



Synthesis and crystal structure of a new copper(II) complex based on 5-ethyl-3-(pyridin-2-yl)-1,2,4-triazole

Yuliia P. Petrenko,^{a*} Dmytro M. Khomenko,^{a,b} Roman O. Doroshchuk,^{a,b} Ilona V. Raspertova,^a Sergiu Shova^c and Rostyslav D. Lampeka^a

Received 17 February 2023

Accepted 3 April 2023

Edited by J. Reibenspies, Texas A & M University, USA

Keywords: copper(II) complex; X-ray crystallography; acetate anion; 3-(2-pyridyl)-1,2,4-triazole; crystal packing.

CCDC reference: 2253664

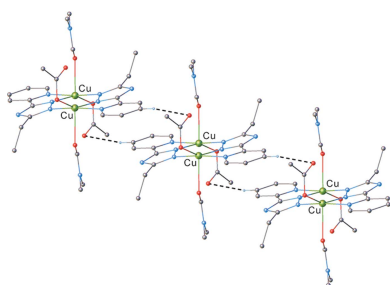
Supporting information: this article has supporting information at journals.iucr.org/e

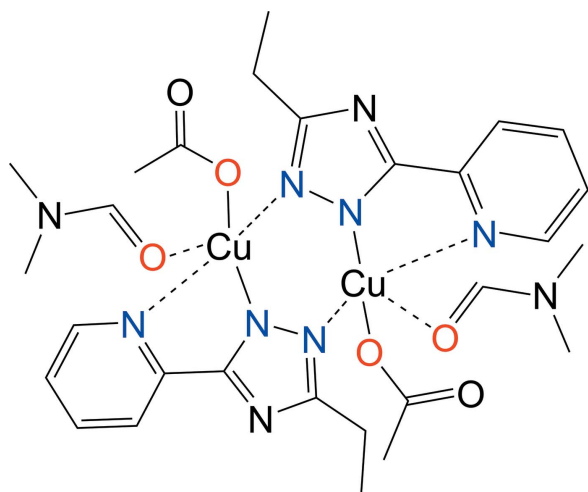
^aDepartment of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska str. 64/13, 01601 Kyiv, Ukraine, ^bEnamine Ltd., Chervonotkatska Street 78, Kyiv 02094, Ukraine, and ^c"PetruPoni" Institute of Macromolecular Chemistry, Aleea Gr., GhicaVoda 41A, 700487 Iasi, Romania. *Correspondence e-mail: p.yuliiapetrenko@gmail.com

The title compound, bis[μ -3-ethyl-5-(pyridin-2-yl)-1*H*-1,2,4-triazol-1-ido]bis[acetato(dimethylformamide)copper(II)], [Cu₂(C₉H₉N₄)₂(C₂H₃O₂)₂(C₃H₇NO)₂] or [Cu₂(L^{Et})₂(OAc)₂(dmf)₂], is a triazolate complex, which contains two 3-(2-pyridyl)-5-ethyl-triazolates (L^{Et})⁻ in bidentate-bridged coordination modes. Both copper atoms are involved in the formation of a planar six-membered metallocycle Cu–[N–N]₂–Cu. The inversion center of the complex is located at the mid-point of the Cu···Cu vector. Each Cu^{II} atom has a distorted trigonal-bipyramidal environment formed by the three nitrogen atoms of the deprotonated bridging 3-(2-pyridyl)-5-ethyl-triazolate unit, oxygen atoms of the OAc⁻ group and dmf molecule. In the crystal, C–H···O hydrogen bonds link the molecules into chains running along the *c*-axis direction.

1. Chemical context

The design and construction of coordination complexes based on dinuclear copper(II) compounds have been the subject of intensive study over the past decades (Li *et al.*, 2018; Cui *et al.*, 2019; Doroshchuk, 2016). N-containing ligands with polypyridyl (Lee *et al.*, 2017), triazolyl (Kucheriv *et al.*, 2016) and pyridyl moieties (Bartual-Murgui *et al.*, 2020) have been widely used for this purpose. Much interest has been focused on functional materials with the presence of a triazole ring, which demonstrate interesting properties such as catalytic ability (Petrenko *et al.*, 2021), anticancer activity (Muhammad & Guo, 2014) and magnetism (Kuzevanova *et al.*, 2021). Although a variety of triazolate frameworks with intriguing topologies (Govor *et al.*, 2010; Senchyk *et al.*, 2012; Lysenko *et al.*, 2016) have been synthesized to date, making rational control in the construction of coordination compounds is a great challenge in crystal engineering. Derivatives of 3-(2-pyridyl)-1,2,4-triazole are among the most widely used ligands that form stable Cu^{II} coordination compounds. There are about 127 examples in the Cambridge Structural Database that exhibit this type of ligand, 37 of which complexes include the binuclear unit [Cu₂(trz-py)₂] with a Cu–[N–N]₂–Cu bridge. Among the reported binuclear compounds, there are few reports of 3-(2-pyridyl)-1,2,4-triazole compounds obtained with copper(II) acetate (Petrenko *et al.*, 2021; Li *et al.*, 2010). In all cases, the equatorial coordination consists of metalcentres linked by two deprotonated triazole ligands, where additional ligands (acetate anions or solvent) axially coordinate the copper atom.





