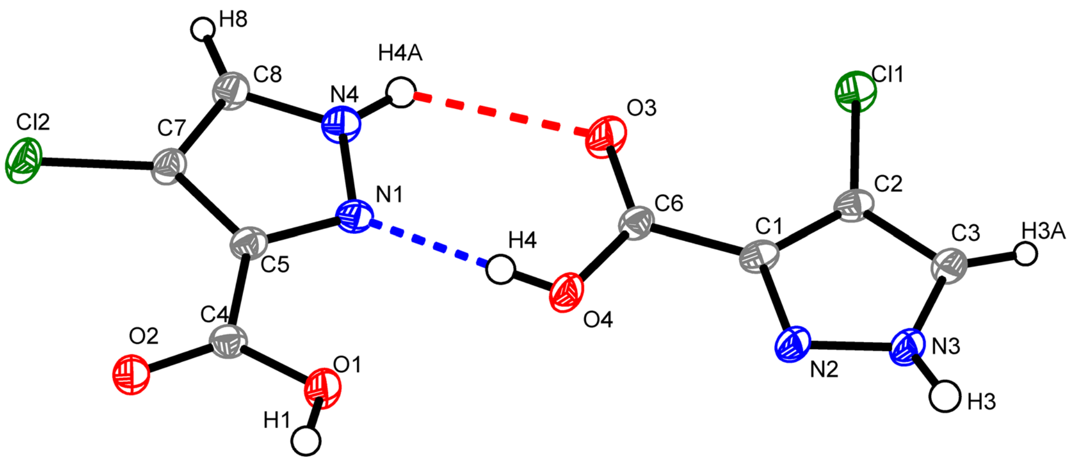
DaoHang Du, ShiHong Zhu, Chao Feng, YunHua Jiang, Jia Yang, Ting Tao, ShuLi Yu and Hong Zhao*

The crystal structure of 4-chloro-1*H*-pyrazole-3-carboxylic acid, $C_4H_3ClN_2O_2$



https://doi.org/10.1515/ncrs-2025-0093
Received February 25, 2025; accepted April 17, 2025;
published online April 30, 2025

Abstract

$C_4H_3ClN_2O_2$, monoclinic, $C2/c$ (no. 15), a = 25.4370(17) Å, b = 6.9155(5) Å, c = 13.0629(7) Å, β = 110.558 (6)°, V = 2151.6 (3) Å^3, Z = 16, $R_{gt}(F)$ = 0.0552, w$R_{ref}(F^2)$ = 0.2177, T = 293 K.

CCDC no.: 2424717

The molecular structure is depicted in the figure. Table 1 summarizes the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Clear light white needle
Size:	0.50 × 0.16 × 0.13 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.62 mm^{-1}
Diffractometer, scan mode:	Bruker Apex 2, φ and ω scans
θ_{max}, completeness:	25.0°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10791, 1895, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,641
$N(param)_{refined}$:	173
Programs:	Bruker,[1] Olex2,[2] SHELX,[3,4] Diamond[5]

1 Source of materials

The title compound was synthesized starting from 1*H*-pyrazole-3-carboxylic acid (10 g, 89.30 mmol) dissolved in acetic acid (100 ml). Concentrated HCl (11.17 ml) was added dropwise under stirring at 40 °C in an oil bath for 15 min, followed by the slow addition of an aqueous solution of sodium chlorate ($NaClO_3$, 2.37 g in 20 ml H_2O) over 30 min. The reaction mixture was stirred at 40 °C for 5 h (monitored by TLC). After completion, the mixture was concentrated under reduced pressure, treated with ice-water (150 ml), and filtered under vacuum. The resulting solid was washed with cold water and dried to yield 4-chloro-1*H*-pyrazole-3-carboxylic acid as a white crystalline solid (9.5184 g, 72.75 %). Single crystals were obtained by slow evaporation using an ethyl acetate/methanol

***Corresponding author: Hong Zhao**, School of Chemistry and Chemical Engineering, Southeast University, Nanjing, JiangSu, 210096, P.R. China, E-mail: zhaohong@seu.edu.cn. https://orcid.org/0000-0001-6596-6867
DaoHang Du, ShiHong Zhu, YunHua Jiang, Jia Yang, Ting Tao and ShuLi Yu, School of Chemistry and Chemical Engineering, Southeast University, Nanjing, JiangSu, 210096, P.R. China, E-mail: 15254701061@163.com (D. Du), 193419839@qq.com (S. Zhu), 220222908@seu.edu.cn (Y. Jiang), 220233119@seu.edu.cn (J. Yang), taoting1923@163.com (T. Tao), 1982259984@qq.com (S. Yu)
Chao Feng, School of Materials and Chemical Engineering, Bengbu University, Bengbu, 233030, P.R. China, E-mail: fchg042@163.com. https://orcid.org/0000-0003-2773-0997

mixed solvent system. ^{1}H-NMR (600 MHz, DMSO) δ 13.63 (s, 2H), 7.94 (s, 1H).

