

Di- μ -chlorido-bis[(2,2'-bipyridine-5,5'-dicarboxylic acid- κ^2N,N')chlorido-copper(II)] dimethylformamide tetrasolvate

Sigurd Øien,* David Stephen Wragg, Karl Petter Lillerud and Mats Tilset

inGAP Centre for Research Based Innovation, Department of Chemistry, University of Oslo, 0315 Oslo, Norway

Correspondence e-mail: sigurdoi@kjemi.uio.no

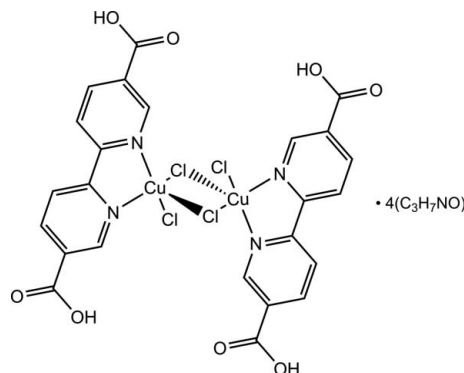
Received 15 November 2012; accepted 20 December 2012

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in solvent or counterion; R factor = 0.029; wR factor = 0.068; data-to-parameter ratio = 16.4.

In the title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4)_2] \cdot 4\text{C}_3\text{H}_7\text{NO}$, which contains a chloride-bridged centrosymmetric Cu^{II} dimer, the Cu^{II} atom is in a distorted square-pyramidal $4 + 1$ coordination geometry defined by the N atoms of the chelating 2,2'-bipyridine ligand, a terminal chloride and two bridging chloride ligands. Of the two independent dimethylformamide molecules, one is hydrogen bonded to a single $-\text{COOH}$ group, while one links two adjacent $-\text{COOH}$ groups *via* a strong accepted $\text{O}-\text{H} \cdots \text{O}$ and a weak donated $\text{C}(\text{O})-\text{H} \cdots \text{O}$ hydrogen bond. Two of these last molecules and the two $-\text{COOH}$ groups form a centrosymmetric hydrogen-bonded ring in which the $\text{CH}=\text{O}$ and the $-\text{COOH}$ groups by disorder adopt two alternate orientations in a 0.44:0.56 ratio. These hydrogen bonds link the Cu^{II} complex molecules and the dimethylformamide solvent molecules into infinite chains along $[\bar{1}11]$. Slipped $\pi-\pi$ stacking interactions between two centrosymmetric pyridine rings (centroid-centroid distance = 3.63 Å) contribute to the coherence of the structure along $[0\bar{1}1]$.

Related literature

For related structures with similar coordination geometry around the copper atoms, see: Goddard *et al.* (1990); Tynan *et al.* (2005); Han *et al.* (2008); Liu *et al.* (2009); Qi *et al.* (2009). For other related structures of chloro bipyridine copper complexes, see: Wang *et al.* (2004); Zhao *et al.* (2010).



Experimental

Crystal data

$[\text{Cu}_2\text{Cl}_4(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4)_2] \cdot 4\text{C}_3\text{H}_7\text{NO}$
 $M_r = 1049.66$
 Triclinic, $P\bar{1}$
 $a = 8.917$ (5) Å
 $b = 11.030$ (6) Å
 $c = 12.179$ (7) Å
 $\alpha = 83.171$ (6)°
 $\beta = 73.903$ (6)°

$\gamma = 68.332$ (6)°
 $V = 1069.4$ (11) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 1.32$ mm⁻¹
 $T = 100$ K
 $0.20 \times 0.15 \times 0.02$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\text{min}} = 0.789$, $T_{\text{max}} = 0.974$

9231 measured reflections
 4824 independent reflections
 3969 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 1.02$
 4824 reflections

295 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------|-------------|----------------------|-------------|
| N1—Cu1 | 2.0337 (18) | Cl2—Cu1 ⁱ | 2.2804 (10) |
| N2—Cu1 | 2.0361 (17) | Cl2—Cu1 | 2.7183 (12) |
| Cl1—Cu1 | 2.2525 (10) | | |

Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|---|--------------|---------------------|--------------|-----------------------|
| $\text{O}2-\text{H}2 \cdots \text{O}6\text{B}^{\text{ii}}$ | 0.82 | 1.72 | 2.515 (3) | 161 |
| $\text{O}1-\text{H}1 \cdots \text{O}6\text{A}^{\text{iii}}$ | 0.82 | 1.75 | 2.536 (4) | 161 |
| $\text{O}3-\text{H}3 \cdots \text{O}5$ | 0.82 | 1.72 | 2.541 (2) | 177 |
| $\text{C}21\text{A}-\text{H}21\text{A} \cdots \text{O}2^{\text{iv}}$ | 0.93 | 2.71 | 3.591 (3) | 158 |
| $\text{C}21\text{B}-\text{H}21\text{B} \cdots \text{O}1^{\text{iii}}$ | 0.93 | 2.72 | 3.603 (3) | 159 |

Symmetry codes: (ii) $x + 1, y - 1, z - 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x - 1, y + 1, z + 1$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

DIAMOND (Brandenburg, 2006) and *Materials Studio* (Accelrys, 2010); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

This work is part of the inGAP and CLIMIT, which receive financial support from the Norwegian Research Council under contract Nos. 174893 and 215735, respectively.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QK2049).