2. Structural commentary

The results of the X-ray diffraction study are depicted in Fig. 1. The crystal is built from discrete dinuclear units $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$, where the $\text{Cu}\cdots\text{Cu}'$ separation is of 4.0159 (8) Å. There are no co-crystallized solvent molecules in the crystals. The complex molecule has its own crystallographically imposed symmetry, being assembled around the inversion centers located at the mid-point of the $\text{Cu1}\cdots\text{Cu1}'$ distances. Each copper(II) atom exhibits an N_3O_2 coordination environment in a slightly distorted trigonal-bipyramidal geometry provided by three nitrogen atoms of the organic ligands and two oxygen atoms from the dmf molecule and the monodentate acetate anion.

The inner ($\text{Cu1}/\text{N2}/\text{N3}-\text{Cu1}'/\text{N2}'/\text{N3}'$) core has an almost planar conformation in $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$, although

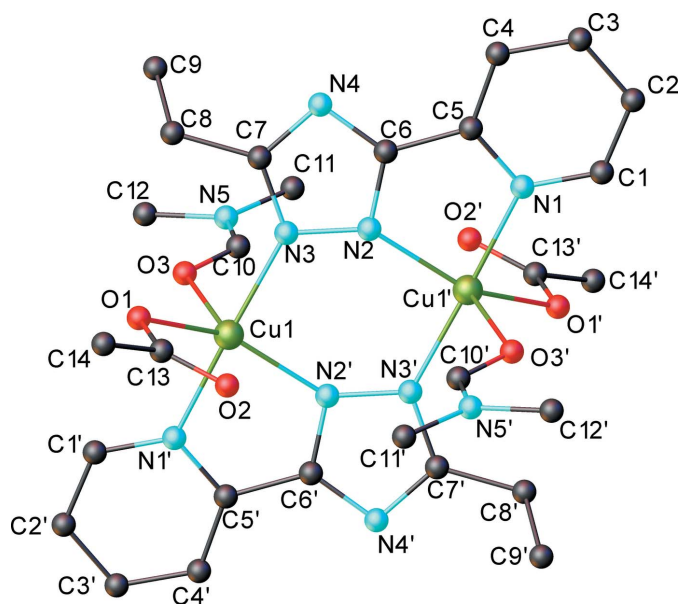


Figure 1
X-ray molecular structure with atom labelling for $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$.

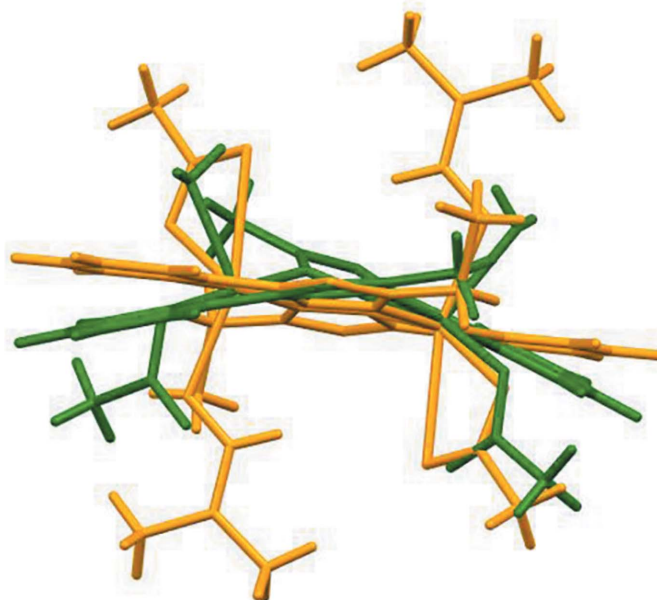


Figure 2
Overlay diagram of the molecular structures $[\text{Cu}_2(\text{L}^{\text{Me}})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ (green) and $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$ (yellow), showing the difference in the spatial arrangement of the ligands.

