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Chloridobis[2-(pyridin-2-yl-κN)benzo[*b*][1,5]-naphthyridine-κN^1]copper(II) perchlorate acetonitrile disolvate

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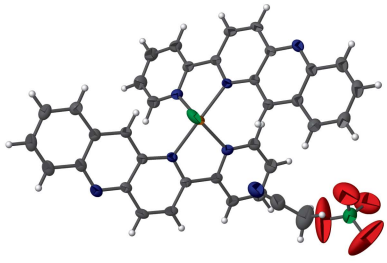
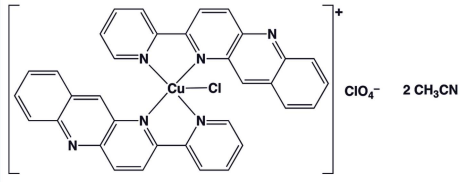
Structural data: full structural data are available from iucrdata.iucr.org

The copper(II) ion in the title complex, $[CuCl(C_{17}H_{11}N_3)_2]ClO_4\cdot 2CH_3CN$, is coordinated by four N atoms from two pbn ligands and one Cl^- ion in a distorted trigonal–bipyramidal geometry (τ = 0.84). The asymmetric unit comprises half of the cationic complex molecule, and complete molecules are generated by twofold rotation symmetry with the corresponding axis running through the Cu atom and the coordinating Cl atom. The perchlorate anion is also located on a twofold rotation axis (passing through the Cl atom). In the crystal, there are π–π stacking interactions between the benzonaphthyridine rings of the pbn ligand of neighbouring cations.

3D view



Chemical scheme



Structure description

Understanding the relationship between coordination geometry and reactivity of complexes containing the NAD$^+$/NADH-analogous ligand pbn [pbn = 2-(pyridin-2-yl)benzo[*b*][1,5]naphthyridine] is of great interest and importance in order to develop a photorenewable hydride reagent. In our previous studies, photocatalytic CO_2 reduction using the pbn complex has proved to be successful (Ohtsu & Tanaka, 2012), and control over the reaction rate of the CO_2 hydride reduction using a pbn complex has been accomplished by tuning of the basicity of the bases (Ohtsu *et al.*, 2015). As part of our ongoing research on transition-metal complexes containing a pbn ligand, we have synthesized a new copper(II) pbn complex and its structure determination has been undertaken.

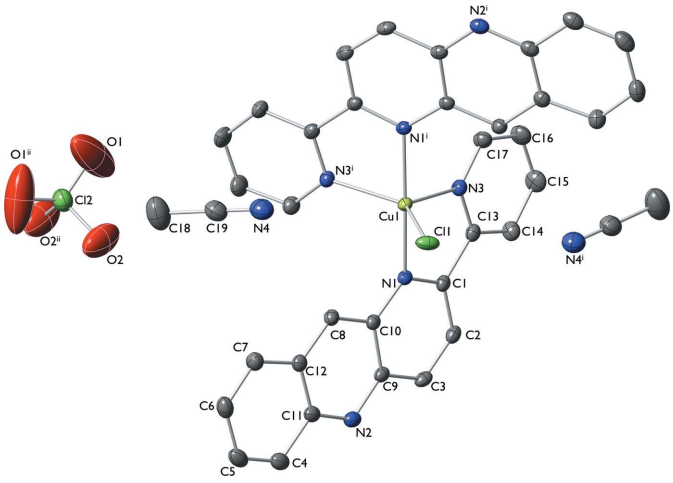


Figure 1
The molecular structure of the title complex, with displacement ellipsoids at the 30% probability level [symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, -y, z$]. H atoms have been omitted for clarity.