References

Accelrys (2010). *Materials Studio*. Accelrys Inc., San Diego, California, USA.

- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Goddard, R., Hemalatha, B. & Rajasekharan, M. V. (1990). *Acta Cryst.* **C46**, 33–35.
- Han, K.-F., Wu, H.-Y., Wang, Z.-M. & Guo, H.-Y. (2008). *Acta Cryst.* **E64**, m1607–m1608.
- Liu, Y.-F., Rong, D.-F., Xia, H.-T. & Wang, D.-Q. (2009). *Acta Cryst.* **E65**, m1492.
- Qi, Z.-P., Wang, A.-D., Zhang, H. & Wang, X.-X. (2009). *Acta Cryst.* **E65**, m1507–m1508.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tynan, E., Jensen, P., Lees, A. C., Moubaraki, B., Murray, K. S. & Kruger, P. E. (2005). *CrystEngComm*, **7**, 90–95.
- Wang, Y.-Q., Bi, W.-H., Li, X. & Cao, R. (2004). *Acta Cryst.* **E60**, m876–m877.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zhao, J., Shi, D., Cheng, H., Chen, L., Ma, P. & Niu, J. (2010). *Inorg. Chem. Commun.* **13**, 822–827.

supplementary materials

Acta Cryst. (2013). E69, m73–m74 [doi:10.1107/S1600536812051422]

Di- μ -chlorido-bis[(2,2'-bipyridine-5,5'-dicarboxylic acid- κ^2N,N')chloridocopper(II)] dimethylformamide tetrasolvate

Sigurd Øien, David Stephen Wragg, Karl Petter Lillerud and Mats Tilset

Comment

In recent years, linear dicarboxylic acids have attracted much attention for their usage as linkers in metal-organic frameworks. This diverse class of porous materials can be utilized as heterogeneous catalysts or selective adsorbents, by incorporating active species onto the linkers. The reported compound (Fig. 1) consists of centrosymmetric dinuclear Cu complexes hydrogen bonded to four DMF molecules *via* O—H \cdots O and C—H \cdots O links. These Cu dimers and the DMF molecules create hydrogen bonded chains parallel to $[\bar{1}11]$ (Fig. 2). The copper atoms have a slightly distorted square-pyramidal coordination by two N and three Cl atoms (two short and one long Cu—Cl bonds; Table 1), as observed in similar copper dimer complexes reported for instance by Goddard *et al.* (1990), Tynan *et al.* (2005), Han *et al.* (2008), Liu *et al.* (2009) and Qi *et al.* (2009). Fig. 1 and Fig. 2 show that the COOH group of O1–C7–O2 and the second DMF molecule (C21, O6A/O6B, N21, C15, C16) form a centrosymmetric hydrogen bond ring with alternating strong O—H \cdots O(DMF) and weak C(DMF)—H \cdots O hydrogen bonds. Due to a synchronous orientation disorder of the COOH groups and the DMF molecules the hydrogen bonds in these rings can adopt a clock or an anticlockwise sense in 0.44/0.56 ratio. Consequently, the observed bond distances C7—O1 = 1.261 (3) Å and C7—O2 = 1.264 (3) Å are approximately an average of the single and double bond distances of an ordered COOH group (e.g. C11=O4 = 1.209 (3) and C11—O3 = 1.311 (3) Å in the title compound). Apart from hydrogen bonding the structure of the title compound is held together by slipped π - π stacking interactions between centrosymmetric pairs of pyridine ring 1 (N1–C1–C8–C9–C10–C12). They show stacking distances of ca. 3.33 Å which are effective along $[0\bar{1}1]$ (Fig. 3). A polymeric copper(II) complex with the same organoligand as in (I) but with a Cu/Cl ratio of 1:1 has been reported by Zhao *et al.* (2010).

Experimental

5,5'-dimethyl-2,2'-bipyridine was purchased from Sigma-Aldrich and oxidized with $K_2Cr_2O_7$ to 2,2'-bipyridine-5,5'-dicarboxylic acid according to literature methods. $CuCl_2 \cdot 2H_2O$ (>99%, Sigma-Aldrich) and dimethylformamide (DMF) (>99.5%, Merck) were used as received. 100 mg (0.41 mmol) H_2bpydc was dissolved in 10 ml of water, using a minimal amount of KOH. 70 mg (0.41 mmol) $CuCl_2 \cdot 2H_2O$ was dissolved in water. When the two solutions were combined, a blue precipitate was immediately formed. Dilute HCl was added until pH was 4. The blue microcrystalline precipitate (96 mg) was recovered, dried and dissolved in 5 ml of DMF along with 50 μL conc. HCl, giving a green solution. 1 ml of the solution was transferred to a small vial. The crystals were precipitated by vapor diffusion, using water as antisolvent.

