Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# 3,5-Pyrazoledicarboxylic acid monohydrate

**Nancy Ching, Long Pan, Xiao-Ying Huang and Jing Li***

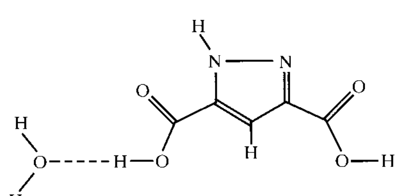
Department of Chemistry, Rutgers University, Camden, NJ 08102, USA
Correspondence e-mail: jingli@crab.rutgers.edu

Received 5 January 2000
Accepted 22 May 2000

In the title compound, $C_5H_4N_2O_4{\cdot}H_2O$, the 3,5-pyrazoledicarboxylic acid ($H_3pdc$) molecules are joined into one-dimensional chains by O—H···O and N—H···O hydrogen bonds, with distances of 2.671 (2) and 2.776 (2) Å, respectively. The one-dimensional chains form a three-dimensional structure via O—H···O*W* and O*W*—H*W*···N hydrogen bonds, with distances of 2.597 (3) and 2.780 (3) Å, respectively. In addition to the potential for forming open-channel frameworks, access to the six coordination atoms of $H_3pdc$ can be directly controlled by varying the pH of the reaction environment, allowing further control over the design and synthesis of novel coordination polymers using various metal centers.

## Comment

The incorporation of hydrogen bonds into metal–organic coordination frameworks is becoming more prevalent because of their strength and stability. The hydrogen bond has played a significant role in the construction of supramolecular organic systems because its strength contributes to crystallization, which is essential for crystallographic structural determination of new compounds (Desiraju, 1995). In designing two- and three-dimensional structures, choosing organic molecules with the ability to form hydrogen bonds has become considerably important (Fitzgerald & Gerkin, 1997; Gong *et al.*, 1999; Ranganathan *et al.*, 1998; Russell *et al.*, 1997; Pedireddi *et al.*, 1997). The structures of many coordination polymers being reported contain symmetric ligands. For example, trimesic acid has been proven to successfully contribute to very stable large-channeled three-dimensional structures through both hydrogen bonds and direct coordination (Duchamp & Marsh, 1969; Kolotuchin *et al.*, 1999; Yaghi *et al.*, 1996). However, there have been few reports concerning asymmetric ligands (Dobson & Gerkin, 1998).



$H_3pdc$

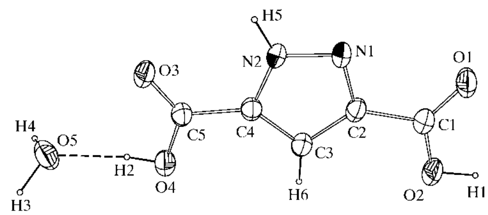



**Figure 1**
Displacement ellipsoid plot (50% probability) of $H_3pdc$ with the atomic labeling.

During the course of rational synthesis and reactivity study of coordination polymers, we have become interested in several asymmetric ligands, 3,5-pyrazoledicarboxylic acid, $H_3pdc$, being one example. Its two carboxylic acid groups and two pyrazole N atoms allow it to function as both a proton acceptor and donor. The irregularly shaped molecule can form various O—H···O*W*, N—H···O, O*W*—H···N and O*W*—H···O*W* hydrogen bonds in water solution. The degree of deprotonation for this asymmetric ligand can often be controlled by varying the pH of the reaction, yielding crystal structures of one, two and three dimensions (Pan *et al.*, 2000*a*,*b*). While this ligand has reacted actively with a number of metal centers to form numerous coordination networks, its crystal structure has not been reported previously. In this paper, we describe the synthesis and determination of the crystal structure of this molecule.

The $H_3pdc$ crystal has a three-dimensional structure formed entirely by hydrogen bonding between the molecule itself and the lattice water molecules. For purposes of description, its three-dimensional structure can be simplified into one-dimensional chains. Graph-set notations, $R^a_d(n)$ and $C^a_d(n)$, designate the patterns formed *via* hydrogen bonding, where *R* and *C* specify whether the pattern is a ring or chain, *a* is the number of hydrogen-bond acceptors, *d* is the number of