for the previously described complex $[\text{Cu}_2(\text{L}^{\text{Me}})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ [$\text{HL}^{\text{Me}} = 5\text{-methyl-3-(2-pyridyl)-1,2,4-triazole}$], a twist-boat conformation was observed (Petrenko *et al.*, 2021) for the non-planar six-membered Cu_2N_4 metal ring. The structures were compared (Fig. 2) using *OLEX2* software (Dolomanov *et al.*, 2009). It was found that in $[\text{Cu}_2(\text{L}^{\text{Me}})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$, the water molecules are axially coordinated by the central atom from one side of the Cu_2N_4 plane, and the acetates from the other. Thus, the non-coordinated oxygen of the acetate anion is involved in an intermolecular hydrogen bond with the coordinated water molecule of an adjacent complex, giving rise to an essentially different crystal motif than was observed for $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$. In the newly reported compound $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$, the copper atoms coordinate the dmf molecules and acetate anions in the axial positions in such a manner that they reflect in the symmetry center, which is typical for such a kind of binuclear species. Notably, both $[\text{Cu}_2(\text{L}^{\text{Me}})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$ were synthesized using the same conditions. These features can be probably induced by different substituents in the 5-position of the 3-(2-pyridyl)-1,2,4-triazole ring in these two compounds, indicating that even negligible changes of the non-coordinating part of the ligand could significantly influence the structure of the complex. The non-typical molecular structure of $[\text{Cu}_2(\text{L}^{\text{Me}})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ is supported by the formation of intermolecular hydrogen bonds. In the case of $[\text{Cu}_2(\text{L}^{\text{Et}})_2(\text{OAc})_2(\text{dmf})_2]$, branching of the non-coordinated part leads to the formation of a less-hindered structure of higher symmetry, similar to those of the previously described 37 compounds, indicating a small difference in the energies of these two topologies, which is probably the result of the formation of additional intermolecular contacts.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O2^i$	0.93	2.59	3.513 (4)	170

Symmetry code: (i) $-x + 1, -y, -z + 1$.

3. Supramolecular features

Further analysis of the structure showed that the crystal structure motif is characterized as a parallel packing of discrete supramolecular chains running along the b -axis direction (Fig. 3). Within a chain, the complex molecules interact through weak $C-H\cdots O$ hydrogen bonds, where the pyridine H atom acts as acceptor, and the acetate O atom as donor (Table 1, Fig. 4).

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, update of March 2022; Groom *et al.*, 2016) using *ConQuest* (Bruno *et al.*, 2002) revealed 127 hits for the moiety containing the $Cu_2(trz-py)_2$ unit. In addition, the searches were also limited to structures with low R -factor values ($R < 0.05$). Most similar to the title compound are binuclear copper(II) complexes with two unsubstituted 3-(2-pyridyl)-1,2,4-triazole ligands, two anions and two water molecules in the axial positions [DODRIX, DODRET (Prins *et al.*, 1985); FIVGEY (Matthews *et al.*, 2003)] and with 3,5-bis(2-pyridyl)-1,2,4-triazole ligands (JUDBIV; Du *et al.*, 2017). The compounds most closely related to the title complex are binuclear Cu^{II} complexes with unsubstituted 3-(2-pyridyl)-1,2,4-triazole ligands and a coordinated acetate anion [UQEQU (Li *et al.*, 2011); GUWZEE (Li *et al.*, 2010); CUSHUV (Li *et al.*, 2015) and JUDBOB (Du *et al.*, 2017)].

5. Synthesis and crystallization

Ligand HL^{Et} was prepared according to the synthesis described in the literature (Khomenko *et al.*, 2016; Zakharchenko *et al.*, 2019). Single crystals of $[Cu_2(L^{Et})-2(OAc)_2(dm f)_2]$ were obtained in *dmf*. A solution of $Cu(OAc)_2 \cdot H_2O$ (0.50 g, 10 ml, 2.5 mmol) was added to a solution of HL^{Et} (0.48 g, 5 ml, 2.5 mmol). The resulting