Refinement

All H atoms were placed in geometrically idealized positions, with $C_{sp^2}-H = 0.93$ Å, $C_{sp^3}-H = 0.96$ Å, $O-H = 0.82$ Å and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C_{sp^2})$ or $1.5U_{eq}(C_{sp^3}, O)$. The atoms O6 A/B, C21 A/B and H21 A/B of one DMF molecule and H1/2 of a COOH group are disordered over 2 sites with refined occupancies of

0.437 (4) (part A and H1) and 0.563 (4) (part B and H2).

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *Materials Studio* (Accelrys, 2010); software used to prepare material for publication: *publCIF* (Westrip, 2010).

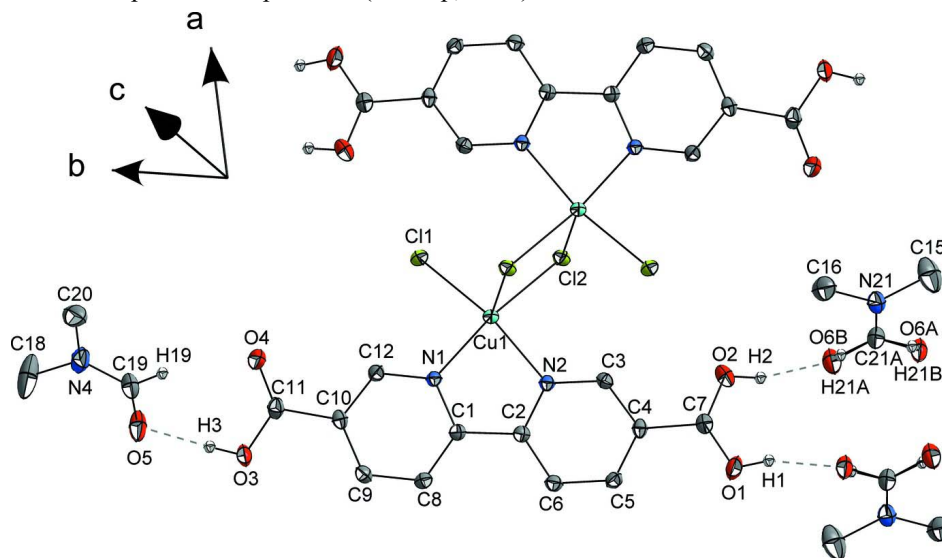


Figure 1

The molecular structure of (**I**), with atom labels and 50% probability displacement ellipsoids for non-H atoms showing also the disorder of one COOH group (C7 etc.) and one DMF molecule (C21A etc.).

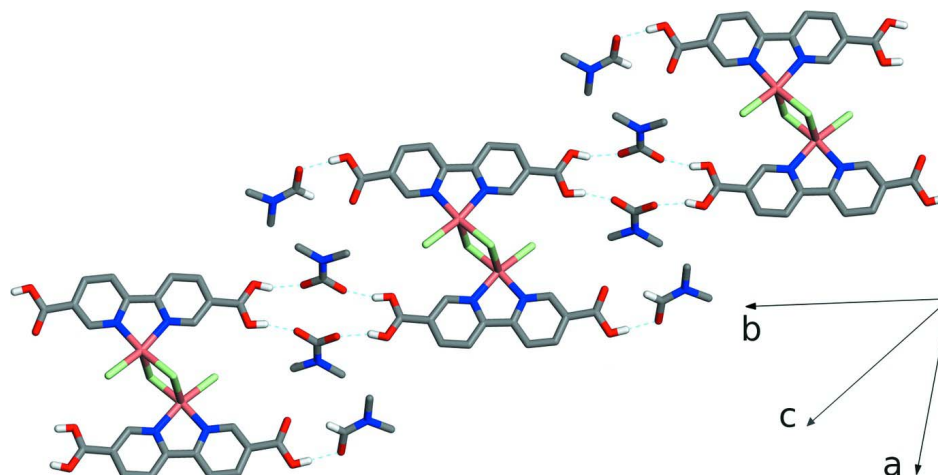
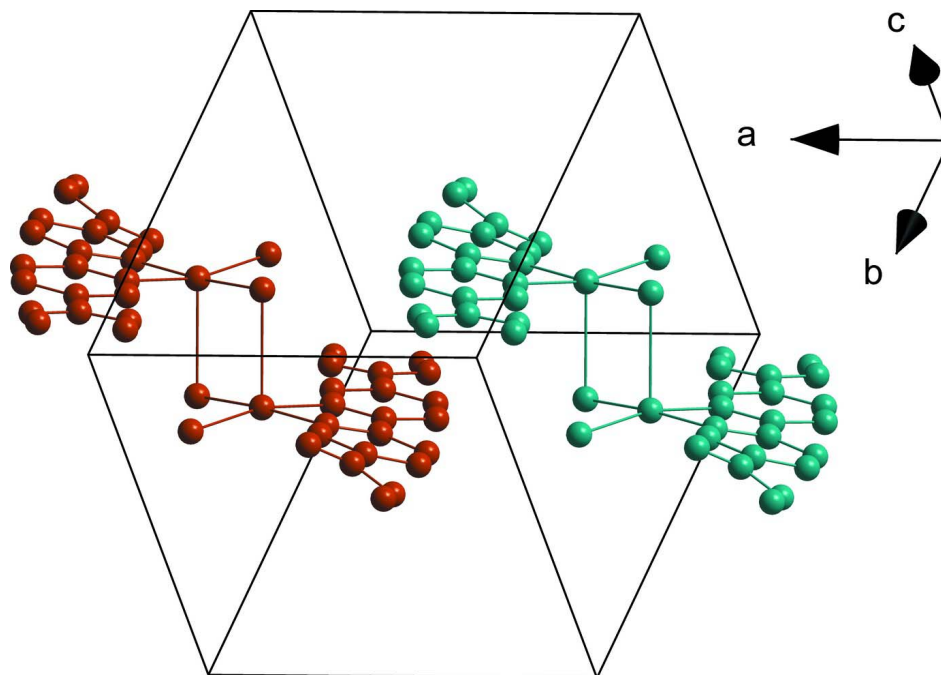


