length (Å) and angles (deg) for L with estimated standard deviations in parentheses.

| Distances |          | Angles   |          |
|-----------|----------|----------|----------|
| C1–N1     | 1.344(2) | C5–C7–O2 | 123.2(2) |
| C5–N1     | 1.337(2) | C5–C7–N4 | 114.8(2) |
| C6–O1     | 1.226(3) | C7–N4–N5 | 116.7(2) |
| C7–O2     | 1.230(2) | O3–N6–O4 | 119.3(2) |
| N2–N3     | 1.413(2) | O4–N6–O5 | 119.7(2) |
| N4–N5     | 1.423(2) | O5–N6–O3 | 121.0(2) |
| N6–O3     | 1.245(2) |          |          |
| N6–O4     | 1.257(2) |          |          |
| N6–O5     | 1.238(2) |          |          |

**Figure 1.** View of the L with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

## RESULTS

In the IR spectrum of L, the absorptions at 3340 and 3215  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric vibrations of  $\text{NH}_3^+$ . Other band at 3160  $\text{cm}^{-1}$  was confirmed the presence of NH. Four bands in the IR spectrum near 1389, 1333, 1011, 856  $\text{cm}^{-1}$  for L can be assigned to vibrations of the nitrate group (respectively the vibrations  $\nu_4$ ,  $\nu_1$ ,  $\nu_2$  and  $\nu_6$ ).

The molecular structure of the L (Figure 1) reveals presence of two protonated portions and three nitrate ions. The plane of pyridine ring with planes of two acetohydrazide moiety including  $\alpha$  (N3/N2/C6/O1) and  $\beta$  (N5/N4/C7/O2) forms the dihedral angles of 12.14° and 1.86°, respectively, which means that the L is not planar (r.m.s. deviation 0.271 Å for O1 atom). In the crystal structure of L, one of the nitrate ions (containing N6 atom) lies closely to plane of cationic portion and makes five interactions with it. The dihedral angle between plane of this nitrate ion (O4/O5/N6/O3) and plane of cationic

portion is 10.47°. In the crystal, the molecules are stabilized due to N–H $\cdots$ O and N–H $\cdots$ N hydrogen bonds (Table 3 and Figure 2). This 3D supramolecular structure is further stabilized by the O $\cdots$  $\pi$ , O $\cdots$ O and N–H $\cdots$  $\pi$  interactions (Figure 2).

