Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Rerefinement of the co-crystal of 4-hydroxypyridine with 4-hydroxypyridinium nitrate

Shan Gao,[a] Zhen-Zhong Lu,[a] Li-Hua Huo,[a] Shariffudin M. Zain[b] and Seik Weng Ng[b]*

[a]College of Chemistry and Chemical Technology, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.037
wR factor = 0.117
Data-to-parameter ratio = 12.4

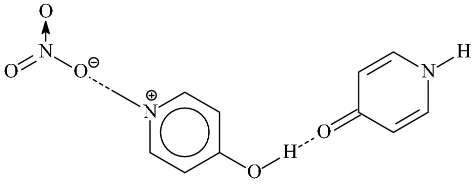
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 25 October 2004
Accepted 26 October 2004
Online 6 November 2004

The crystal structure of the title salt adduct, $C_5H_6NO^+ \cdot NO_3^- \cdot C_5H_5NO$, has a $C_5H_6NO^+/C_5HNO$ cation/molecule assembly (which lies on an inversion center) whose components are linked through their O atoms by a short hydrogen bond [2.446 (3) Å]. The cation is formally the 4-hydroxypyridinium cation and the neutral component the 4-pyridinone molecule, but the two could not be differentiated as they occupy equivalent positions, with the H atom disordered between them. The nitrogen-bound H atom interacts with the nitrate ion [2.840 (1) Å], which lies on another special position of site symmetry 2.

Comment

4-Pyridinone, which exists as a 6/5-hydrate (Jones, 2001), is reported to form a 2:1 adduct with nitric acid; the earlier study had placed an H atom midway between two neutral 4-pyridinone molecules, on a center of inversion (Goodgame *et al.*, 1993). In the present study, the structure was refined without imposing the symmetry constraint on this atom; the structure is consequently interpreted as the title co-crystal (I) (Fig. 1).



(I)

The position of the H atom along the linear internuclear axis, when investigated by a *PM*3 potential calculation carried out with *HYPERCHEM* (Hypercube, 2000), coincides with the minimum energy when it is off center, at about 1 Å from the single-bonded O atom. The calculations assumed a structure where one ring has a hydroxy group and the other has a double-bonded carbonyl O atom. The published structure (Goodgame *et al.*, 1993) with symmetrical O···H bonds is probably chemically less appropriate.

Experimental

The title co-crystal was the unexpected compound isolated from the reaction of cadmium nitrate tetrahydrate (3.08 g, 10 mmol) and 4-hydroxypyridine (1.4 g, 15 mmol) in ethanol. The solvent was allowed to evaporate over several days to furnish colorless prismatic crystals of the organic compound. Calculated for $C_{10}H_{10}N_3O_5$: C 47.62, H 4.00, N 16.66%; found: C 47.58, H 3.94, N 16.5%. The reaction of the heterocycle with cobalt nitrate had yielded the water-coordinated bis-adduct (Lu *et al.*, 2004).

Crystal data

$C_5H_6NO^+ \cdot NO_3^- \cdot C_5H_5NO$
$M_r = 253.22$
Monoclinic, $C2/c$
$a = 17.993$ (4) Å
$b = 6.528$ (1) Å
$c = 12.501$ (3) Å
$\beta = 127.74$ (3)°
$V = 1161.2$ (4) Å^3
$Z = 4$
$D_x = 1.448$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5340 reflections
$\theta = 3.3$–$27.5°$
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.38 × 0.24 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.858$, $T_{\max} = 0.979$
5541 measured reflections
1338 independent reflections
1010 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 27.5°$
$h = -23 \rightarrow 23$
$k = -7 \rightarrow 8$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.117$
$S = 1.08$
1338 reflections
108 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.2278P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.005 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.291 (2)	C2—C3	1.403 (2)
N1—C1	1.339 (2)	C3—C4	1.411 (2)
N1—C5	1.339 (2)	C4—C5	1.358 (2)
C1—C2	1.354 (2)		
C1—N1—C5	120.6 (1)	O1—C3—C4	123.3 (1)
N1—C1—C2	121.5 (2)	C2—C3—C4	116.8 (1)
C1—C2—C3	120.0 (1)	C3—C4—C5	120.1 (1)
O1—C3—C2	119.9 (1)	N1—C5—C4	121.0 (1)

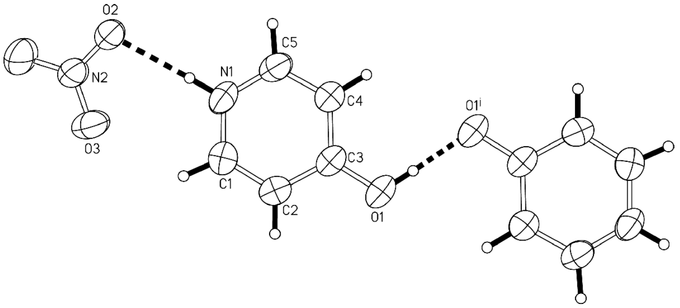


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

The carbon-bound H atoms were refined with a distance restraint of 0.95 (1) Å; the nitrogen-bound H atom was refined with a restraint of 0.85 (1) Å. The final H atom that would balance the charges was initially located on the $\overline{1}$ site ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$), the atom being midway between the O atom of the cation and that of the symmetry-related neutral molecule. This H atom was then allowed to refine without this symmetry constraint, but with a distance restraint of 0.85 (1) Å. The H atom is thus disordered over two positions, and the cation and neutral molecule are disordered on equivalent sites..

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

We thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund for Remarkable Teachers of Heilongjiang Province (No. 1054G036) and the University of Malaya for supporting this study.

References

Goodgame, D. M. L., Lalia-Kantouri, M. & Williams, D. J. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 373–380.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hypercube (2000). *HYPERCHEM*. Release 6.01 for Windows. Hypercube Inc., Ontario, Canada.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jones, P. G. (2001). *Acta Cryst.* C**57**, 880–882.
Lu, Z.-Z., Gao, S., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst.* E**60**, m811–m813.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

o2196 Shan Gao *et al.* • $C_5H_6NO^+ \cdot NO_3^- \cdot C_5H_5NO$ *Acta Cryst.* (2004). E**60**, o2195–o2196