Figure 2

The packing of (**I**), showing the hydrogen bonded chains. Hydrogen atoms (except amide and carboxylic) are omitted and hydrogen bonds are shown as dashed lines.


Figure 3

Slipped π - π stacking interaction between the pyridine rings 1 (N1–C1–C8–C9–C10–C12) of two neighboring Cu complexes related by inversion (**I**).

Di- μ -chlorido-bis[(2,2'-bipyridine-5,5'-dicarboxylic acid- κ^2N,N')chloridocopper(II)] dimethylformamide tetrasolvate

Crystal data

$[\text{Cu}_2\text{Cl}_4(\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4)_2] \cdot 4\text{C}_3\text{H}_7\text{NO}$

$M_r = 1049.66$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 8.917$ (5) Å

$b = 11.030$ (6) Å

$c = 12.179$ (7) Å

$\alpha = 83.171$ (6)°

$\beta = 73.903$ (6)°

$\gamma = 68.332$ (6)°

$V = 1069.4$ (11) Å³

$Z = 1$

$F(000) = 538$

$D_x = 1.627$ Mg m⁻³

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

Cell parameters from 3373 reflections

$\theta = 2.5$ – 27.4 °

$\mu = 1.32$ mm⁻¹

$T = 100$ K

Prism, green

$0.20 \times 0.15 \times 0.02$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.789$, $T_{\max} = 0.974$

9231 measured reflections

4824 independent reflections

3969 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 27.9$ °, $\theta_{\min} = 1.7$ °

$h = -11 \rightarrow 11$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.068$

$S = 1.02$

4824 reflections

295 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 0.590P]$

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

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

$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|------------|--------------|--------------|----------------------------------|-----------|
| C1 | 0.5061 (2) | 0.75714 (18) | 0.49804 (17) | 0.0142 (4) | |
| C2 | 0.5665 (2) | 0.64520 (18) | 0.42163 (16) | 0.0141 (4) | |
| C3 | 0.7981 (2) | 0.47716 (18) | 0.32901 (16) | 0.0150 (4) | |
| H3A | 0.9128 | 0.4329 | 0.3112 | 0.018* | |
| C4 | 0.6997 (3) | 0.43285 (18) | 0.28504 (17) | 0.0157 (4) | |
| C5 | 0.5292 (2) | 0.49803 (19) | 0.31204 (17) | 0.0168 (4) | |
| H5 | 0.4611 | 0.4698 | 0.2838 | 0.020* | |
| C6 | 0.4604 (3) | 0.60601 (19) | 0.38163 (17) | 0.0170 (4) | |
| H6 | 0.3459 | 0.6511 | 0.4010 | 0.020* | |
| C7 | 0.7786 (3) | 0.31742 (19) | 0.20877 (17) | 0.0174 (4) | |
| C8 | 0.3416 (3) | 0.84090 (19) | 0.52720 (17) | 0.0175 (4) | |
| H8 | 0.2620 | 0.8292 | 0.4980 | 0.021* | |
| C9 | 0.2973 (3) | 0.94225 (19) | 0.60049 (18) | 0.0178 (4) | |
| H9 | 0.1884 | 1.0014 | 0.6192 | 0.021* | |
| C10 | 0.4173 (3) | 0.95414 (18) | 0.64538 (17) | 0.0161 (4) | |
| C11 | 0.3799 (3) | 1.0583 (2) | 0.72813 (18) | 0.0202 (4) | |
| C12 | 0.5801 (3) | 0.86824 (19) | 0.61159 (17) | 0.0164 (4) | |
| H12 | 0.6608 | 0.8774 | 0.6412 | 0.020* | |
| C15 | 0.3041 (4) | 0.7442 (2) | 1.1227 (2) | 0.0452 (7) | |
| H15A | 0.3318 | 0.7211 | 1.0441 | 0.068* | |
| H15B | 0.2396 | 0.6952 | 1.1693 | 0.068* | |
| H15C | 0.4047 | 0.7248 | 1.1465 | 0.068* | |
| C16 | 0.1570 (3) | 0.9324 (3) | 1.2499 (2) | 0.0327 (6) | |
| H16A | 0.0844 | 1.0220 | 1.2507 | 0.049* | |
| H16B | 0.2539 | 0.9263 | 1.2734 | 0.049* | |
| H16C | 0.0992 | 0.8818 | 1.3016 | 0.049* | |