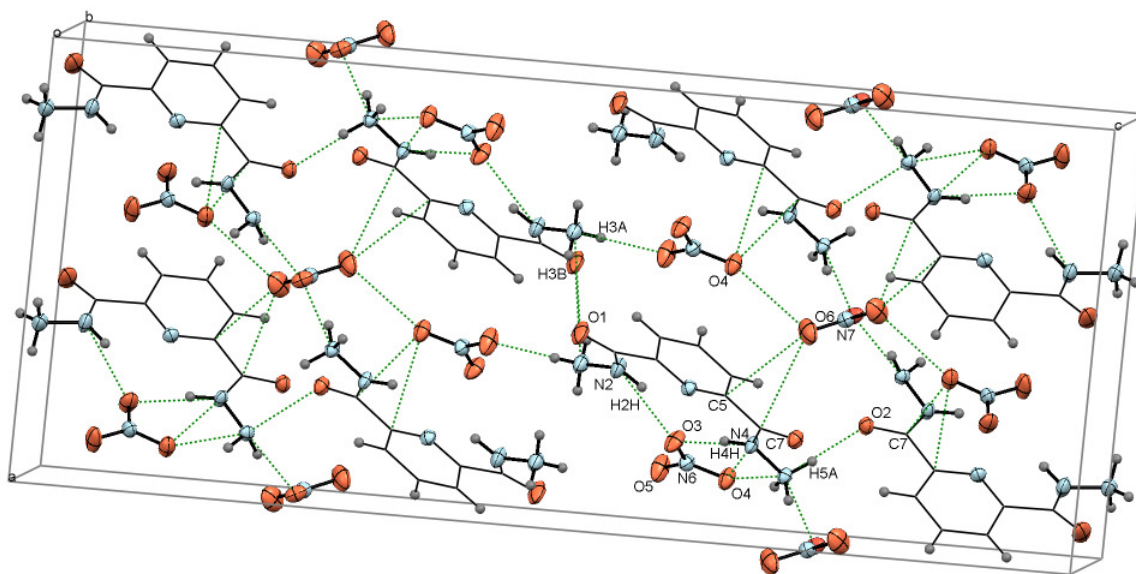
## DISCUSSION

Free nitrate ion has  $D_{3h}$  symmetry and three infrared active vibrations but it was lowered to  $C_{2v}$  and  $C_s$  upon interaction of two and one oxygen atoms in complex, respectively (Drago, 1992; Nakamoto, 2009) with six infrared active vibrations. In L, nitrate groups did not coordinate to metal atom and must have  $D_{3h}$  symmetry but the interactions such as hydrogen bonds and others influenced the nitrates geometry and lowered it. In title compound the bond lengths and angles are normal and are comparable to the values observed in similar compound (Jia et al., 2006).

**Table 3.** Hydrogen-bond geometry (Å, °).

| D–H...A             | d(D–H) | d(H...A) | d(D...A)   | <(DHA) |
|---------------------|--------|----------|------------|--------|
| N(3)–H(3A)···O(5)#1 | 0.91   | 2.01     | 2.883(2)   | 160    |
| N(3)–H(3B)···O(1)#2 | 0.91   | 2.29     | 2.990(2)   | 134    |
| N(3)–H(3B)···O(1)#3 | 0.91   | 2.52     | 3.313(2)   | 147    |
| N(3)–H(3C)···N(3)#1 | 0.91   | 1.83     | 2.741(3)   | 175    |
| N(3)–H(3C)···N(2)#1 | 0.91   | 2.65     | 3.469(2)   | 150    |
| N(5)–H(5A)···O(2)#4 | 0.91   | 1.88     | 2.785(2)   | 170    |
| N(5)–H(5B)···O(4)   | 0.91   | 2.00     | 2.796(2)   | 145    |
| N(5)–H(5B)···O(6)#3 | 0.91   | 2.32     | 2.987(2)   | 130    |
| N(5)–H(5C)···O(7)   | 0.91   | 1.89     | 2.7746(18) | 163    |
| N(4)–H(4H)···O(3)   | 0.917  | 1.919    | 2.820(2)   | 167    |
| N(4)–H(4H)···O(4)   | 0.917  | 2.57     | 3.035(2)   | 111.7  |
| N(4)–H(4H)···N(6)   | 0.917  | 2.60     | 3.352(2)   | 140    |
| N(2)–H(2H)···O(3)   | 0.915  | 2.010    | 2.888(2)   | 160    |

Symmetry transformations used to generate equivalent atoms: #1  $-x+1.5, -y+1.5, -z+1$ ; #2  $-x+1, -y+1, -z+1$ ; #3  $x, y+1, z$ ; #4  $-x+1.5, y+0.5, -z+1.5$ .

**Figure 2.** Packing of crystal, showing the hydrogen bonded chain formation and short contacts in the *ac* plane.

## Conclusion

In this paper, preparation of the pyridine-2,6-dicarbohydrazide nitrate salt, L, was presented and its spectral and structural properties were described. The crystal structure determination of L revealed that this crystal consist of two protonated pyridine-2,6-dicarbohydrazide and three nitrate ions. In the crystal of L, hydrogen bonds and weak interactions such as  $N-H\cdots N_{\text{nitrate}}$ ,  $N-H\cdots O_{\text{nitrate}}$ ,  $O\cdots\pi$ ,  $O\cdots O$  and  $N-H\cdots\pi$  gave rise to a supramolecular network. The synthesis of complexes with the pyridine-2,6-dicarbohydrazide is

continued by our research group.

CCDC 833546 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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