The molecular structure of the title complex is shown in Fig. 1. The copper(II) ion of the cation has a pentacoordinate structure formed by four N atoms from two pbn ligands and one Cl ligand. The complex cation exhibits point group symmetry 2, with the twofold rotation axis running through Cu1 and Cl1. The perchlorate anion is also located on a twofold rotation axis (passing through Cl2). The bond lengths from the copper to each of donor N atoms and chloride are Cu1—N1 2.0230 (18) Å, Cu1—N3 2.0778 (19) Å, and Cu1—Cl1 2.2795 (9) Å. The quantitative difference in five-coordinate geometry is indicated by the τ parameter, the value of which can range from $\tau = 1$ for a perfect trigonal–bipyramidal geometry to $\tau = 0$ for a perfect square-pyramidal geometry (Addison *et al.*, 1984). The τ value for the copper(II) ion of the cation in the title complex is calculated to be 0.84 using the equation $\tau = (\beta - \alpha)/60$ (Addison *et al.*, 1984), where α = N3—Cu1—Cl1 [125.66 (5)°] and β = N1—Cu1—N1^{i} [175.78 (11)°; symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}-z$). Thus, the coordination environment of the copper(II) ion in $[Cu(pbn)_2Cl]^+$ is slightly distorted trigonal–bipyramidal.

The crystal packing of the title complex is shown in Fig. 2. The relatively short interplanar distances between the benzonaphthyridine rings of the pbn ligand of neighbouring cations indicate intermolecular π–π stacking interactions [distance between the centroids of the (C8/N2/C9–C12) and (C2/N1/C1/C9/C10/C3)^{ii} rings = 3.6070 (3) Å; symmetry code: (ii) $-\frac{1}{2}+x, y, 1-z$].

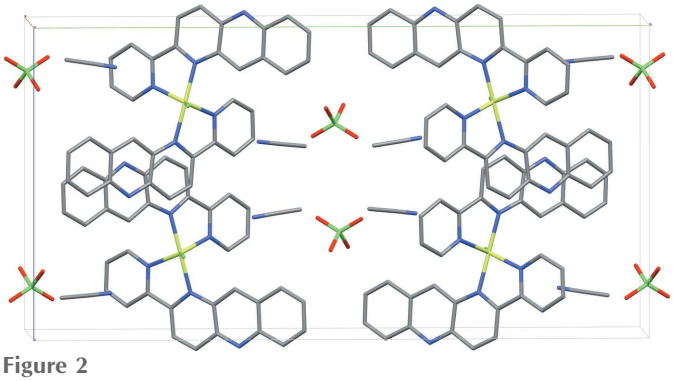


Figure 2
The crystal packing of the title complex, viewed along the *a* axis. H atoms have been omitted for clarity.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[CuCl(C_{17}H_{11}N_3)_2]ClO_4\cdot 2C_2H_3N$
M_r	795.14
Crystal system, space group	Orthorhombic, *Pnna*
Temperature (K)	173
a, *b*, *c* (Å)	7.53614 (16), 30.5246 (6), 15.4918 (4)
V (Å^3)	3563.71 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.82
Crystal size (mm)	0.25 × 0.23 × 0.02
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.751, 0.984
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	32886, 4072, 3235
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.132, 1.06
No. of reflections	4072
No. of parameters	242
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.81, −0.50

Computer programs: *RAPID-AUTO* (Rigaku, 2001), *SIR2011* (Burla *et al.*, 2012), *SHELXL2016* (Sheldrick, 2015), *CrystalStructure* (Rigaku, 2016), *Mercury* (Macrae *et al.*, 2008), *CrystalMaker* (Palmer, 2007) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

The NAD$^+$/NADH-analogous ligand pbn [pbn = 2-(pyridin-2-yl)benzo[*b*][1,5]naphthyridine] was prepared according to the procedure of Koizumi & Tanaka (2005). To a dichloromethane solution (4 ml) of pbn (50.0 mg, 0.19 mmol) was added dropwise a mixture of $CuCl_2\cdot 2H_2O$ (8.3 mg, 0.05 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (19.9 mg, 0.05 mmol) in acetonitrile (4 ml). The resulting pale yellow–green precipitate was filtered and dissolved in hot acetonitrile for recrystallization. After the solution was left to stand for a few weeks at room temperature, pale yellow–green crystals of the title complex, $[Cu(pbn)_2Cl]ClO_4\cdot 2CH_3CN$, were obtained (yield: 33.7 mg, 48.6%). Elemental analysis found: C 53.40, H 3.55, N 10.83%; calculated for $C_{34}H_{28}Cl_2CuN_6O_7$: C 53.24, H 3.68, N 10.96%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. & Spagna, R. (2012). *J. Appl. Cryst.* **45**, 357–361.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Koizumi, T.-a. & Tanaka, K. (2005). *Angew. Chem. Int. Ed.* **44**, 5891–5894.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Ohtsu, H. & Tanaka, K. (2012). *Angew. Chem. Int. Ed.* **51**, 9792–9795.