| | | | | | |
|------|--------------|--------------|--------------|--------------|-----------|
| C18 | 0.2042 (5) | 1.4697 (3) | 1.0417 (2) | 0.0590 (10) | |
| H18A | 0.1608 | 1.5052 | 0.9764 | 0.088* | |
| H18B | 0.2955 | 1.4971 | 1.0395 | 0.088* | |
| H18C | 0.1180 | 1.5003 | 1.1103 | 0.088* | |
| C19 | 0.2560 (3) | 1.2678 (2) | 0.95630 (19) | 0.0272 (5) | |
| H19 | 0.2955 | 1.1771 | 0.9602 | 0.033* | |
| C20 | 0.3184 (3) | 1.2590 (3) | 1.1386 (2) | 0.0434 (7) | |
| H20A | 0.3579 | 1.1668 | 1.1265 | 0.065* | |
| H20B | 0.2275 | 1.2811 | 1.2059 | 0.065* | |
| H20C | 0.4073 | 1.2827 | 1.1483 | 0.065* | |
| C21A | 0.1675 (3) | 0.9574 (2) | 1.04753 (19) | 0.0242 (5) | 0.437 (4) |
| H21A | 0.1017 | 1.0445 | 1.0620 | 0.029* | 0.437 (4) |
| O6A | 0.2100 (5) | 0.9214 (3) | 0.9473 (3) | 0.0255 (11) | 0.437 (4) |
| C21B | 0.1675 (3) | 0.9574 (2) | 1.04753 (19) | 0.0242 (5) | 0.563 (4) |
| H21B | 0.1983 | 0.9165 | 0.9781 | 0.029* | 0.563 (4) |
| O6B | 0.0912 (4) | 1.0793 (3) | 1.0485 (2) | 0.0304 (9) | 0.563 (4) |
| N1 | 0.6254 (2) | 0.77252 (15) | 0.53787 (14) | 0.0139 (3) | |
| N2 | 0.7337 (2) | 0.58081 (15) | 0.39584 (14) | 0.0140 (3) | |
| N4 | 0.2618 (3) | 1.32944 (19) | 1.04017 (16) | 0.0293 (4) | |
| N21 | 0.2077 (2) | 0.88264 (17) | 1.13500 (15) | 0.0227 (4) | |
| O1 | 0.6831 (2) | 0.27950 (15) | 0.17378 (14) | 0.0278 (4) | |
| H1 | 0.7387 | 0.2161 | 0.1329 | 0.042* | 0.437 (4) |
| O2 | 0.93592 (19) | 0.26688 (15) | 0.18333 (14) | 0.0293 (4) | |
| H2 | 0.9662 | 0.2047 | 0.1415 | 0.044* | 0.563 (4) |
| O3 | 0.23516 (19) | 1.15187 (14) | 0.73405 (13) | 0.0233 (3) | |
| H3 | 0.2215 | 1.2066 | 0.7795 | 0.035* | |
| O4 | 0.4777 (2) | 1.05397 (17) | 0.78151 (15) | 0.0347 (4) | |
| O5 | 0.2021 (2) | 1.32076 (15) | 0.87227 (13) | 0.0337 (4) | |
| Cl1 | 0.97529 (6) | 0.78040 (5) | 0.52466 (4) | 0.01868 (11) | |
| Cl2 | 0.88428 (6) | 0.47339 (5) | 0.63849 (4) | 0.01680 (11) | |
| Cu1 | 0.86273 (3) | 0.65512 (2) | 0.46635 (2) | 0.01421 (7) | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0145 (10) | 0.0134 (9) | 0.0158 (10) | -0.0059 (8) | -0.0049 (8) | 0.0017 (7) |
| C2 | 0.0139 (10) | 0.0138 (9) | 0.0148 (10) | -0.0054 (8) | -0.0038 (8) | 0.0010 (7) |
| C3 | 0.0136 (10) | 0.0149 (9) | 0.0153 (10) | -0.0035 (8) | -0.0042 (8) | 0.0005 (8) |
| C4 | 0.0191 (10) | 0.0127 (9) | 0.0153 (10) | -0.0062 (8) | -0.0034 (8) | -0.0001 (7) |
| C5 | 0.0177 (10) | 0.0170 (10) | 0.0187 (10) | -0.0082 (8) | -0.0067 (8) | -0.0007 (8) |
| C6 | 0.0137 (10) | 0.0173 (10) | 0.0199 (11) | -0.0050 (8) | -0.0050 (8) | 0.0000 (8) |
| C7 | 0.0195 (11) | 0.0152 (9) | 0.0159 (10) | -0.0055 (8) | -0.0030 (8) | -0.0006 (8) |
| C8 | 0.0151 (10) | 0.0181 (10) | 0.0209 (11) | -0.0062 (8) | -0.0064 (8) | -0.0013 (8) |
| C9 | 0.0139 (10) | 0.0158 (10) | 0.0207 (11) | -0.0031 (8) | -0.0027 (8) | -0.0011 (8) |
| C10 | 0.0180 (10) | 0.0138 (9) | 0.0151 (10) | -0.0054 (8) | -0.0023 (8) | 0.0000 (8) |
| C11 | 0.0207 (11) | 0.0207 (10) | 0.0176 (11) | -0.0079 (9) | 0.0002 (9) | -0.0046 (8) |
| C12 | 0.0167 (10) | 0.0174 (10) | 0.0164 (10) | -0.0071 (8) | -0.0042 (8) | -0.0018 (8) |
| C15 | 0.0600 (19) | 0.0260 (13) | 0.0336 (15) | -0.0043 (13) | -0.0032 (14) | 0.0031 (11) |
| C16 | 0.0285 (13) | 0.0451 (15) | 0.0223 (12) | -0.0123 (11) | -0.0022 (10) | -0.0053 (11) |
| C18 | 0.116 (3) | 0.0361 (16) | 0.0334 (16) | -0.0372 (18) | -0.0143 (18) | -0.0073 (13) |

