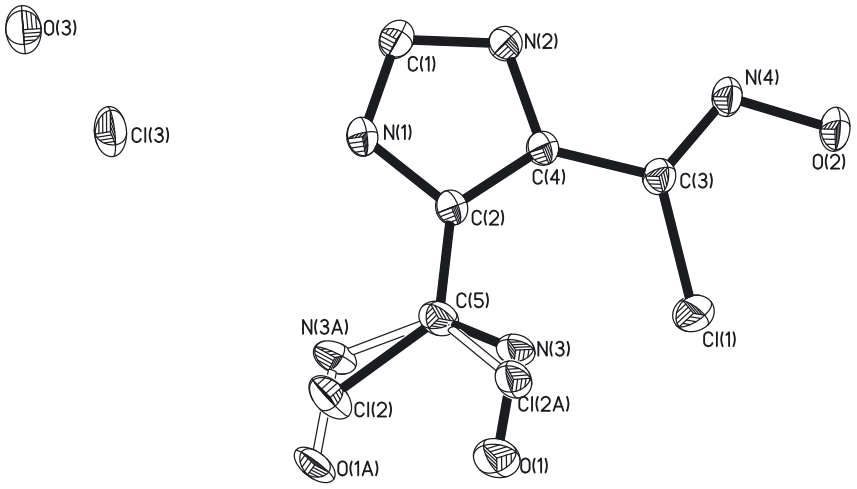
Yunlu Li*, Rui Zhou, Bo Wang and Shengping Fan

The crystal structure of 4,5-bis((*Z*)-chloro(hydroxyimino)methyl)-1*H*-imidazol-3-ium chloride monohydrate



https://doi.org/10.1515/ncrs-2024-0316
Received July 25, 2024; accepted October 10, 2024;
published online October 23, 2024

Abstract

$C_5H_7Cl_3N_4O_3$, monoclinic, $P2_1/c$ (no. 14), a = 5.745(3) Å, b = 29.120(13) Å, c = 6.813(3) Å, β = 107.649(6)°, V = 1086.1(9) Å^3, Z = 4, $R_{gt}(F)$ = 0.0411, w$R_{ref}(F^2)$ = 0.1163, T = 296 K.

CCDC no.: 2389954

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:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.84 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.6°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6479, 2502, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,118
$N(param)_{refined}$:	167
Programs:	Olex2[1], SHELX[2,3], Bruker[4]

1 Source of material

Add 0.01 mol 4,5-dicyanoimidazole and 0.04 mol hydroxylamine aqueous solution to the reactor. The temperature of the reactor was maintained at 298.15 K and the reaction is for 2 h. After the reaction is completed, the reaction solution is filtered. Remove the filtrate and retain the precipitate. Add 0.01 mol above solid and 20 mL $NaNO_2$ to the reactor. The temperature of the reactor was maintained at 273 K. 10 mL 37 % hydrochloric acid is slowly added dropwise into the reaction for 2 h. After the reaction is completed, the reaction solution is filtered. Remove the filtrate and retain the white solid. The white solid is dissolved in methanol and is

***Corresponding author: Yunlu Li**, School of Environment and Safety Engineering, North University of China, Taiyuan 030051, Shanxi Province, P.R. China, E-mail: liyunlu@nuc.edu.cn. https://orcid.org/0000-0003-1998-4292
Rui Zhou, School of Environment and Safety Engineering, North University of China, Taiyuan 030051, Shanxi Province, P.R. China
Bo Wang and Shengping Fan, Subunit 51 of the 32272nd Unit of the Chinese People's Liberation Army, Lanzhou 730100, Gansu Province, P.R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7127 (5)	0.69011 (8)	0.2759 (4)	0.0431 (6)
H1	0.713916	0.720247	0.230982	0.052*
N1	0.8127 (4)	0.65474 (7)	0.2121 (3)	0.0401 (4)
H1A	0.889877	0.655881	0.122033	0.048*
Cl1	0.71267 (14)	0.55584 (2)	0.70060 (10)	0.0547 (2)
C2	0.7749 (4)	0.61569 (7)	0.3115 (3)	0.0320 (4)
O2	0.3570 (4)	0.60339 (6)	0.8231 (3)	0.0483 (4)
H2	0.254784	0.618127	0.858413	0.072*
N2	0.6108 (4)	0.67580 (6)	0.4138 (3)	0.0367 (4)
H2A	0.532247	0.692765	0.475578	0.044*
C5	0.8502 (4)	0.57083 (8)	0.2584 (3)	0.0387 (5)
Cl2[a]	1.12042 (19)	0.56408 (4)	0.2188 (2)	0.0477 (4)
N3[a]	0.6892 (15)	0.5369 (2)	0.2383 (18)	0.0354 (15)
O1[a]	0.7811 (4)	0.49535 (8)	0.1912 (4)	0.0505 (7)
H1B[a]	0.683178	0.474733	0.189115	0.076*
Cl2A[b]	0.7215 (16)	0.5264 (2)	0.2397 (19)	0.0389 (16)
N3A[b]	1.086 (2)	0.5794 (4)	0.231 (2)	0.042 (2)
O1A[b]	1.1701 (14)	0.5372 (3)	0.1728 (13)	0.0438 (18)
H1AA[b]	1.317674	0.538749	0.190988	0.066*
C3	0.5725 (4)	0.60623 (7)	0.6026 (3)	0.0317 (4)
Cl3	1.04629 (13)	0.68544 (2)	−0.11491 (10)	0.0495 (2)
O3	1.3573 (4)	0.77021 (6)	0.1020 (3)	0.0570 (5)
H3A	1.278113	0.786170	0.177639	0.085*
H3B	1.244903	0.747670	0.059739	0.085*
N4	0.4138 (4)	0.62623 (6)	0.6663 (3)	0.0365 (4)
C4	0.6498 (4)	0.62945 (7)	0.4433 (3)	0.0302 (4)