Ohtsu, H., Tsuge, K. & Tanaka, K. (2015). *J. Photochem. Photobiol. Chem.* **313**, 163–167.

Palmer, D. (2007). *CrystalMaker*. CrystalMaker Software, Bicester, England.

Rigaku (2001). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku (2016). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2016). **1**, x161562 [https://doi.org/10.1107/S2414314616015625]

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Crystal data

$[CuCl(C_{17}H_{11}N_3)_2]ClO_4·2C_2H_3N$
M_r = 795.14
Orthorhombic, *Pnna*
a = 7.53614 (16) Å
b = 30.5246 (6) Å
c = 15.4918 (4) Å
V = 3563.71 (13) Å^3
Z = 4
F(000) = 1628.00
D_x = 1.482 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71075 Å
Cell parameters from 21593 reflections
θ = 3.0–27.5°
μ = 0.82 mm^{-1}
T = 173 K
Platelet, yellowish green
0.25 × 0.23 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.751, T_{max} = 0.984
32886 measured reflections
4072 independent reflections
3235 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.043
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −8→9
k = −39→39
l = −20→20

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.132
S = 1.06
4072 reflections
242 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
$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 2.7626P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Special details

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

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
CU1	0.27555 (5)	0.250000	0.250000	0.02241 (13)
CL1	−0.02693 (11)	0.250000	0.250000	0.0367 (2)
CL2	0.750000	0.000000	0.16427 (8)	0.0533 (3)
O1	0.8062 (9)	0.03461 (19)	0.1220 (6)	0.244 (4)
O2	0.6099 (6)	0.01641 (18)	0.2183 (3)	0.1367 (17)
N1	0.2854 (2)	0.23357 (6)	0.37642 (12)	0.0233 (4)
N2	0.1294 (3)	0.15656 (7)	0.54355 (13)	0.0294 (4)
N3	0.4363 (3)	0.30003 (6)	0.29646 (12)	0.0271 (4)
N4	0.1061 (4)	0.13340 (10)	0.12987 (17)	0.0557 (7)
C1	0.3578 (3)	0.26382 (7)	0.42751 (14)	0.0241 (5)
C2	0.3555 (3)	0.26007 (8)	0.51920 (15)	0.0283 (5)
H2	0.407636	0.282244	0.553951	0.034*
C3	0.2785 (3)	0.22473 (8)	0.55655 (14)	0.0282 (5)
H3	0.275313	0.222235	0.617656	0.034*
C4	−0.0133 (3)	0.08709 (8)	0.53424 (18)	0.0357 (6)
H4	−0.017468	0.085455	0.595443	0.043*
C5	−0.0791 (4)	0.05395 (9)	0.48647 (19)	0.0403 (6)
H5	−0.129111	0.029212	0.514602	0.048*
C6	−0.0750 (4)	0.05533 (8)	0.3947 (2)	0.0408 (6)
H6	−0.120543	0.031392	0.362345	0.049*
C7	−0.0063 (4)	0.09064 (8)	0.35284 (17)	0.0353 (6)
H7	−0.005778	0.091390	0.291536	0.042*
C8	0.1360 (3)	0.16370 (7)	0.36126 (15)	0.0268 (5)
H8	0.135199	0.166429	0.300175	0.032*
C9	0.2028 (3)	0.19150 (7)	0.50445 (15)	0.0250 (5)
C10	0.2084 (3)	0.19688 (7)	0.41263 (14)	0.0232 (4)
C11	0.0629 (3)	0.12479 (8)	0.49334 (16)	0.0287 (5)
C12	0.0652 (3)	0.12666 (7)	0.40064 (15)	0.0280 (5)
C13	0.4470 (3)	0.30072 (7)	0.38324 (15)	0.0266 (5)
C14	0.5399 (4)	0.33320 (8)	0.42694 (17)	0.0347 (6)
H14	0.545306	0.333179	0.488203	0.042*
C15	0.6248 (4)	0.36570 (9)	0.37968 (19)	0.0424 (7)
H15	0.688212	0.388422	0.408040	0.051*
C16	0.6153 (4)	0.36437 (9)	0.2907 (2)	0.0414 (6)
H16	0.673472	0.386018	0.256982	0.050*
C17	0.5203 (3)	0.33121 (9)	0.25129 (16)	0.0334 (5)
H17	0.514287	0.330496	0.190050	0.040*
C18	0.2394 (6)	0.05650 (14)	0.1102 (4)	0.0886 (15)
H18A	0.256040	0.050434	0.048564	0.106*
H18B	0.158888	0.034679	0.135016	0.106*
H18C	0.354269	0.055080	0.139691	0.106*

