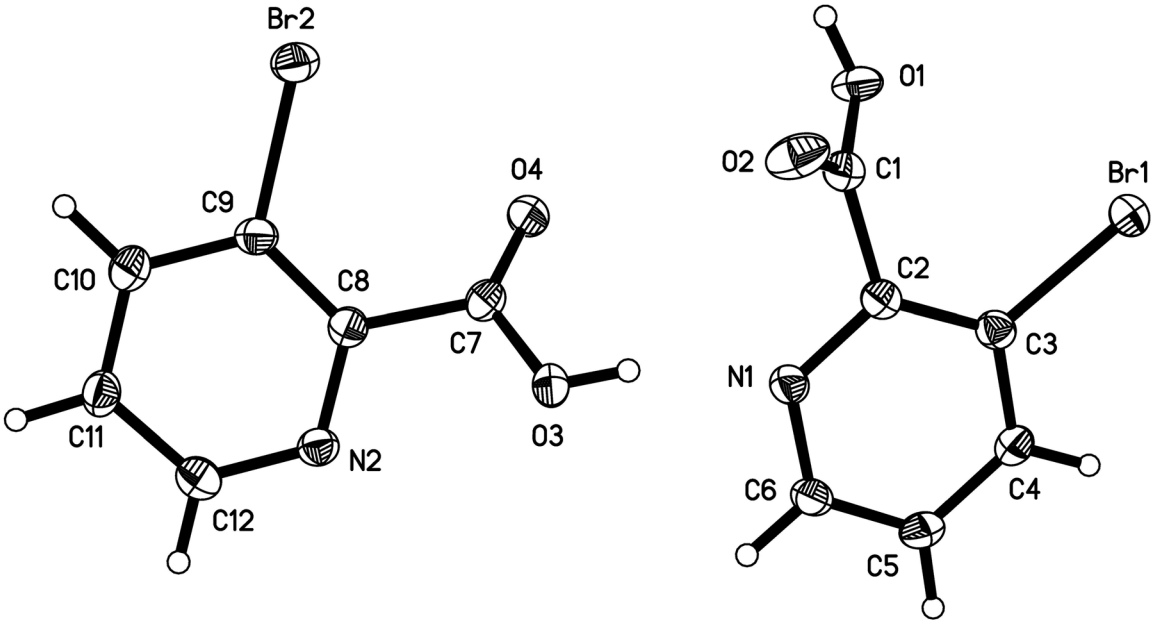
Guang Huang*

The crystal structure of 3-bromopicolinic acid, $C_6H_4BrNO_2$



https://doi.org/10.1515/ncrs-2021-0343
Received August 28, 2021; accepted October 5, 2021;
published online October 14, 2021

Abstract

$C_6H_4BrNO_2$, orthorhombic, $Pna2_1$ (no. 33), $a = 14.3975(12)$ Å, $b = 7.5773(7)$ Å, $c = 12.2500(10)$ Å, $\beta = 90°$, $V = 1336.4(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0281$, $wR_{ref}(F^2) = 0.0536$, $T = 150(2)$ K.

CCDC no.: 2113913

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.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.25 × 0.15 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	6.08 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15,847, 2696, 0.054
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2341
$N(param)_{refined}$:	183
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

All starting materials were used as received. For the recrystallization 2.01 g (10 mmol) 3-bromopicolinic acid was mixed with 10 mL tetrahydrofuran and 1 mL deionized water under room temperature and was stirred to form a clear solution. The solution was filtered and evaporated naturally. Several days later, colorless block crystals of the title compound were obtained, yield 82% (based on the raw 3-bromopicolinic acid).

Experimental details

The structure was solved by direct methods with the SHELXS-2018 program. All H-atoms from C and N atoms were positioned with idealized geometry and refined

***Corresponding author: Guang Huang**, Sino-Portugal Belt and Road Joint Laboratory on Science of Cultural Heritage Conservation, City University of Macau, Macau, P. R. China; Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, Guangdong, P. R. China, E-mail: ghuang@cityu.mo. https://orcid.org/0000-0002-9171-3641

