Z. Kristallogr. NCS 221 (2006) 539-540 / DOI 10.1524/ncrs.2006.0189

Crystal structure of 4-oxo-3,5-dinitropyridine-*N*-hydroxide monohydrate, $C_5NH_2(NO_2)_2O(OH) \cdot H_2O$

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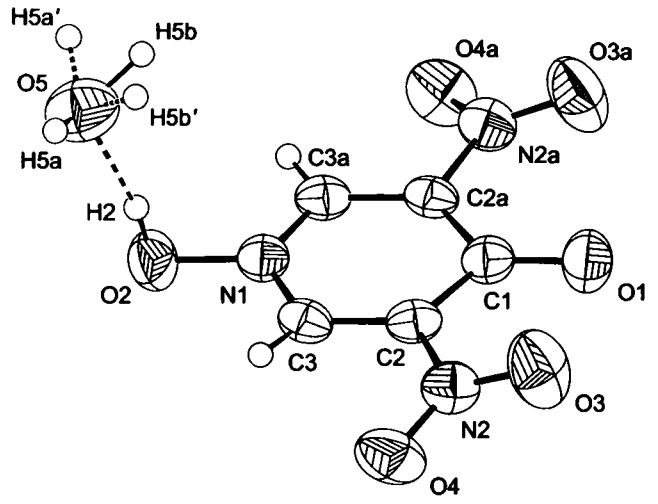
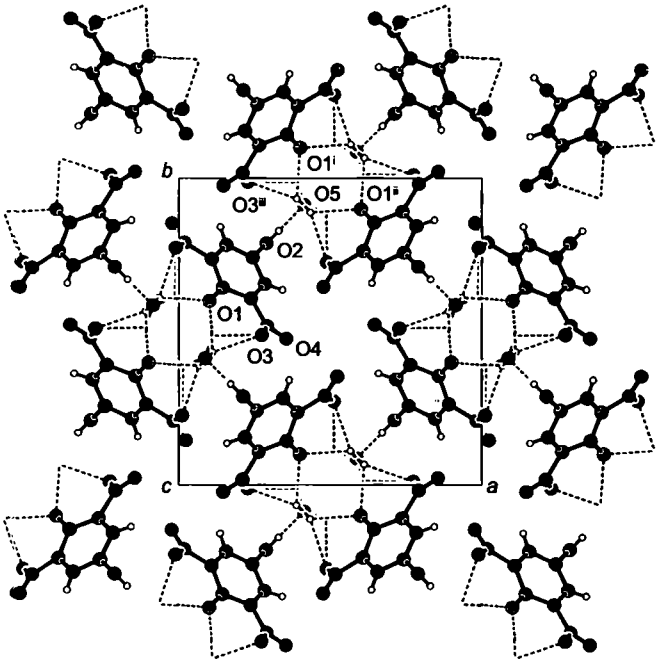
Received October 23, 2006, accepted and available on-line December 19, 2006; CCDC no. 1267/1920





Abstract

$C_5H_5N_3O_7$, tetragonal, $P\bar{4}2_1m$ (no. 113), a = 13.113(5) Å, c = 4.941(3) Å, V = 849.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.137, T = 298 K.

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Source of material

Under stirring 4-hydroxypyridine *N*-oxide (1.0 g, 0.009 mol) was dissolved in 10 ml glacial acetic acid, followed by slow addition of 5 ml concentrated nitric acid. The temperature of the solution was raised to 50 °C, then gradually heated to 80 °C with the reaction process and kept at this temperature for one hour. After lowering to RT, the solution was poured on 20 g ice, whereupon a pale yellow solid formed. The solid was filtered, the mother liquor was extracted two times with $CHCl_3$, and one part of the pale yellow solid was cropped. All of the solid was collected and recrystallized from ethanol and 1.25 g (75 %) pale yellow solid was obtained. Single crystals suitable for X-ray diffraction analysis were grown from a water solution after several weeks.

Experimental details

The H atoms were located from Fourier difference maps and refined. The water molecule was found to be disordered via symmetry and refined using restraints for bond lengths and angle.