C19	0.1648 (5)	0.09945 (11)	0.1207 (2)	0.0506 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
CU1	0.0261 (2)	0.0236 (2)	0.0175 (2)	0.000	0.000	−0.00087 (14)
CL1	0.0256 (4)	0.0562 (6)	0.0283 (4)	0.000	0.000	0.0163 (4)
CL2	0.0604 (7)	0.0417 (5)	0.0579 (7)	−0.0012 (5)	0.000	0.000
O1	0.189 (6)	0.131 (4)	0.412 (11)	0.034 (4)	0.106 (6)	0.162 (6)
O2	0.118 (3)	0.190 (4)	0.102 (3)	0.080 (3)	0.014 (2)	0.006 (3)
N1	0.0255 (10)	0.0250 (9)	0.0192 (9)	0.0038 (8)	−0.0017 (7)	−0.0003 (7)
N2	0.0269 (10)	0.0343 (11)	0.0269 (10)	0.0065 (8)	0.0020 (8)	0.0043 (8)
N3	0.0275 (10)	0.0282 (9)	0.0257 (10)	−0.0009 (8)	0.0001 (8)	−0.0038 (8)
N4	0.0638 (18)	0.0584 (17)	0.0449 (15)	−0.0029 (14)	−0.0009 (13)	0.0052 (13)
C1	0.0235 (11)	0.0258 (10)	0.0230 (11)	0.0055 (9)	−0.0033 (9)	−0.0024 (8)
C2	0.0256 (12)	0.0351 (12)	0.0243 (11)	0.0042 (9)	−0.0046 (9)	−0.0079 (9)
C3	0.0271 (12)	0.0388 (13)	0.0187 (10)	0.0069 (10)	−0.0013 (9)	−0.0014 (9)
C4	0.0305 (13)	0.0373 (13)	0.0393 (13)	0.0066 (11)	0.0048 (11)	0.0095 (11)
C5	0.0330 (14)	0.0333 (13)	0.0545 (17)	0.0014 (11)	0.0074 (12)	0.0125 (12)
C6	0.0384 (14)	0.0281 (12)	0.0559 (17)	−0.0023 (11)	0.0018 (13)	−0.0029 (12)
C7	0.0365 (14)	0.0319 (12)	0.0375 (13)	−0.0006 (11)	0.0021 (11)	−0.0029 (10)
C8	0.0308 (12)	0.0259 (11)	0.0236 (10)	0.0034 (9)	−0.0018 (9)	−0.0012 (9)
C9	0.0243 (11)	0.0290 (11)	0.0219 (10)	0.0073 (9)	−0.0001 (8)	−0.0001 (9)
C10	0.0228 (11)	0.0246 (10)	0.0223 (10)	0.0054 (9)	−0.0014 (8)	0.0002 (8)
C11	0.0253 (12)	0.0302 (11)	0.0305 (12)	0.0072 (10)	0.0029 (9)	0.0047 (9)
C12	0.0258 (11)	0.0273 (11)	0.0310 (12)	0.0047 (9)	0.0006 (10)	0.0003 (9)
C13	0.0249 (11)	0.0273 (11)	0.0276 (11)	0.0046 (9)	−0.0034 (9)	−0.0040 (9)
C14	0.0391 (14)	0.0323 (12)	0.0327 (13)	−0.0006 (11)	−0.0080 (11)	−0.0057 (10)
C15	0.0439 (16)	0.0360 (14)	0.0472 (16)	−0.0102 (12)	−0.0105 (13)	−0.0064 (12)
C16	0.0385 (15)	0.0383 (14)	0.0473 (16)	−0.0134 (12)	0.0009 (12)	0.0009 (12)
C17	0.0326 (13)	0.0359 (13)	0.0316 (12)	−0.0066 (11)	0.0025 (10)	0.0000 (10)
C18	0.075 (3)	0.058 (2)	0.132 (4)	0.005 (2)	−0.007 (3)	0.001 (3)
C19	0.0528 (18)	0.0517 (18)	0.0473 (17)	−0.0038 (16)	−0.0015 (15)	0.0086 (14)