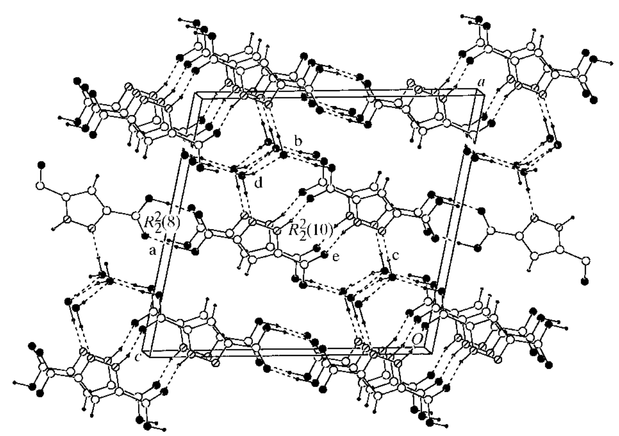



**Figure 2**
One-dimensional chains of $H_3pdc$ molecules through $R^2_2(8)$ and $R^2_2(10)$ graph sets along [01$\bar{1}$] and [0$\bar{1}\bar{1}$] alternately. The C atoms are designated by open circles, and N and O atoms by shaded and solid circles, respectively. The small solid circles represent H atoms. Hydrogen bonds are indicated by dotted lines (**a** = 2.671, **b** = 2.597, **c** = 2.780, **d** = 2.933 and **e** = 2.776 Å).

hydrogen-bond donors, and $n$ is the number of atoms in the ring, also called the degree of the pattern (Bernstein *et al.*, 1995). As shown in Fig. 2, one-dimensional chains with the pattern $C_2^2(14)[R_2^2(8)R_2^2(10)]$ are formed by the hydrogen bond, **a**, of the carboxyl group of one molecule to the hydroxyl group of a second molecule and the hydrogen bond, **e**, of the carboxyl group of the second molecule to the protonated nitrogen of a third molecule. The graph set $R_2^2(8)$ consists only of **a**, while graph set $R_2^2(10)$ consists of **e**. Every $R_2^2(10)$ ring in each one-dimensional chain connects to four adjacent one-dimensional chains through two $C_2^2(8)$ graph sets consisting of hydrogen bonds **b** and **c**, giving rise to the three-dimensional structure of $H_3$pdc. The $C(2)$ hydrogen-bonded chain, **d**, of water molecules lies along the $2_1$ screw axis.

## Experimental

3,5-Pyrazoledicarboxylic acid monohydrate (100 mg) was dissolved in hot deionized water (10 ml). The solution was allowed to evaporate slowly over several days. Colorless crystals suitable for single-crystal X-ray diffraction study were collected once all of the solution had evaporated.

### *Crystal data*

| | |
|---|---|
| $C_5H_4N_2O_4{\cdot}H_2O$ | $D_x$ = 1.641 Mg m$^{-3}$ |
| $M_r$ = 174.12 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 20 reflections |
| $a$ = 13.386 (3) Å | $\theta$ = 7.09–12.14° |
| $b$ = 3.7500 (10) Å | $\mu$ = 0.149 mm$^{-1}$ |
| $c$ = 14.350 (3) Å | $T$ = 293 (2) K |
| $\beta$ = 101.88 (3)° | Columnar, colorless |
| $V$ = 704.9 (3) Å$^3$ | 0.30 × 0.10 × 0.08 mm |
| $Z$ = 4 | |