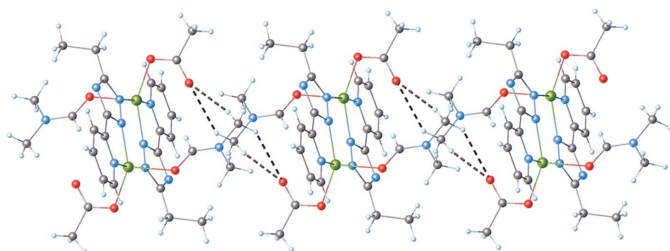


Figure 3
One-dimensional coordination network viewed along the b -axis.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_9H_9N_4)_2(C_2H_3O_2)_2 \cdot (C_3H_7NO)_2]$
M_r	737.76
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	9.4445 (5), 8.9404 (4), 20.2237 (9)
β (°)	93.257 (4)
V (Å ³)	1704.88 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.30
Crystal size (mm)	0.3 × 0.2 × 0.15
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2019)
T_{min}, T_{max}	0.876, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7405, 3007, 2382
R_{int}	0.034
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.085, 1.05
No. of reflections	3007
No. of parameters	212
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.31, -0.27

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

mixture was stirred with heating for 15 min, and then left in the air for crystallization. The green crystals obtained were filtered off, washed with *dmf* and dried in air. Yield 0.507 g (55%). Analysis calculated for $C_{28}H_{38}Cu_2N_{10}O_6$ (%): C 45.58, H 5.19, N 18.99; found: C 45.57, H 5.17, N 18.96.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

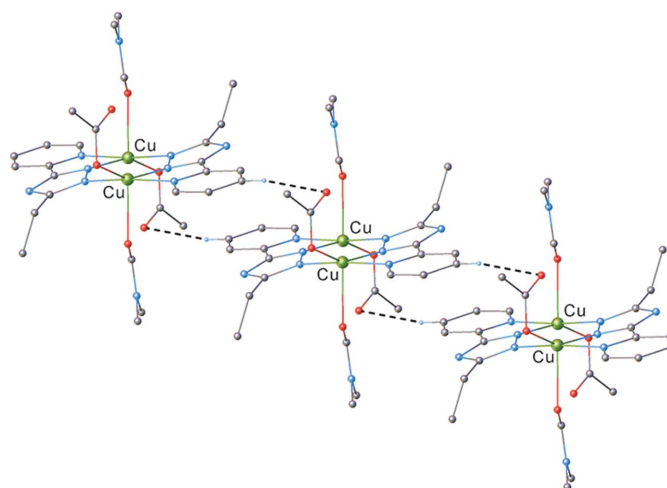


Figure 4
Partial view of the crystal packing showing hydrogen-bond contacts between adjacent molecules.

Funding information

This work was supported by grants 22BF037–06 obtained from the Ministry of Education and Science of Ukraine.

