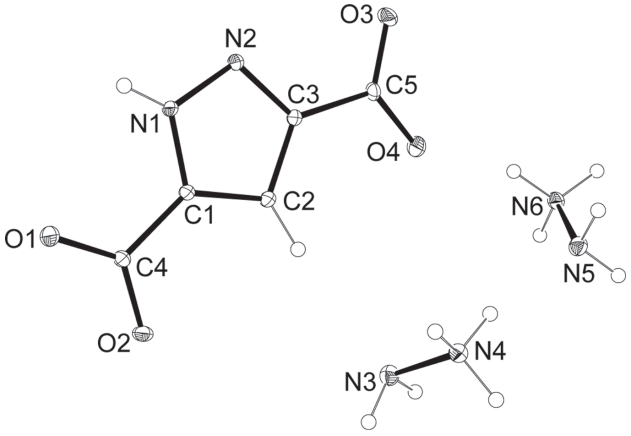
Nedeljko Latinović, Sladjana B. Novaković, Goran A. Bogdanović, Vlatko Kastratović, Gerald Giester and Željko K. Jaćimović*

Crystal structure of dihydrazinium 1*H*-pyrazole-3,5-dicarboxylate, $C_5H_{12}N_6O_4$



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Abstract

$C_5H_{12}N_6O_4$, monoclinic, $P2_1/n$ (no. 14), $a = 4.3368(6)$ Å, $b = 15.483(2)$ Å, $c = 13.8852(19)$ Å, $\beta = 97.714(3)°$, $V = 923.9(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0411$, $wR_{ref}(F^2) = 0.1109$, $T = 200(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Željko K. Jaćimović,** Faculty of Metallurgy and Technology, Džordža Vašingtona bb, University of Montenegro, Podgorica, Montenegro, e-mail: zeljkoj@ucg.ac.me
Nedeljko Latinović: Biotechnical Faculty, Mihaila Lalića 1, University of Montenegro, Podgorica, Montenegro
Sladjana B. Novaković and Goran A. Bogdanović: Vinča Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, University of Belgrade, PO Box 522, 11001 Belgrade, Serbia
Vlatko Kastratović: Faculty of Natural Sciences and Mathematics, Džordža Vašingtona bb, University of Montenegro, Podgorica, Montenegro
Gerald Giester: Institut für Mineralogie und Kristallographie, Althanstraße 14, Universität Wien – Geozentrum, Wien, Austria

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.22 × 0.16 × 0.07 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.14 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	33.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	32710, 3560, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2985
$N(param)_{refined}$:	184
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

In an attempt to synthesize the intermediates of 1*H*-pyrazole-3,5-dicarbohydrazide with direct synthesis starting from 3,5-pyrazoledicarboxylic acid monohydrate and hydrazine monohydrate in a stoichiometric relationship, a microcrystalline light yellow mixture was obtained with a pair of monocrystals that were mechanically isolated from the mixture and prepared for X-ray analysis.

Experimental details

All hydrogen atoms were identified in difference Fourier map and were refined isotropically.

Discussion

Pyrazole-related molecules have attracted much attention because of their diverse pharmacological properties [4], and also because of their increased use in the synthesis of new functional materials [5]. The derivatives of 3,5-pyrazoledicarboxylic acid (H_3PZDC) are known as building components of either purely organic or organometallic materials. As ligands the H_3PZDC derivatives can display up to six metal coordination sites and various bridging modes [6] that is utilized for the synthesis of polynuclear magnetic solids [7] and MOFs [8]. On the other hand, the uncoordinated H_3PZDC possesses multiple hydrogen bonding sites and can generate extensive hydrogen bonding important for supramolecular organic networks. [9] As a continuation of our research on pyrazole-derived molecules [10, 11], the present

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	1.0208(2)	0.37998(5)	0.00034(6)	0.02391(18)
O2	0.95263(19)	0.27289(5)	0.10278(5)	0.01774(16)
O3	0.3217(2)	0.57757(5)	0.34723(6)	0.02178(17)
O4	0.3622(2)	0.43877(6)	0.39166(6)	0.02606(19)
N1	0.7665(2)	0.49729(5)	0.12136(6)	0.01619(17)
N2	0.6304(2)	0.54007(5)	0.18837(6)	0.01656(17)
N3	0.4105(2)	0.19896(6)	0.30831(7)	0.01824(17)
N4	0.0802(2)	0.21603(6)	0.29600(7)	0.01688(17)
N5	−0.1350(2)	0.31100(6)	0.45979(7)	0.01783(17)
N6	0.0646(2)	0.36462(6)	0.52751(6)	0.01631(17)
C1	0.7787(2)	0.41106(6)	0.13768(7)	0.01305(17)
C2	0.6380(2)	0.39651(6)	0.21949(7)	0.01395(17)
C3	0.5512(2)	0.47861(6)	0.24878(7)	0.01327(17)
C4	0.9279(2)	0.35062(6)	0.07503(7)	0.01376(17)
C5	0.3981(2)	0.50030(6)	0.33578(7)	0.01423(17)
H1	0.836(4)	0.5238(11)	0.0767(13)	0.028(4)*
H2	0.601(3)	0.3413(10)	0.2477(11)	0.019(3)*
H31	0.448(4)	0.1762(11)	0.3700(13)	0.028(4)*
H32	0.428(4)	0.1547(11)	0.2676(12)	0.027(4)*
H41	0.035(4)	0.2515(11)	0.3457(13)	0.026(4)*
H42	0.032(4)	0.2416(11)	0.2356(13)	0.027(4)*
H43	−0.042(4)	0.1653(12)	0.3002(12)	0.031(4)*
H51	0.216(4)	0.3295(11)	0.5599(11)	0.023(4)*
H52	−0.046(4)	0.3928(11)	0.5707(13)	0.032(4)*
H53	0.163(4)	0.4018(11)	0.4929(13)	0.031(4)*
H61	−0.290(4)	0.3452(11)	0.4301(12)	0.027(4)*
H62	−0.218(4)	0.2750(11)	0.4960(13)	0.031(4)*

work describes the crystal structure of novel hydrazinium(+1) salt of 3,5-pyrazoledicarboxylic acid, $(N_2H_5)_2$·HPZDC.

The crystal structures of two hydrazine salts of H_3PZDC have been reported previously. These salts are of the type N_2H_6·$(H_2PZDC)_2$ [12] and N_2H_5·H_2PZDC·H_2O [9] and both contain the monocarboxylate H_2PZDC^- anion. The asymmetric unit of title salt $(N_2H_5)_2$·HPZDC contains the dicarboxylate dianion of H_3PZDC and two hydrazinium counterions. In comparison to previous structures [12, 13] the geometry of species shows expected differences arising from their different protonation states. The crystal structure is stabilized by extensive N—H···O and N—H···N hydrogen bonding between the charged species with H···A distances ranging from 1.84(2) to 2.32(2) Å. The HPZDC anions alone form N1—H1···O1 centrosymmetric dimer [N1—H1···O1^{i} = 161(2)°, H1···O1 = 1.98(2) Å, (i) = 2 − x, 1 − x, −z].

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