### *Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int}$ = 0.044 |
| $\omega$ scans | $\theta_{max}$ = 26.01° |
| Absorption correction: $\psi$ scan (Kopfmann & Huber, 1968) | $h = 0 \rightarrow 16$ |
| $T_{min}$ = 0.96, $T_{max}$ = 1.00 | $k = -4 \rightarrow 4$ |
| 2883 measured reflections | $l = -17 \rightarrow 17$ |
| 1388 independent reflections | 3 standard reflections frequency: 250 min |
| 856 reflections with $I > 2\sigma(I)$ | intensity decay: ±2.8% |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + 0.2500P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.040 | $(\Delta/\sigma)_{max}$ < 0.001 |
| $wR(F^2)$ = 0.079 | $\Delta\rho_{max}$ = 0.17 e Å$^{-3}$ |
| $S$ = 1.18 | $\Delta\rho_{min}$ = −0.23 e Å$^{-3}$ |
| 1388 reflections | Extinction correction: *SHELXL*97 (Sheldrick, 1997) |
| 128 parameters | Extinction coefficient: 0.0109 (12) |
| H atoms treated by a mixture of independent and constrained refinement | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C1 | 1.221 (3) | N2—C4 | 1.342 (3) |
| O2—C1 | 1.294 (3) | C1—C2 | 1.477 (3) |
| O3—C5 | 1.211 (2) | C2—C3 | 1.388 (3) |
| O4—C5 | 1.300 (3) | C3—C4 | 1.373 (3) |
| N1—N2 | 1.330 (2) | C4—C5 | 1.467 (3) |
| N1—C2 | 1.337 (3) | | |
| N2—N1—C2 | 104.20 (18) | C4—C3—C2 | 104.3 (2) |
| N1—N2—C4 | 112.88 (18) | N2—C4—C3 | 106.77 (19) |
| O1—C1—O2 | 125.3 (2) | N2—C4—C5 | 118.43 (18) |
| O1—C1—C2 | 120.6 (2) | C3—C4—C5 | 134.7 (2) |
| O2—C1—C2 | 114.1 (2) | O3—C5—O4 | 124.9 (2) |
| N1—C2—C3 | 111.82 (18) | O3—C5—C4 | 121.8 (2) |
| N1—C2—C1 | 117.2 (2) | O4—C5—C4 | 113.30 (19) |
| C3—C2—C1 | 130.9 (2) | | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H1···O1$^{i}$ | 0.95 (3) | 1.72 (3) | 2.671 (2) | 178 (3) |
| O4—H2···O5 | 0.96 (2) | 1.64 (2) | 2.597 (3) | 178 (2) |
| O5—H3···N1$^{ii}$ | 0.90 (3) | 1.90 (3) | 2.780 (3) | 165 (3) |
| O5—H4···O5$^{iii}$ | 0.82 (3) | 2.18 (3) | 2.933 (3) | 153 (3) |
| N2—H5···O3$^{iv}$ | 0.90 (2) | 1.91 (2) | 2.776 (2) | 162 (2) |

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $-\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (iv) $-x, 1-y, -z$.

All H atoms were located from difference Fourier map synthesis. Their positional parameters were refined with their isotropic displacement parameters set equal to 1.2 times the $U_{eq}$ value of the parent non-H atoms. The distance between O5 and H4 was restrained to 0.95 Å with an s.u. of 0.05 Å.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *XCAD*-4/*PC* (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SCHAKAL*92 (Keller, 1992); software used to prepare material for publication: *SHELXL*97.

The authors wish to thank the National Science Foundation for its generous support through grant DMR-9553066 and the REU Supplement funds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1520). Services for accessing these data are described at the back of the journal.

## References


Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Desiraju, G. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
Dobson, A. J. & Gerkin, R. E. (1998). *Acta Cryst.* C**54**, 253–256.
Duchamp, D. J. & Marsh, R. E. (1969). *Acta Cryst.* B**25**, 5–19.
Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fitzgerald, L. J. & Gerkin, R. E. (1997). *Acta Cryst.* C**53**, 967–969.
Gong, B., Yan, Y., Zeng, H., Skrzypczak-Jankunn, E., Kim, Y. W., Zhu, J. & Ickes, H. (1999). *J. Am. Chem. Soc.* **121**, 5607–5608.
Harms, K. (1997). *XCAD-4/PC*. University of Marburg, Germany.
Keller, E. (1992). *SCHAKAL92*. University of Freiburg, Germany.
Kolotuchin, S. V., Thiessen, P. A., Fenlon, E. E., Wilson, S. R., Loweth, C. J. & Zimmerman, S. C. (1999). *Chem. Eur. J.* **5**, 2537–2547.
Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–351.
Pan, L., Huang, X. Y. & Li, J. (2000*a*). *Angew. Chem. Int. Ed. Engl.* **39**, 527–530.
Pan, L., Huang, X. Y. & Li, J. (2000*b*). *J. Solid State Chem.* **152**, 236–246.
Pedireddi, V. R., Chatterjee, S., Ranganathan, A. & Rao, C. N. R. (1997). *J. Am. Chem. Soc.* **119**, 10867–10868.
Ranganathan, A., Pedireddi, V. R. & Rao, C. N. R. (1998). *J. Am. Chem. Soc.* **121**, 1752–1753.
Russell, V. A., Evans, C. C., Li, W. & Ward, M. D. (1997). *Science*, **276**, 575–579.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Yaghi, O. M., Li, H. & Groy, T. L. (1996). *J. Am. Chem. Soc.* **118**, 9096–9101.