References

- Bartual-Murgui, C., Rubio-Giménez, V., Meneses-Sánchez, M., Valverde-Muñoz, F. J., Tatay, S., Martí-Gastaldo, C., Muñoz, M. C. & Real, J. A. (2020). *Appl. Mater. Interfaces*, **12**, 29461–29472.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Cui, Y., Wu, L., Yue, W., Lian, F. & Qu, J. (2019). *J. Mol. Struct.* **1191**, 145–151.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Doroschuk, R. (2016). *Acta Cryst.* **E72**, 486–488.
- Du, C.-C., Fan, J.-Z., Li, J.-P. & Wang, D. Z. (2017). *Chin. J. Inorg. Chem.* **33**, 1352–1353.
- Govor, E. V., Lysenko, A. B., Rusanov, E. B., Chernega, A. N., Krautscheid, H. & Domasevitch, K. V. (2010). *Z. Anorg. Allg. Chem.* **636**, 209–217.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Khomenko, D. M., Doroshchuk, R. O., Vashchenko, O. V. & Lampeka, R. D. (2016). *Chem. Heterocycl. Compd.* **52**, 402–408.
- Kucheriv, O. I., Oliynyk, V. V., Zagorodnii, V. V., Launets, V. L. & Gural'skiy, I. A. (2016). *Sci. Rep.* **6**, 1–7.
- Kuzevanova, I. S., Kucheriv, O. I., Hiiuk, V. M., Naumova, D. D., Shova, S., Shylin, S. I., Kotsyubynsky, V. O., Rotaru, A., Fritsky, I. O. & Gural'skiy, I. A. (2021). *Dalton Trans.* **50**, 9250–9258.
- Lee, L. C. C., Leung, K. K. & Lo, K. K. (2017). *Dalton Trans.* **46**, 16357–16380.
- Li, C. H., Li, W., Hu, H. X. & Hu, B. N. (2015). *Chin. J. Struct. Chem.* **34**, 1553–1557.
- Li, Ch.-H., Tan, X.-W., Li, W. & Yang, Y.-Q. (2011). *Chin. J. Struct. Chem.* **30**, 289.
- Li, W., Zhang, J., Li, C. & Yang, Y. (2010). *Z. Kristallogr.* **225**, 181–182.
- Li, Y., Chen, Y., Liu, Y., Jia, L. & Chen, Y. (2018). *Transit. Met. Chem.* **43**, 731–737.
- Lysenko, A. B., Senchyk, G. A., Lukashuk, L. V., Domasevitch, K. V., Handke, M., Lincke, J., Krautscheid, H., Rusanov, E. B., Krämer, K. W., Decurtins, S. & Liu, S. X. (2016). *Inorg. Chem.* **55**, 239–250.
- Matthews, C. J., Horton, P. N. & Hursthouse, M. B. (2003). University of Southampton, Crystal Structure Report Archive, 986.
- Muhammad, N. & Guo, Z. (2014). *Curr. Opin. Chem. Biol.* **19**, 144–153.
- Petrenko, Y. P., Piasta, K., Khomenko, D. M., Doroshchuk, R. O., Shova, S., Novitchi, G., Toporivska, Y., Gumienna-Kontecka, E., Martins, L. M. D. R. S. & Lampeka, R. D. (2021). *RSC Adv.* **11**, 23442–23449.
- Prins, R., Birker, P. J. M. W. L., Haasnoot, J. G., Verschoor, G. C. & Reedijk, J. (1985). *Inorg. Chem.* **24**, 4128–4133.
- Rigaku OD (2019). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Senchyk, G. A., Lysenko, A. B., Boldog, I., Rusanov, E. B., Chernega, A. N., Krautscheid, H. & Domasevitch, K. V. (2012). *Dalton Trans.* **41**, 8675–8689.
- Zakharchenko, B. V., Khomenko, D. M., Doroshchuk, R. O., Raspertova, I. V., Starova, V. S., Trachevsky, V. V., Shova, S., Severynovska, O. V., Martins, L. M. D. R. S., Pombeiro, A. J. L., Arion, V. B. & Lampeka, R. D. (2019). *New J. Chem.* **43**, 10973–10984.

supporting information

Acta Cryst. (2023). E79, 432-435 [https://doi.org/10.1107/S2056989023003079]

Synthesis and crystal structure of a new copper(II) complex based on 5-ethyl-3-(pyridin-2-yl)-1,2,4-triazole

Yuliia P. Petrenko, Dmytro M. Khomenko, Roman O. Doroshchuk, Ilona V. Raspertova, Sergiu Shova and Rostyslav D. Lampeka

Computing details

Data collection: *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019); data reduction: *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Olex2* 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* 1.5 (Dolomanov *et al.*, 2009).

Bis[μ -3-ethyl-5-(pyridin-2-yl)-1H-1,2,4-triazol-1-ido]bis[acetato(dimethylacetamide)copper(II)]

Crystal data

$[\text{Cu}_2(\text{C}_9\text{H}_9\text{N}_4)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_3\text{H}_7\text{NO})_2]$

$M_r = 737.76$

Monoclinic, $P2_1/c$

$a = 9.4445$ (5) Å

$b = 8.9404$ (4) Å

$c = 20.2237$ (9) Å

$\beta = 93.257$ (4)°

$V = 1704.88$ (14) Å³

$Z = 2$

$F(000) = 764$

$D_x = 1.437$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2231 reflections

$\theta = 2.0$ – 25.3 °

$\mu = 1.30$ mm⁻¹

$T = 293$ K

Prism, clear dark blue

$0.3 \times 0.2 \times 0.15$ mm

Data collection

Xcalibur, Eos
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlisPro*; Rigaku OD, 2019)