[a]Occupancy: 0.772(4), [b]Occupancy: 0.228(4).

volatilized at room temperature to obtain clear colourless block crystals.

2 Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. All the non-hydrogen atoms were refined anisotropically.

3 Comment

Imidazole compounds and their energetic salts are research hotspots in the field of energetic materials in various countries.[5–8] 4,5-Dicyanoimidazole is an important imidazole compound that has been extensively studied.[9,10] The title compound was obtained by reacting 4,5-dicyanoimidazole, hydroxylamine aqueous solution and 37 % hydrochloric acid. The title compound is an organic compound with high research value in the preparation of imidazole energetic salts.

The bond lengths and angles in the title molecule are in the expected ranges.[11] The four atoms Cl2, C5, N3, O1 are in the same plane and the four atoms Cl1, C3, N4, O2 are also in the same plane. The dihedral angle formed by imidazole ring and place of Cl2, C5, N3, O1 is 41.514° and the dihedral angle formed by imidazole ring and place of Cl1, C3, N4, O2 is 21.1°.

The title compound was obtained by reacting 4,5-dicyanoimidazole, hydroxylamine aqueous solution and 37 % hydrochloric acid. During the reaction, hydroxylamine molecules are free in solution in the form $-NH_2$ and –OH and hydrochloric acid is free in solution in the form –Cl. The –CN triple bond of 4,5-dicyanoimidazole becomes double bond, with the C atom connected to –Cl and the N atom connected to –OH, generating the (4*Z*,5*E*)-*N*′4,*N*′5-dihydroxy-1*H*-imidazole-4,5-bis(carbimidoyl) dichloride molecule. Due to the presence of a large amount of hydrochloric acid in the solution, the title salt was obtained.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by National Science Foundation of China under grant 22105023.

Conflict of interest statement: The authors declare no conflicts of interest regarding 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. Cryst.* **2009**, *42*, 339–341.
2. Sheldrick, G. M. SHELXT – Integrated Space-Group Andcrystal-Structure Determination. *Acta Crystallogr.* **2015**, *71*, 3–8.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *71*, 3–8.
4. BRUKER SAINT, APEX*2 and* SADABS; Bruker AXS Inc.: Madison, WI, USA, 2016.
5. Windler, G. K.; Scott, B. L.; Tomson, N. C.; Leonard, P. W. Crystal Structure of 4,5-Dinitro-1*H*-Imidazole. *Acta Crystallogr.* **2015**, *E71*, o634.
6. Kelley, S. P.; Nuss, J. S.; Rogers, R. D. Nonstoichiometric, Protic Azolium Azolate Ionic Liquids Provide Unique Environments for N-Donor Coordination Chemistry. *Chem. Eur. J.* **2015**, *21*, 17196–17199.
7. Titi, H. M.; Kelley, S. P.; Easton, M. E.; Emerson, S. D.; Rogers, R. D. Formation of Ionic Co-crystals of Amphoteric Azoles Directed by the Ionic Liquid Co-Former 1-Ethyl-3-Methylimidazolium Acetate. *Chem. Commun.* **2017**, *61*, 8569–8572.
8. Easton, M. E.; Li, K.; Titi, H. M.; Kelley, S. P.; Rogers, R. D. Controlling the Interface between Salts, Solvates, Co-Crystals, and Ionic Liquids with Non-Stoichiometric Protic Azolium Azolates. *Cryst. Growth Des.* **2020**, *20*, 2608–2616.
9. Nagatomo, S.; Takeda, S.; Tamura, H.; Nakamura, N. Crystal Structures and Hydrogen Bonding in One-Dimensional Chains of 4,5-

Dicyanoimidazole and 4,5-Dichloroimidazole. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2783–2789.

10. Barni, E.; Bianchi, R.; Gervasio, G.; Peters, A. T.; Viscardi, G. Structural Characterization of 4-Cyanoimidazolium-5-Olate, 4,4-Diphenyl-5-Imidazolinone, and 4,5-Dicyanoimidazole. A Novel Mesoionic Compound and Decoding of Intermolecular Hydrogen Bonds. *J. Org. Chem.* **1997**, *62*, 7037–7043.
11. Luo, Y. H.; Wang, J. W.; Chen, C.; Li, Y. J.; Sun, B. W. Reversibly Stretching Cocrystals by the Application of a Magnetic Field. *Cryst. Growth Des.* **2017**, *17*, 2576–2583.