| | | | | | | |
|------|--------------|--------------|--------------|---------------|---------------|---------------|
| C19 | 0.0318 (13) | 0.0209 (11) | 0.0236 (12) | -0.0049 (10) | -0.0021 (10) | -0.0068 (9) |
| C20 | 0.0328 (15) | 0.0567 (18) | 0.0327 (15) | 0.0025 (13) | -0.0144 (12) | -0.0170 (13) |
| C21A | 0.0257 (12) | 0.0203 (11) | 0.0270 (12) | -0.0070 (9) | -0.0061 (10) | -0.0068 (9) |
| O6A | 0.035 (2) | 0.0194 (19) | 0.020 (2) | -0.0058 (16) | -0.0081 (16) | -0.0050 (14) |
| C21B | 0.0257 (12) | 0.0203 (11) | 0.0270 (12) | -0.0070 (9) | -0.0061 (10) | -0.0068 (9) |
| O6B | 0.0358 (18) | 0.0216 (15) | 0.0283 (17) | -0.0037 (13) | -0.0062 (13) | -0.0056 (12) |
| N1 | 0.0125 (8) | 0.0136 (8) | 0.0165 (8) | -0.0046 (6) | -0.0047 (7) | -0.0003 (6) |
| N2 | 0.0132 (8) | 0.0138 (8) | 0.0152 (8) | -0.0047 (7) | -0.0040 (7) | -0.0001 (6) |
| N4 | 0.0333 (12) | 0.0327 (11) | 0.0208 (10) | -0.0114 (9) | -0.0017 (9) | -0.0097 (8) |
| N21 | 0.0223 (10) | 0.0221 (9) | 0.0213 (10) | -0.0068 (8) | -0.0020 (8) | -0.0032 (7) |
| O1 | 0.0317 (9) | 0.0262 (8) | 0.0302 (9) | -0.0137 (7) | -0.0056 (7) | -0.0114 (7) |
| O2 | 0.0210 (9) | 0.0259 (8) | 0.0344 (9) | 0.0000 (7) | -0.0033 (7) | -0.0114 (7) |
| O3 | 0.0269 (9) | 0.0170 (7) | 0.0219 (8) | -0.0014 (6) | -0.0053 (7) | -0.0074 (6) |
| O4 | 0.0239 (9) | 0.0420 (10) | 0.0379 (10) | -0.0025 (8) | -0.0100 (8) | -0.0239 (8) |
| O5 | 0.0581 (12) | 0.0210 (8) | 0.0189 (8) | -0.0089 (8) | -0.0109 (8) | -0.0028 (7) |
| C11 | 0.0153 (2) | 0.0184 (2) | 0.0249 (3) | -0.00683 (19) | -0.0069 (2) | -0.00293 (19) |
| C12 | 0.0120 (2) | 0.0202 (2) | 0.0173 (2) | -0.00488 (19) | -0.00233 (18) | -0.00277 (19) |
| Cu1 | 0.01079 (13) | 0.01549 (12) | 0.01676 (13) | -0.00388 (9) | -0.00401 (9) | -0.00304 (9) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|----------------------|-------------|
| C1—N1 | 1.355 (3) | C15—H15C | 0.9600 |
| C1—C8 | 1.386 (3) | C16—N21 | 1.453 (3) |
| C1—C2 | 1.478 (3) | C16—H16A | 0.9600 |
| C2—N2 | 1.355 (3) | C16—H16B | 0.9600 |
| C2—C6 | 1.388 (3) | C16—H16C | 0.9600 |
| C3—N2 | 1.333 (3) | C18—N4 | 1.439 (3) |
| C3—C4 | 1.391 (3) | C18—H18A | 0.9600 |
| C3—H3A | 0.9300 | C18—H18B | 0.9600 |
| C4—C5 | 1.382 (3) | C18—H18C | 0.9600 |
| C4—C7 | 1.495 (3) | C19—O5 | 1.242 (3) |
| C5—C6 | 1.388 (3) | C19—N4 | 1.315 (3) |
| C5—H5 | 0.9300 | C19—H19 | 0.9300 |
| C6—H6 | 0.9300 | C20—N4 | 1.456 (3) |
| C7—O1 | 1.261 (3) | C20—H20A | 0.9600 |
| C7—O2 | 1.264 (3) | C20—H20B | 0.9600 |
| C8—C9 | 1.385 (3) | C20—H20C | 0.9600 |
| C8—H8 | 0.9300 | C21A—O6A | 1.241 (4) |
| C9—C10 | 1.381 (3) | C21A—N21 | 1.315 (3) |
| C9—H9 | 0.9300 | C21A—H21A | 0.9300 |
| C10—C12 | 1.386 (3) | N1—Cu1 | 2.0337 (18) |
| C10—C11 | 1.501 (3) | N2—Cu1 | 2.0361 (17) |
| C11—O4 | 1.209 (3) | O1—H1 | 0.8200 |
| C11—O3 | 1.311 (3) | O2—H2 | 0.8200 |
| C12—N1 | 1.339 (3) | O3—H3 | 0.8200 |
| C12—H12 | 0.9300 | C11—Cu1 | 2.2525 (10) |
| C15—N21 | 1.451 (3) | C12—Cu1 ⁱ | 2.2804 (10) |
| C15—H15A | 0.9600 | C12—Cu1 | 2.7183 (12) |
| C15—H15B | 0.9600 | | |