Discussion

Nitropyridine and its derivatives have been paid much attention due to their practical applications. Indeed, there are several patent claims and publications related with 4-hydroxy-3,5-dinitropyridine-*N*-oxide compounds. A variety of substituted nitropyridine-*N*-oxide compounds are used as herbicidal chemicals to control the growth of undesired plants [1]. Moreover, 4-hydroxy-3,5-dinitropyridine-*N*-oxide and its metal complexes have a higher explosion temperature and lower sensitivity, and therefore are used as energetic catalysts for solid propellants in order to adjust and improve their trajectory properties [2].

The X-ray diffraction study of the title crystal structure revealed that the H atom of hydroxy group is moved to the *N*-oxide group of 4-hydroxypyridine *N*-oxide (figure, top). The N1—O2 distance is 1.389(5) Å, and the C1—O1 distance is 1.242(5) Å. The C1—C2 distance of 1.450(5) Å is longer than the corresponding distance in 4-hydroxy-3,5-dinitropyridine (1.39(4) Å [3]), while the N1—C3 and C2—C3 distances of 1.345(4) Å and 1.363(4) Å, respectively, are shorter than the corresponding distances in the above-mentioned compound (1.37(5) Å and 1.39(4) Å, respectively). The mean N—O distance of the nitro group amounts to 1.222(3) Å. Intermolecular hydrogen bonds exist between water molecules, oxo and *N*-hydroxide groups as well as the nitro groups of neighboring molecules (d(O2—H2) = 0.87 Å, d(O2···O5) = 2.527 Å, ∠O2–H2···O5 = 170°; d(O5—H5A) = 1.02 Å, d(O5···O1^{i}) = 2.861 Å, ∠O5–H5A···O1^{i} = 139°; d(O5—H5B) = 1.02 Å, d(O5···O1^{ii}) = 2.861 Å, ∠O5–H5B···O1^{ii} = 116°; d(O5···O3^{iii}) = 2.999 Å, ∠O5–H5B···O3^{iii} = 124°; symmetry codes i: $-y+1,x+1,-z+2$; ii: $y,-x+1,-z+2$; iii: $x+½,-y+½,-z+2$; figure, bottom).

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.39 × 0.41 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.63 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5043, 1026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 620
$N(param)_{refined}$:	92
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	4*e*	0.5	0.329(3)	0.829(3)	0.413(9)	0.04(1)
H(3)	8*f*		0.136(2)	0.842(2)	0.573(5)	0.019(7)
H(5A)	8*f*	0.5	0.390(5)	0.987(3)	0.551(8)	0.05(2)
H(5B)	8*f*	0.5	0.433(4)	0.889(3)	0.718(7)	0.05(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.1003(2)	x+½	1.1743(7)	0.054(1)	U_{11}	0.058(2)	0.003(2)	0.012(1)	U_{13}
O(2)	4*e*	0.2885(2)	x+½	0.3251(7)	0.064(1)	U_{11}	0.036(2)	–0.010(2)	0.003(1)	U_{13}
O(3)	8*f*	–0.0109(2)	0.7734(2)	1.1837(5)	0.086(2)	0.089(2)	0.064(2)	0.033(2)	0.029(2)	0.013(2)
O(4)	8*f*	–0.0228(2)	0.8541(2)	0.8068(6)	0.057(2)	0.075(2)	0.065(2)	0.025(1)	–0.009(1)	0.001(2)
N(1)	4*e*	0.2423(2)	x+½	0.5461(7)	0.040(1)	U_{11}	0.037(2)	–0.005(2)	–0.005(1)	U_{13}
N(2)	8*f*	0.0179(2)	0.7908(2)	0.9537(6)	0.046(2)	0.050(2)	0.049(2)	0.004(1)	–0.002(1)	–0.005(2)
C(1)	4*e*	0.1440(2)	x+½	0.9837(9)	0.040(1)	U_{11}	0.041(3)	–0.004(2)	–0.005(2)	U_{13}
C(2)	8*f*	0.1083(2)	0.7370(2)	0.8563(7)	0.034(2)	0.039(2)	0.038(2)	0.001(1)	–0.006(1)	–0.012(1)
C(3)	8*f*	0.1556(3)	0.7831(3)	0.6433(6)	0.043(2)	0.037(2)	0.036(2)	0.001(2)	–0.011(2)	–0.006(2)
O(5)	4*e*	0.4134(2)	x+½	0.530(1)	0.067(2)	U_{11}	0.085(4)	–0.007(2)	–0.010(2)	U_{13}

Acknowledgment. We thank the Postgraduate-Innovation-Foundation of Shaanxi Normal University for financial support.

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