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.22803 (4)	0.52861 (7)	0.81495 (6)	0.03716 (14)
Br2	0.46236 (4)	0.82636 (10)	0.14898 (5)	0.04430 (17)
C1	0.3262 (4)	0.5618 (8)	0.5733 (5)	0.0336 (14)
C2	0.3808 (4)	0.6122 (8)	0.6736 (5)	0.0307 (14)
C3	0.3489 (4)	0.6082 (8)	0.7803 (5)	0.0317 (13)
C4	0.4073 (4)	0.6555 (8)	0.8646 (5)	0.0349 (14)
H4	0.385729	0.653693	0.937917	0.042*
C5	0.4973 (4)	0.7054 (8)	0.8414 (5)	0.0364 (15)
H5	0.539178	0.737623	0.897911	0.044*
C6	0.5243 (4)	0.7069 (8)	0.7339 (5)	0.0357 (15)
H6	0.585833	0.743315	0.717250	0.043*
C7	0.5299 (4)	0.8165 (8)	0.4021 (5)	0.0333 (13)
C8	0.6007 (3)	0.8671 (7)	0.3169 (5)	0.0308 (11)
C9	0.5811 (4)	0.8806 (8)	0.2070 (5)	0.0328 (14)
C10	0.6498 (4)	0.9304 (8)	0.1339 (5)	0.0372 (14)
H10	0.637243	0.939454	0.057940	0.045*
C11	0.7372 (4)	0.9665 (8)	0.1751 (5)	0.0375 (14)
H11	0.786326	1.000954	0.127834	0.045*
C12	0.7519 (4)	0.9514 (8)	0.2861 (5)	0.0384 (16)
H12	0.811946	0.977176	0.313956	0.046*
N1	0.4685 (3)	0.6596 (6)	0.6511 (6)	0.0326 (9)
N2	0.6860 (3)	0.9025 (7)	0.3558 (4)	0.0325(11)
O1	0.2493 (3)	0.6525 (6)	0.5614 (4)	0.0396 (10)
H1	0.226034	0.630712	0.500027	0.059*
O2	0.3556 (3)	0.4546 (6)	0.5101 (4)	0.0491 (12)
O3	0.5656 (3)	0.7083 (6)	0.4753 (3)	0.0361 (10)
H3	0.525885	0.687403	0.523783	0.054*
O4	0.4513 (3)	0.8729 (6)	0.4024 (4)	0.0449 (11)

isotropic (U_{iso}(H) = 1.2U_{eq}(C)) using a riding model with C–H = 0.95 Å. The H-atoms from O atoms positioned using peaks from the difference Fourier map and refined isotropic with the distance of O1–H1 = 0.84 Å and O3–H3 = 0.84 Å (U_{iso}(H) = 1.5U_{eq}(O)). The distance of Br1 and O4 is 3.034 Å, which indicates a short inter HL···A contact between Br1 and O4, resulting an Alert level B for checkcif. But there is no reasonable hydrogen bond. There may be some intermolecular weak interaction between Br1 and O4.

Comment

Among the mono-bromide-substituted picolinic acids, including 4-, 5- and 6-bromide-substituted picolinic acids and their derivatives, only the crystal structures of 4-bromopicolinic acid and methyl 5-bromo-6-methylpicolinate have been reported [5, 6]. Some of their metal complexes [7–15] and organometal complexes [16–22] have been also reported elsewhere. To the best of our knowledge, the crystal structures of 3-bromide-substituted picolinic acid has not been reported. Herein we reported the crystal structure of 3-bromopicolinic acid.

The asymmetric unit is made of two 3-bromopicolinic acid molecules, which show a slightly different conformation about the C1–C2 and C7–C8 bond, respectively. All bond lengths of the title compound are comparable with the reported results [5–22]. There is one dimensional chain generated by hydrogen bonds O1–H1···N2 and O3–H3···N1.

Author contributions: The author has accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The author declares no conflicts of interest regarding this article.