| | | | |
|---------------|-------------|---------------------------|--------------|
| N1—C1—C8 | 121.94 (18) | H16A—C16—H16C | 109.5 |
| N1—C1—C2 | 114.49 (17) | H16B—C16—H16C | 109.5 |
| C8—C1—C2 | 123.57 (18) | N4—C18—H18A | 109.5 |
| N2—C2—C6 | 122.18 (18) | N4—C18—H18B | 109.5 |
| N2—C2—C1 | 114.96 (16) | H18A—C18—H18B | 109.5 |
| C6—C2—C1 | 122.83 (18) | N4—C18—H18C | 109.5 |
| N2—C3—C4 | 122.29 (19) | H18A—C18—H18C | 109.5 |
| N2—C3—H3A | 118.9 | H18B—C18—H18C | 109.5 |
| C4—C3—H3A | 118.9 | O5—C19—N4 | 125.3 (2) |
| C5—C4—C3 | 118.91 (18) | O5—C19—H19 | 117.3 |
| C5—C4—C7 | 120.96 (18) | N4—C19—H19 | 117.3 |
| C3—C4—C7 | 120.13 (18) | N4—C20—H20A | 109.5 |
| C4—C5—C6 | 119.42 (18) | N4—C20—H20B | 109.5 |
| C4—C5—H5 | 120.3 | H20A—C20—H20B | 109.5 |
| C6—C5—H5 | 120.3 | N4—C20—H20C | 109.5 |
| C5—C6—C2 | 118.45 (19) | H20A—C20—H20C | 109.5 |
| C5—C6—H6 | 120.8 | H20B—C20—H20C | 109.5 |
| C2—C6—H6 | 120.8 | O6A—C21A—N21 | 125.4 (3) |
| O1—C7—O2 | 125.27 (19) | O6A—C21A—H21A | 117.3 |
| O1—C7—C4 | 117.40 (18) | N21—C21A—H21A | 117.3 |
| O2—C7—C4 | 117.32 (18) | C12—N1—C1 | 118.42 (17) |
| C9—C8—C1 | 119.05 (19) | C12—N1—Cu1 | 126.23 (14) |
| C9—C8—H8 | 120.5 | C1—N1—Cu1 | 115.10 (13) |
| C1—C8—H8 | 120.5 | C3—N2—C2 | 118.75 (17) |
| C10—C9—C8 | 118.98 (19) | C3—N2—Cu1 | 126.29 (14) |
| C10—C9—H9 | 120.5 | C2—N2—Cu1 | 114.96 (13) |
| C8—C9—H9 | 120.5 | C19—N4—C18 | 121.5 (2) |
| C9—C10—C12 | 119.08 (18) | C19—N4—C20 | 121.4 (2) |
| C9—C10—C11 | 122.74 (18) | C18—N4—C20 | 117.0 (2) |
| C12—C10—C11 | 118.17 (18) | C21A—N21—C15 | 121.8 (2) |
| O4—C11—O3 | 124.97 (19) | C21A—N21—C16 | 122.4 (2) |
| O4—C11—C10 | 121.63 (19) | C15—N21—C16 | 115.8 (2) |
| O3—C11—C10 | 113.39 (18) | C7—O1—H1 | 109.5 |
| N1—C12—C10 | 122.42 (18) | C7—O2—H2 | 109.5 |
| N1—C12—H12 | 118.8 | C11—O3—H3 | 109.5 |
| C10—C12—H12 | 118.8 | Cu1 ⁱ —Cl2—Cu1 | 90.20 (4) |
| N21—C15—H15A | 109.5 | N1—Cu1—N2 | 79.91 (8) |
| N21—C15—H15B | 109.5 | N1—Cu1—Cl1 | 92.97 (6) |
| H15A—C15—H15B | 109.5 | N2—Cu1—Cl1 | 166.75 (5) |
| N21—C15—H15C | 109.5 | N1—Cu1—Cl2 ⁱ | 171.33 (5) |
| H15A—C15—H15C | 109.5 | N2—Cu1—Cl2 ⁱ | 93.45 (7) |
| H15B—C15—H15C | 109.5 | Cl1—Cu1—Cl2 ⁱ | 92.41 (5) |
| N21—C16—H16A | 109.5 | N1—Cu1—Cl2 | 96.09 (5) |
| N21—C16—H16B | 109.5 | N2—Cu1—Cl2 | 93.10 (6) |
| H16A—C16—H16B | 109.5 | Cl1—Cu1—Cl2 | 98.80 (4) |
| N21—C16—H16C | 109.5 | Cl2 ⁱ —Cu1—Cl2 | 89.80 (4) |
| N1—C1—C2—N2 | -4.8 (2) | C8—C1—N1—Cu1 | -171.55 (15) |
| C8—C1—C2—N2 | 174.95 (18) | C2—C1—N1—Cu1 | 8.2 (2) |