2 Results and discussion

Pyrazole-carboxylic acid compounds serve as versatile molecular platforms,[5–10] where the synergistic combination of the rigid conjugated system in the pyrazole ring and the strong coordination capability of the carboxylic acid group provides structural foundations for the controlled construction of metal complexes while imparting unique physicochemical properties.[11–15] The derived metal-organic frameworks (MOFs) have been extensively applied in environmental sensing and optoelectronic devices, with their proton conductivity offering novel insights for developing advanced energy materials.[16–19] Leveraging the site-tunability and conformational diversity of pyrazole-carboxylic acid derivatives, this work reports a compound incorporating this structural motif.

The asymmetric unit of the title compound comprises two complete 4-chloro-1*H*-pyrazole-3-carboxylic acid molecules linked via O4–H4···N1 (1.8549 Å) and N4–H4A···O3 (2.4830 Å) hydrogen bonds. Structural analysis reveals C···N bond lengths (C1–N2, C3–N3, C8–N4, and C5–N1) ranging from 1.335 Å to 1.348 Å, consistent with values reported for 4-bromopyrazole analogues.[20] The C–Cl bond length of 1.712 Å aligns with typical ranges for analogous compounds,[21,22] further supporting the structural integrity of the framework. Intermolecular interactions dominate the extended architecture. Within the *bc*-plane, a two-dimensional grid is formed through three distinct hydrogen-bonding motifs: (i) pyrazole N···N interactions (N4–H4A···N2, 2.1654 Å), (ii) carboxyl O–pyrazole N interactions (N3–H3···O3, 2.2106 Å and N4–H4A···O3, 2.4830 Å), and (iii) carboxylic acid O···O interactions (O1–H1···O2, 1.8189 Å). Adjacent two-dimensional grids stack into a three-dimensional framework via N3–H3···O4 hydrogen bonds (2.8014 Å). These interactions, while within expected van der Waals distances, highlight the role of hydrogen bonding in stabilizing the supramolecular assembly.

Author contributions: The authors have acknowledged full accountability for the entirety of the content presented in this submitted manuscript and have given their approval for its submission.
Research funding: This work was supported by Jiangsu Ainaji Neoenergy Science & Technology Co., Ltd. (8507040091), and the National Natural Science Foundation of China (81703366).
Conflict of interest: The author hereby declares that there are no conflicts of interest pertaining to this article.