$T_{\min} = 0.876$, $T_{\max} = 1.000$

7405 measured reflections

3007 independent reflections

2382 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 2.0$ °

$h = -11 \rightarrow 10$

$k = -8 \rightarrow 10$

$l = -18 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.085$

$S = 1.05$

3007 reflections

212 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.6113P]$

where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.48907 (4)	0.60148 (4)	0.58814 (2)	0.03442 (13)
O1	0.4294 (2)	0.5477 (2)	0.67766 (10)	0.0415 (5)
O2	0.2385 (3)	0.4889 (3)	0.61484 (12)	0.0601 (7)
O3	0.7170 (2)	0.6884 (3)	0.60652 (12)	0.0528 (6)
N1	0.5774 (3)	0.1842 (3)	0.39823 (12)	0.0353 (6)
N2	0.5539 (2)	0.3380 (3)	0.50737 (11)	0.0327 (6)
N3	0.5690 (2)	0.4020 (2)	0.56906 (11)	0.0327 (6)
N4	0.6816 (3)	0.1801 (3)	0.57376 (12)	0.0404 (6)
N5	0.9247 (3)	0.7291 (3)	0.55819 (14)	0.0521 (7)
C1	0.5741 (3)	0.1078 (4)	0.34135 (16)	0.0457 (8)
H1	0.537481	0.154425	0.302982	0.055*
C2	0.6226 (4)	-0.0369 (4)	0.33712 (17)	0.0544 (9)
H2	0.618426	-0.086813	0.296711	0.065*
C3	0.6776 (4)	-0.1069 (4)	0.39395 (19)	0.0551 (10)
H3	0.712383	-0.204028	0.392220	0.066*
C4	0.6800 (3)	-0.0302 (3)	0.45327 (17)	0.0461 (8)
H4	0.715879	-0.075095	0.492185	0.055*
C5	0.6281 (3)	0.1149 (3)	0.45383 (15)	0.0355 (7)
C6	0.6231 (3)	0.2074 (3)	0.51308 (14)	0.0337 (7)
C7	0.6464 (3)	0.3047 (3)	0.60695 (15)	0.0376 (7)
C8	0.6944 (4)	0.3322 (4)	0.67766 (16)	0.0512 (9)
H8A	0.656363	0.254626	0.705100	0.061*
H8B	0.656717	0.427334	0.691653	0.061*
C9	0.8546 (4)	0.3344 (5)	0.6883 (2)	0.0881 (14)
H9A	0.892006	0.418177	0.665222	0.132*
H9B	0.892983	0.243409	0.671529	0.132*
H9C	0.880205	0.342977	0.734718	0.132*
C10	0.7957 (3)	0.6721 (3)	0.56038 (17)	0.0453 (8)
H10	0.761756	0.615416	0.524331	0.054*
C11	1.0110 (4)	0.7075 (4)	0.5014 (2)	0.0706 (12)
H11A	1.096094	0.654624	0.515113	0.106*
H11B	1.035153	0.803030	0.483543	0.106*
H11C	0.958395	0.650492	0.468059	0.106*
C12	0.9843 (5)	0.8163 (6)	0.6132 (2)	0.0978 (16)
H12A	0.975052	0.920858	0.603018	0.147*
H12B	1.082830	0.791748	0.620908	0.147*
H12C	0.934694	0.794217	0.652151	0.147*

C13	0.3033 (4)	0.4974 (3)	0.66937 (16)	0.0407 (8)
C14	0.2343 (4)	0.4436 (4)	0.73102 (18)	0.0660 (11)
H14A	0.221006	0.337203	0.728592	0.099*
H14B	0.144052	0.491720	0.733999	0.099*
H14C	0.294255	0.467671	0.769470	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0376 (2)	0.0393 (2)	0.0265 (2)	0.00146 (18)	0.00264 (15)	0.00220 (17)
O1	0.0415 (14)	0.0516 (13)	0.0316 (12)	−0.0047 (11)	0.0043 (10)	−0.0001 (10)
O2	0.0539 (16)	0.0787 (17)	0.0469 (15)	−0.0069 (13)	−0.0063 (12)	−0.0004 (13)
O3	0.0386 (14)	0.0636 (15)	0.0570 (16)	−0.0071 (11)	0.0085 (12)	−0.0052 (12)
N1	0.0375 (15)	0.0373 (14)	0.0314 (15)	−0.0007 (12)	0.0051 (11)	−0.0003 (12)
N2	0.0348 (15)	0.0356 (13)	0.0276 (14)	0.0014 (11)	0.0016 (11)	0.0052 (11)
N3	0.0357 (15)	0.0376 (13)	0.0247 (13)	0.0019 (12)	0.0009 (11)	0.0038 (11)
N4	0.0430 (16)	0.0435 (15)	0.0345 (15)	0.0071 (13)	0.0000 (12)	0.0061 (13)
N5	0.0349 (17)	0.0643 (18)	0.057 (2)	−0.0065 (14)	0.0026 (14)	0.0023 (15)
C1	0.051 (2)	0.049 (2)	0.0379 (19)	−0.0010 (16)	0.0040 (16)	−0.0029 (16)
C2	0.071 (3)	0.048 (2)	0.045 (2)	−0.0043 (19)	0.0099 (19)	−0.0101 (18)
C3	0.063 (3)	0.0392 (18)	0.064 (3)	0.0001 (17)	0.010 (2)	−0.0086 (18)
C4	0.048 (2)	0.0411 (18)	0.049 (2)	0.0041 (16)	0.0020 (16)	0.0061 (16)
C5	0.0305 (17)	0.0371 (17)	0.0396 (18)	−0.0026 (14)	0.0069 (13)	0.0016 (14)
C6	0.0298 (17)	0.0393 (17)	0.0322 (17)	0.0000 (14)	0.0046 (13)	0.0061 (14)
C7	0.0348 (18)	0.0452 (18)	0.0327 (18)	−0.0012 (15)	0.0003 (14)	0.0082 (15)
C8	0.059 (2)	0.059 (2)	0.0346 (19)	0.0106 (18)	−0.0078 (16)	0.0043 (17)
C9	0.072 (3)	0.133 (4)	0.056 (3)	−0.007 (3)	−0.025 (2)	0.010 (3)
C10	0.037 (2)	0.0445 (19)	0.054 (2)	−0.0045 (16)	−0.0035 (16)	0.0055 (17)
C11	0.050 (2)	0.088 (3)	0.076 (3)	−0.006 (2)	0.016 (2)	0.006 (2)
C12	0.065 (3)	0.135 (4)	0.094 (4)	−0.042 (3)	0.009 (3)	−0.035 (3)
C13	0.046 (2)	0.0380 (18)	0.038 (2)	0.0015 (16)	0.0051 (16)	0.0002 (14)
C14	0.064 (3)	0.082 (3)	0.054 (2)	−0.018 (2)	0.023 (2)	0.005 (2)

