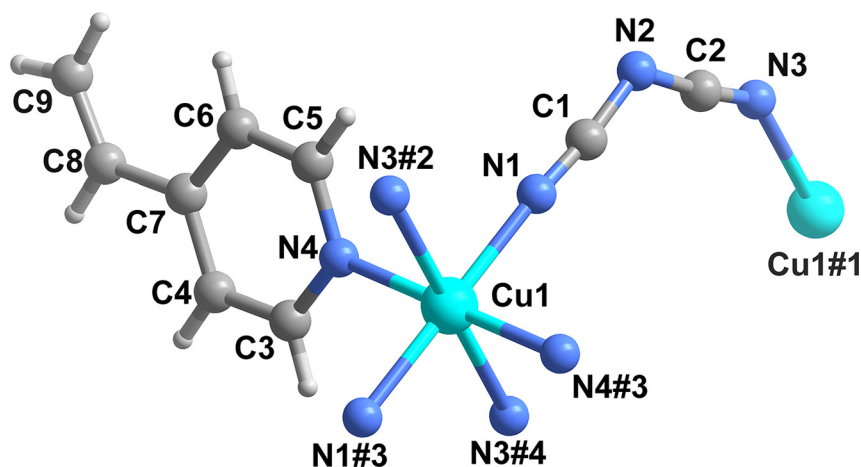


Chong Tan, Tong Zhang and Xiaodong Yi*

Crystal structure of *catena*-poly [bis(μ_2 -dicyanamide- $\kappa^2 N:N'$)-bis(4-vinylpyridine- κN)-copper(II)], $C_{18}H_{14}CuN_8$



<https://doi.org/10.1515/ncrs-2023-0100>

Received March 3, 2023; accepted March 24, 2023;
published online April 12, 2023

Abstract

$C_{18}H_{14}CuN_8$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2431(5)$ Å, $b = 7.3783(5)$ Å, $c = 9.8740(6)$ Å, $\alpha = 110.174(6)^\circ$, $\beta = 105.036(5)^\circ$, $\gamma = 92.219(5)^\circ$, $V = 473.55(6)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0409$, $wR_{ref}(F^2) = 0.1272$, $T = 293(2)$ K.

CCDC no.: 2245520

Table 1: Data collection and handling.

Crystal:	Green flaky
Size:	0.48 × 0.30 × 0.10 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	1.79 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	78.1°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	4781, 1910, 0.031
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1707
$N(param)_{refined}$:	124
Programs:	CrysAlis ^{PRO} [1], SHELX [2]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Xiaodong Yi**, CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 350002 Fuzhou, Fujian, P.R. China,

E-mail: yixiaodong@fjirsm.ac.cn. <https://orcid.org/0000-0002-6206-7804>

Chong Tan, College of Chemical Engineering, Fuzhou University, 350108, Fuzhou, Fujian, P. R. China; and College of Chemical Engineering, Fuzhou University, 350108, Fuzhou, Fujian, P. R. China. <https://orcid.org/0009-0001-0866-0658>

Tong Zhang, School of Chemical Engineering and Technology, North University of China, 030051 Taiyuan, Shanxi, P.R. China. <https://orcid.org/0000-0001-7977-5260>

1 Source of material

The 10 mL of $Cu(ClO_4)_2 \cdot 6H_2O$ (116 mg, 0.5 mmol) and 4-vinylpyridine (105 mg, 1.0 mmol) ethanol solution was added to a 10 mL aqueous solution of sodium dicyanamide (89 mg, 1 mmol) with severely stirring at 80 °C. The mixture was stirred for 10 min and then cooled to room temperature. After few minutes, green flaky crystals were collected, washed by ethanol, and dried in air, yield 60% (based on 4-vinylpyridine).

2 Experimental details

The structure was solved by Direct Methods and refined by full-matrix least-squares method on F^2 with anisotropic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.6756 (5)	0.6146 (4)	0.8808 (3)	0.0539 (7)
C2	0.7038 (5)	0.3042 (5)	0.8647 (3)	0.0569 (7)
C3	0.0990 (5)	0.8996 (5)	0.8057 (4)	0.0630 (8)
H3	0.073409	0.944071	0.898388	0.076 [*]
C4	−0.0544 (5)	0.8346 (6)	0.6765 (4)	0.0671 (9)
H4	−0.179890	0.836007	0.683699	0.081 [*]
C5	0.3136 (5)	0.8367 (5)	0.6697 (3)	0.0553 (7)
H5	0.440650	0.836950	0.666057	0.066 [*]
C6	0.1672 (5)	0.7691 (5)	0.5358 (3)	0.0590 (8)
H6	0.196614	0.724446	0.444629	0.071 [*]
C7	−0.0237 (5)	0.7676 (5)	0.5366 (3)	0.0563 (7)
C8	−0.1879 (5)	0.6990 (6)	0.3983 (4)	0.0717 (9)
H8	−0.310322	0.706631	0.411502	0.086 [*]
C9	−0.1812 (6)	0.6299 (7)	0.2617 (4)	0.0822 (11)
H9A	−0.062582	0.618937	0.241866	0.099 [*]
H9B	−0.294868	0.590820	0.182522	0.099 [*]
Cu01	0.500000	1.000000	1.000000	0.0494 (2)
N1	0.6281 (4)	0.7643 (4)	0.9217 (3)	0.0596 (7)
N2	0.7320 (6)	0.4499 (5)	0.8229 (5)	0.0967 (13)
N3	0.6832 (5)	0.1683 (4)	0.8900 (4)	0.0750 (8)
N4	0.2815 (4)	0.9019 (3)	0.8043 (3)	0.0498 (5)