| | | | |
|----------------|--------------|--|--------------|
| N1—C1—C2—C6 | 173.40 (18) | C4—C3—N2—C2 | -0.1 (3) |
| C8—C1—C2—C6 | -6.9 (3) | C4—C3—N2—Cu1 | 179.64 (14) |
| N2—C3—C4—C5 | -0.4 (3) | C6—C2—N2—C3 | 0.6 (3) |
| N2—C3—C4—C7 | 178.92 (17) | C1—C2—N2—C3 | 178.81 (16) |
| C3—C4—C5—C6 | 0.3 (3) | C6—C2—N2—Cu1 | -179.13 (15) |
| C7—C4—C5—C6 | -179.00 (18) | C1—C2—N2—Cu1 | -0.9 (2) |
| C4—C5—C6—C2 | 0.2 (3) | O5—C19—N4—C18 | -0.3 (4) |
| N2—C2—C6—C5 | -0.7 (3) | O5—C19—N4—C20 | 176.4 (2) |
| C1—C2—C6—C5 | -178.74 (18) | O6A—C21A—N21—C15 | -2.5 (4) |
| C5—C4—C7—O1 | -2.5 (3) | O6A—C21A—N21—C16 | 178.3 (3) |
| C3—C4—C7—O1 | 178.22 (18) | C12—N1—Cu1—N2 | 179.08 (17) |
| C5—C4—C7—O2 | 176.55 (19) | C1—N1—Cu1—N2 | -6.78 (13) |
| C3—C4—C7—O2 | -2.7 (3) | C12—N1—Cu1—Cl1 | -12.18 (16) |
| N1—C1—C8—C9 | -0.9 (3) | C1—N1—Cu1—Cl1 | 161.96 (13) |
| C2—C1—C8—C9 | 179.35 (18) | C12—N1—Cu1—Cl2 | 87.00 (16) |
| C1—C8—C9—C10 | -2.2 (3) | C1—N1—Cu1—Cl2 | -98.86 (14) |
| C8—C9—C10—C12 | 3.1 (3) | C3—N2—Cu1—N1 | -175.67 (17) |
| C8—C9—C10—C11 | -178.12 (19) | C2—N2—Cu1—N1 | 4.05 (13) |
| C9—C10—C11—O4 | 166.9 (2) | C3—N2—Cu1—Cl1 | 126.0 (2) |
| C12—C10—C11—O4 | -14.3 (3) | C2—N2—Cu1—Cl1 | -54.2 (3) |
| C9—C10—C11—O3 | -14.0 (3) | C3—N2—Cu1—Cl2 ⁱ | 9.96 (16) |
| C12—C10—C11—O3 | 164.78 (18) | C2—N2—Cu1—Cl2 ⁱ | -170.32 (13) |
| C9—C10—C12—N1 | -0.9 (3) | C3—N2—Cu1—Cl2 | -80.03 (16) |
| C11—C10—C12—N1 | -179.79 (18) | C2—N2—Cu1—Cl2 | 99.69 (13) |
| C10—C12—N1—C1 | -2.2 (3) | Cu1 ⁱ —Cl2—Cu1—N1 | 173.62 (5) |
| C10—C12—N1—Cu1 | 171.82 (14) | Cu1 ⁱ —Cl2—Cu1—N2 | 93.44 (6) |
| C8—C1—N1—C12 | 3.1 (3) | Cu1 ⁱ —Cl2—Cu1—Cl1 | -92.40 (5) |
| C2—C1—N1—C12 | -177.18 (16) | Cu1 ⁱ —Cl2—Cu1—Cl2 ⁱ | 0.0 |

Symmetry code: (i) $-x+2, -y+1, -z+1$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| O2—H2 \cdots O6B ⁱⁱ | 0.82 | 1.72 | 2.515 (3) | 161 |
| O1—H1 \cdots O6A ⁱⁱⁱ | 0.82 | 1.75 | 2.536 (4) | 161 |
| O3—H3 \cdots O5 | 0.82 | 1.72 | 2.541 (2) | 177 |
| C21A—H21A \cdots O2 ^{iv} | 0.93 | 2.71 | 3.591 (3) | 158 |
| C21B—H21B \cdots O1 ⁱⁱⁱ | 0.93 | 2.72 | 3.603 (3) | 159 |

Symmetry codes: (ii) $x+1, y-1, z-1$; (iii) $-x+1, -y+1, -z+1$; (iv) $x-1, y+1, z+1$.