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341.
2. Sheldrick, G. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A* **2015**, *71* (1), 3–8.
3. Sheldrick, G. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr. Section C* **2015**, *71* (1), 3–8.
4. Brandenburg, K.; Putz, H. Diamond. *Crystal Impact GbR, Bonn, Germany* 2006.
5. Kumar Gupta, R.; Kallem, P.; Luo, G.–G.; Cui, P.; Wang, Z.; Banat, F.; Tung, C.–H.; Sun, D. 1H-Pyrazole-4-carboxylic Acid-based metal–organic Frameworks: Multifaceted Materials. *Coord. Chem. Rev.* **2023**, *497*, 215436.
6. Tokumasu, K.; Yazaki, R.; Ohshima, T. Direct Catalytic Chemoselective *α*-Amination of Acylpyrazoles: A Concise Route to Unnatural *α*-Amino Acid Derivatives. *J. Am. Chem. Soc.* **2016**, *138* (8), 2664–2669.
7. Somakala, K.; Amir, M. Synthesis, Characterization and Pharmacological Evaluation of Pyrazolyl Urea Derivatives as Potential Anti-inflammatory Agents. *Acta Pharm. Sin. B* **2017**, *7* (2), 230–240.
8. Wang, B.; Wang, H.; Liu, H.; Xiong, L.; Yang, N.; Zhang, Y.; Li, Z. Synthesis and Structure-insecticidal Activity Relationship of Novel Phenylpyrazole Carboxylic Acid Derivatives Containing Fluorine Moiety. *Chin. Chem. Lett.* **2020**, *31* (3), 739–745.
9. Utochnikova, V. V.; Abramovich, M. S.; Latipov, E. V.; Dalinger, A. I.; Goloveshkin, A. S.; Vashchenko, A. A.; Kalyakina, A. S.; Vatsadze, S. Z.; Schepers, U.; Bräse, S.; Kuzmina, N. P. Brightly Luminescent Lanthanide Pyrazolecarboxylates: Synthesis, Luminescent Properties and Influence of Ligand Isomerism. *J. Lumin.* **2019**, *205*, 429–439.
10. Utochnikova, V. V.; Latipov, E. V.; Dalinger, A. I.; Nelyubina, Y. V.; Vashchenko, A. A.; Hoffmann, M.; Kalyakina, A. S.; Vatsadze, S. Z.; Schepers, U.; Bräse, S.; Kuzmina, N. P. Lanthanide Pyrazolecarboxylates for OLEDs and Bioimaging. *J. Lumin.* **2018**, *202*, 38–46.
11. Lin, C.–L.; Chen, Y.–F.; Qiu, L.–J.; Zhu, B.; Wang, X.; Luo, S.–P.; Shi, W.; Yang, T.–H.; Lei, W. Synthesis, Structure and Photocatalytic Properties of Coordination Polymers Based on Pyrazole Carboxylic Acid Ligands. *CrystEngComm* **2020**, *22* (41), 6847–6835.
12. Radi, S.; El-Massaoudi, M.; Benaissa, H.; Adarsh, N. N.; Ferbinteanu, M.; Devlin, E.; Sanakis, Y.; Garcia, Y. Crystal Engineering of a Series of Complexes and Coordination Polymers Based on pyrazole-carboxylic Acid Ligands. *New J. Chem.* **2017**, *41* (16), 8232–8241.
13. Dahmani, M.; Et-Touhami, A.; Yahyi, A.; Harit, T.; Eddike, D.; Tillard, M.; Benabbes, R. Synthesis, Characterization, X-Ray Structure and in Vitro Antifungal Activity of Triphenyltin Complexes Based on Pyrazole Dicarboxylic Acid Derivatives. *J. Mol. Struct.* **2021**, *1225*, 129137.
14. Scatena, R.; Massignani, S.; Lanza, A. E.; Zorzi, F.; Monari, M.; Nestola, F.;; Pettinari, C.; Pandolfo, L. Synthesis of Coordination Polymers and Discrete Complexes from the Reaction of Copper(II) Carboxylates with Pyrazole: Role of Carboxylates Basicity. *Cryst. Growth Des.* **2021**, *22* (2), 1032–1044.
15. Yang, J. Pyrazole–3–carboxylates Assisted N–heterocyclic Carbene Palladium Complexes: Synthesis, Characterization, and Catalytic Activities Towards Arylation of Azoles with Arylsulfonyl Hydrazides. *Appl. Organomet. Chem.* **2020**, *34* (3), e5450.
16. Kumar, S.; Arora, A.; Kumar, A.; Tomar, K. An Unsymmetrical Tritopic Pyrazole Carboxylate Ligand Based Porous Cd(II) MOF Sensor for Acetone Molecule. *Inorg. Chem. Commun.* **2018**, *96*, 16–19.

17. Kumar, A.; Bains, O.; Langyan, R.; Kumar, R.; Kumar, V.; Chetti, P.; Kamal, R.; Synthesis, C. Optoelectronic Properties and DFT Studies of Novel 4,5–Diarylpyrazole-1–Carboxylates. *ChemistrySelect* **2024**, *9* (4), e202303934.
18. Yıldız, B.; Güzel, E.; Akyüz, D.; Arslan, B. S.; Koca, A.; Şener, M. K. Unsymmetrically pyrazole-3-carboxylic Acid Substituted Phthalocyanine-based Photoanodes for Use in Water Splitting Photoelectrochemical and dye-sensitized Solar Cells. *Sol. Energy* **2019**, *191*, 654–662.
19. Hegde, V.; Sreekala, C. O.; Kulkarni, N. V.; Mathew, J. Bis(pyrazolyl) methane Supported Cobalt (II) Complexes as Sensitizers in dye-sensitized Solar Cells. *J. Photochem. Photobiol., A: Chem.* **2023**, *449*, 115389.
20. Foces-Foces, C.; Llamas-Saiz, A.; Elguero, J. Crystal Structures of Two 4-bromopyrazole Derivatives. *Z. Kristallogr. Cryst. Mater.* **1999**, *214* (4), 237–241.
21. Rue, K.; Raptis, R. G. Low-Temperature Crystal Structure of 4-chloro-1H-pyrazole. *Acta Crystallogr. Section E Cryst. Commun.* **2021**, *77*, 955–957.
22. Jaćimović, željko; Kosović, M.; Kastratović, V.; Barta Holló, B.; Szécsényi, K. M.; Szilágyi, I. M.; Latinović, N.; Vojinović-Ješić, L.; Rodić, M. Synthesis and Characterization of Copper, Nickel, Cobalt, Zinc Complexes with 4-nitro-3-pyrazolecarboxylic Acid Ligand. *J. Therm. Anal. Calorim.* **2018**, *133*, 813.