thermal parameters for all non-hydrogen atoms. The hydrogen atom positions were determined by theoretical calculations and refined with an isotropic displacement factor.

3 Comment

Metal-based coordination polymers have attracted much attention in the fields of coordination chemistry and crystal engineering. Nitrogen-containing organic ligands containing unsaturated groups have been used to assemble hypergolic fuels due to their unique activities. Moreover, high-energy dicandiamine ions (DCA) also have great advantages in regulating the structure and properties of compounds. In this work, we present a 1D coordination polymer based on 4-vinylpyridine and DCA [3–11].

The title crystal structure belongs to the triclinic space group *P* $\bar{1}$ (no. 2), and features a 1D chain. Each asymmetric unit contains half a Cu(II) atom, a bridging dicyanamide anion and a 4-vinylpyridine. The Cu1 atom is six-coordinated by two nitrogen atoms (N4, N4#3) from two 4-vinylpyridine ligands and four nitrogen atoms (N3#2, N1, N3#4, N1#3) from four dicyanamide anions, forming a distorted octahedral geometry with the Cu–N distances being in the normal range of 2.013(3)–2.456(4) Å. Each dicyanamide anion displays a

μ 2-coordination style (see the figure) to link the neighboring Cu(II) atom to form an infinite 1D chain with a Cu(II) ... Cu(II) distance of 7.3783(5) Å along the *b*-axis. The N–Cu–N angles vary from 88.11(11) to 180.0°. These values match with the previously reported Cu(II) compounds. Furthermore, these chains are stacked *via* van der Waals forces to produce a 3D supramolecular structure along the *b*-axis.

Acknowledgements: We thank the Center of Testing and Analysis, Fujian Institute of Research on the Structure of Matter, for support.

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

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- Agilent Technologies. *CrysAlis^{PRO}*. Agilent Technologies: Santa Clara, CA, USA, 2017.
- Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
- Jin Y., Shi Y., Zhang W., Qi X., Xia H., Zhang Q. Cationic effect on properties related to thermal stability and ignition delay for hypergolic ionic liquids. *J. Mol. Liq.* 2021, *336*, 116572.
- Li Z., Zhong Y., Liang L., Feng Y., Zhang J., Zhang T., Zhang Y. Hypergolic coordination compounds as modifiers for ionic liquid propulsion. *Chem. Eng. J.* 2021, *423*, 130187.
- Liu F.-Q., Li R.-X., Li S.-X., Sun L.-S., Liu G.-Y., Tetra- μ -acetato- κ^8 O':O'-bis [(4-vinylpyridine- κ N)copper(II)](Cu–Cu). *Acta Crystallogr.* 2007, *E63*, m2455.
- Liu T., Qi X., Huang S., Jiang L., Li J., Tang C., Zhang Q. Exploiting hydrophobic borohydride-rich ionic liquids as faster-igniting rocket fuels. *Chem. Commun.* 2016, *52*, 2031–2034.
- Taş M., Karabağ E., Titiz A., Kaya M., Ataseven M., Dal H. Synthesis and characterization of tetrakis- μ -[*N*-phenylanthranilate](*O,O'*)-bis [(4-vinylpyridine copper(II))] complex. *Z. für Kristallogr. Cryst. Mater.* 2013, *228*, 92–99.
- Volz D., Nieger M., Friedrichs J., Baumann T., Bräse S. Small change, big red shift: syntheses, structure and photoluminescence of Cu₂Br₂(Ph₃P)₂py₂ (py=pyridine, 4-vinylpyridine). *Inorg. Chem. Commun.* 2013, *37*, 106–109.
- Xu Y., Wang Y., Zhong Y., Lei G., Li Z., Zhang J., Zhang T. High-energy metal-organic frameworks with a dicyanamide linker for hypergolic fuels. *Inorg. Chem.* 2021, *60*, 5100–5106.
- Yang R., Sun Y., Zhao D., Guo L. Synthesis of asymmetric binuclear copper(I) complexes containing 4-vinylpyridine and bis(diphenylphosphino) methane. *J. Coord. Chem.* 2010, *56*, 1169–1177.
- Zhao J. Tetrakis(μ -2-chloro-benzoato- κ O':O')bis-[(4-vinyl-pyridine- κ N)copper(II)]. *Acta Crystallogr.* 2008, *E64*, m1336.