References

1. Bruker. SAINT (v8.37A); Bruker AXS Inc: Madison, Wisconsin, USA, 2015.
2. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. Using phases to determine the space group. *Acta Crystallogr.* 2018, *A74*, a353.
5. Cai B., Zhu M.-E., Bai X., Lin Y.-R., Guo Q.-Q., Mneg Y.-N. The crystal structure of 5-bromopicolinic acid monohydrate, $C_6H_6BrNO_3$. *Z. Kristallogr. NCS* 2020, *235*, 399–400.
6. Wu Y.-M., Wu C.-M., Wang Y. Methyl 5-bromo-6-methylpicolinate. *Acta Crystallogr.* 2009, *E65*, o134.
7. Li J.-X., Du Z.-X., Bai R.-F. Crystal structure of aqua-bis(5-bromo-6-methyl-picolinato- κ^2N,O) zinc(II) dihydrate, $C_{14}H_{16}Br_2N2O_7Zn$. *Z. Kristallogr. NCS* 2020, *235*, 63–65.
8. Chai J., Liu Y., Liu B., Yang B. Effect of substituent groups (R = CH_3, Br and CF_3) on the structure, stability and redox property of $[Cr(R\text{-}pic)_2(H_2O)_2]NO_3{\cdot}H_2O$ complexes. *J. Mol. Struct.* 2017, *1150*, 307–315.
9. Chai J., Liu Y., Dong J., Liu B., Yang B. Synthesis, structure, chemical and bioactivity behavior of eight chromium(III) picolinate derivatives $Cr(R\text{-}pic)_3$. *Inorg. Chim. Acta.* 2017, *466*, 151–159.
10. Baroud A. A., Mihajlovic-Lalic L. E., Gligorijevic N., Arandelovic S., Stankovic D., Radulovic S., Van Hecke K., Grguric-Sipka S. Ruthenium(II) bipyridine complexes: from synthesis and crystal structures to electrochemical and cytotoxicity investigation. *J. Coord. Chem.* 2017, *70*, 831–847.
11. Kukovec B.-M., Popovic Z. Pseudopolymorphism in nickel(II) complexes with 6-bromopicolinic acid. synthesis, structural and thermal studies. *J. Mol. Struct.* 2009, *930*, 121–125.
12. Rachford A. A., Jeffrey L., Petersen J. L., Rack J. J. Efficient energy conversion in photochromic ruthenium DMSO complexes. *Inorg. Chem.* 2006, *45*, 5953–5960.

13. Hu F.-L., Yue Z., Yan M., Luo W.-Q., Yin X.-H. Aquabis-(6-bromopicolinato-κ^2*N,O*)copper(II). *Acta Crystallogr.* 2009, *E65*, m45–m46.
14. Kukovec B.-M., Popovic Z. Polymorphism of cobalt(II) complex with 6-bromopicolinic acid: the influence of the solution pH value on the formation of polymorphs. *J. Mol. Struct.* 2009, *930*, 174–178.
15. Kukovec B.-M., Popovic Z., Kozlevcar B., Jaglicic Z. 3D supramolecular architectures of copper(II) complexes with 6-methylpicolinic and 6-bromopicolinic acid: synthesis, spectroscopic, thermal and magnetic properties. *Polyhedron* 2008, *27*, 3631–3638.
16. Poljarevic J. M., Gal G. T., May N. V., Spengler V., Domotor O., Savic A. R., Grguric-Sipka S., Enyedy E. A. Comparative solution equilibrium and structural studies of half-sandwich ruthenium(II) (η^6-toluene) complexes of picolinate derivatives. *J. Inorg. Biochem.* 2018, *181*, 74–85.
17. Davidson R., Hsu Y.-T., Bhagani Yufit D., Beeby A. Exploring the chemistry and photophysics of substituted picolinates positional isomers in iridium(III) bisphenylpyridine complexes. *Organometallics* 2017, *36*, 2727–2735.
18. Quan L., Yin H., Wang D. Bis(5-bromopyridine-2-carboxylato-*O*) triphenyl-antimony(V). *Acta Crystallogr.* 2008, *E64*, m1503.
19. Silva J. A., Magalhaes A. P., Silva M. R., Sobral A. J. F. N., Pereira L. C. J. Diaqua-(6-bromopicolinato-κ^2*N,O*) (nitrato-κ^2*O,O*) copper(II). *Acta Crystallogr.* 2011, *E67*, m160.
20. Ivanovic I., Jovanovic K. K., Gligorijevic N., Radulovic S., Arion V. B., Sheweshein K. S. A. M., Tesic Z. L., Grguric-Sipka S. Ruthenium(II)-arene complexes with substituted picolinato ligands: synthesis, structure, spectroscopic properties and antiproliferative activity. *J. Organomet. Chem.* 2014, *749*, 343–349.
21. Hong M., Yin D.-H., Zhang Y.-W., Jiang J., Li C. Coordination geometry of monomeric, dimeric and polymeric organotin(IV) compounds constructed from 5-bromopyridine-2-carboxylic acid and mono-, di- or tri-organotin precursors. *J. Mol. Struct.* 2009, *1036*, 244–251.
22. Van Rijt S. H., Anna F. A., Peacock A. F. A., Russell D. L., Johnstone R. D. L., Simon Parsons S., Sadler P. J. Organometallic osmium(II) arene anticancer complexes containing picolinate derivatives. *Inorg. Chem.* 2009, *48*, 1753–1762.