Geometric parameters (Å, °)

Cu1—O1	1.985 (2)	C3—C4	1.381 (4)
Cu1—O3	2.299 (2)	C4—H4	0.9300
Cu1—N1 ⁱ	2.040 (2)	C4—C5	1.387 (4)
Cu1—N2 ⁱ	2.025 (2)	C5—C6	1.459 (4)
Cu1—N3	1.983 (2)	C7—C8	1.496 (4)
O1—C13	1.276 (4)	C8—H8A	0.9700
O2—C13	1.233 (4)	C8—H8B	0.9700
O3—C10	1.234 (4)	C8—C9	1.516 (5)
N1—C1	1.337 (4)	C9—H9A	0.9600
N1—C5	1.348 (4)	C9—H9B	0.9600
N2—N3	1.373 (3)	C9—H9C	0.9600
N2—C6	1.340 (3)	C10—H10	0.9300
N3—C7	1.347 (3)	C11—H11A	0.9600

N4—C6	1.339 (3)	C11—H11B	0.9600
N4—C7	1.351 (4)	C11—H11C	0.9600
N5—C10	1.323 (4)	C12—H12A	0.9600
N5—C11	1.459 (4)	C12—H12B	0.9600
N5—C12	1.446 (5)	C12—H12C	0.9600
C1—H1	0.9300	C13—C14	1.518 (4)
C1—C2	1.377 (4)	C14—H14A	0.9600
C2—H2	0.9300	C14—H14B	0.9600
C2—C3	1.384 (5)	C14—H14C	0.9600
C3—H3	0.9300		
O1—Cu1—O3	104.24 (9)	N4—C6—N2	114.3 (3)
O1—Cu1—N1 ⁱ	89.93 (9)	N4—C6—C5	128.2 (3)
O1—Cu1—N2 ⁱ	151.98 (9)	N3—C7—N4	113.0 (3)
N1 ⁱ —Cu1—O3	87.31 (9)	N3—C7—C8	124.2 (3)
N2 ⁱ —Cu1—O3	101.48 (9)	N4—C7—C8	122.7 (3)
N2 ⁱ —Cu1—N1 ⁱ	80.29 (10)	C7—C8—H8A	109.1
N3—Cu1—O1	95.20 (9)	C7—C8—H8B	109.1
N3—Cu1—O3	88.40 (9)	C7—C8—C9	112.5 (3)
N3—Cu1—N1 ⁱ	173.99 (10)	H8A—C8—H8B	107.8
N3—Cu1—N2 ⁱ	96.46 (9)	C9—C8—H8A	109.1
C13—O1—Cu1	106.07 (19)	C9—C8—H8B	109.1
C10—O3—Cu1	115.9 (2)	C8—C9—H9A	109.5
C1—N1—Cu1 ⁱ	127.1 (2)	C8—C9—H9B	109.5
C1—N1—C5	118.2 (3)	C8—C9—H9C	109.5
C5—N1—Cu1 ⁱ	114.60 (19)	H9A—C9—H9B	109.5
N3—N2—Cu1 ⁱ	139.50 (18)	H9A—C9—H9C	109.5
C6—N2—Cu1 ⁱ	112.67 (19)	H9B—C9—H9C	109.5
C6—N2—N3	105.1 (2)	O3—C10—N5	125.1 (3)
N2—N3—Cu1	122.07 (17)	O3—C10—H10	117.4
C7—N3—Cu1	132.1 (2)	N5—C10—H10	117.4
C7—N3—N2	105.8 (2)	N5—C11—H11A	109.5
C6—N4—C7	101.8 (2)	N5—C11—H11B	109.5
C10—N5—C11	122.1 (3)	N5—C11—H11C	109.5
C10—N5—C12	120.1 (3)	H11A—C11—H11B	109.5
C12—N5—C11	117.8 (3)	H11A—C11—H11C	109.5
N1—C1—H1	118.6	H11B—C11—H11C	109.5
N1—C1—C2	122.8 (3)	N5—C12—H12A	109.5
C2—C1—H1	118.6	N5—C12—H12B	109.5
C1—C2—H2	120.5	N5—C12—H12C	109.5
C1—C2—C3	118.9 (3)	H12A—C12—H12B	109.5
C3—C2—H2	120.5	H12A—C12—H12C	109.5
C2—C3—H3	120.5	H12B—C12—H12C	109.5
C4—C3—C2	119.0 (3)	O1—C13—C14	116.4 (3)
C4—C3—H3	120.5	O2—C13—O1	123.5 (3)
C3—C4—H4	120.6	O2—C13—C14	120.0 (3)
C3—C4—C5	118.9 (3)	C13—C14—H14A	109.5
C5—C4—H4	120.6	C13—C14—H14B	109.5

N1—C5—C4	122.1 (3)	C13—C14—H14C	109.5
N1—C5—C6	113.5 (2)	H14A—C14—H14B	109.5
C4—C5—C6	124.4 (3)	H14A—C14—H14C	109.5
N2—C6—C5	117.5 (3)	H14B—C14—H14C	109.5
Cu1—O1—C13—O2	-0.5 (4)	N3—C7—C8—C9	-118.2 (4)
Cu1—O1—C13—C14	178.2 (2)	N4—C7—C8—C9	59.2 (4)
Cu1—O3—C10—N5	172.0 (2)	C1—N1—C5—C4	1.8 (4)
Cu1 ⁱ —N1—C1—C2	179.5 (2)	C1—N1—C5—C6	-178.5 (3)
Cu1 ⁱ —N1—C5—C4	-178.8 (2)	C1—C2—C3—C4	1.0 (5)
Cu1 ⁱ —N1—C5—C6	0.9 (3)	C2—C3—C4—C5	-0.4 (5)
Cu1 ⁱ —N2—N3—Cu1	20.3 (4)	C3—C4—C5—N1	-1.0 (5)
Cu1 ⁱ —N2—N3—C7	-158.4 (2)	C3—C4—C5—C6	179.3 (3)
Cu1 ⁱ —N2—C6—N4	165.50 (19)	C4—C5—C6—N2	-171.7 (3)
Cu1 ⁱ —N2—C6—C5	-13.5 (3)	C4—C5—C6—N4	9.4 (5)
Cu1—N3—C7—N4	-179.03 (19)	C5—N1—C1—C2	-1.2 (5)
Cu1—N3—C7—C8	-1.4 (5)	C6—N2—N3—Cu1	178.70 (18)
N1—C1—C2—C3	-0.2 (5)	C6—N2—N3—C7	0.1 (3)
N1—C5—C6—N2	8.5 (4)	C6—N4—C7—N3	0.8 (3)
N1—C5—C6—N4	-170.3 (3)	C6—N4—C7—C8	-176.8 (3)
N2—N3—C7—N4	-0.6 (3)	C7—N4—C6—N2	-0.8 (3)
N2—N3—C7—C8	177.1 (3)	C7—N4—C6—C5	178.1 (3)
N3—N2—C6—N4	0.5 (3)	C11—N5—C10—O3	-178.9 (3)
N3—N2—C6—C5	-178.5 (2)	C12—N5—C10—O3	1.0 (5)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O2 ⁱⁱ	0.93	2.59	3.513 (4)	170

Symmetry code: (ii) $-x+1, -y, -z+1$.