Geometric parameters (Å, º)

CU1—N1	2.0230 (18)	C4—H4	0.9500
CU1—N1^{i}	2.0230 (18)	C5—C6	1.423 (4)
CU1—N3	2.0778 (19)	C5—H5	0.9500
CU1—N3^{i}	2.0779 (19)	C6—C7	1.360 (4)
CU1—CL1	2.2795 (9)	C6—H6	0.9500
CL2—O1^{ii}	1.313 (5)	C7—C12	1.431 (3)
CL2—O1	1.313 (5)	C7—H7	0.9500
CL2—O2	1.438 (4)	C8—C12	1.391 (3)
CL2—O2^{ii}	1.438 (4)	C8—C10	1.399 (3)
N1—C1	1.333 (3)	C8—H8	0.9500
N1—C10	1.381 (3)	C9—C10	1.433 (3)
N2—C11	1.341 (3)	C11—C12	1.437 (3)

N2—C9	1.345 (3)	C13—C14	1.390 (3)
N3—C17	1.340 (3)	C14—C15	1.389 (4)
N3—C13	1.347 (3)	C14—H14	0.9500
N4—C19	1.136 (4)	C15—C16	1.380 (4)
C1—C2	1.425 (3)	C15—H15	0.9500
C1—C13	1.480 (3)	C16—C17	1.382 (4)
C2—C3	1.355 (4)	C16—H16	0.9500
C2—H2	0.9500	C17—H17	0.9500
C3—C9	1.416 (3)	C18—C19	1.436 (6)
C3—H3	0.9500	C18—H18A	0.9800
C4—C5	1.348 (4)	C18—H18B	0.9800
C4—C11	1.434 (3)	C18—H18C	0.9800

N1—CU1—N1^{i}	175.78 (11)	C6—C7—C12	120.4 (2)
N1—CU1—N3	79.95 (8)	C6—C7—H7	119.8
N1^{i}—CU1—N3	97.56 (7)	C12—C7—H7	119.8
N1—CU1—N3^{i}	97.57 (7)	C12—C8—C10	119.3 (2)
N1^{i}—CU1—N3^{i}	79.95 (8)	C12—C8—H8	120.4
N3—CU1—N3^{i}	108.69 (11)	C10—C8—H8	120.4
N1—CU1—CL1	92.11 (5)	N2—C9—C3	118.5 (2)
N1^{i}—CU1—CL1	92.11 (5)	N2—C9—C10	123.4 (2)
N3—CU1—CL1	125.66 (5)	C3—C9—C10	118.2 (2)
N3^{i}—CU1—CL1	125.65 (5)	N1—C10—C8	121.3 (2)
O1^{ii}—CL2—O1	120.2 (9)	N1—C10—C9	120.6 (2)
O1^{ii}—CL2—O2	109.5 (4)	C8—C10—C9	118.1 (2)
O1—CL2—O2	104.3 (4)	N2—C11—C4	118.3 (2)
O1^{ii}—CL2—O2^{ii}	104.3 (4)	N2—C11—C12	123.1 (2)
O1—CL2—O2^{ii}	109.5 (4)	C4—C11—C12	118.6 (2)
O2—CL2—O2^{ii}	108.8 (4)	C8—C12—C7	122.8 (2)
C1—N1—C10	119.52 (19)	C8—C12—C11	118.4 (2)
C1—N1—CU1	114.72 (15)	C7—C12—C11	118.8 (2)
C10—N1—CU1	125.38 (15)	N3—C13—C14	121.8 (2)
C11—N2—C9	117.8 (2)	N3—C13—C1	115.0 (2)
C17—N3—C13	118.8 (2)	C14—C13—C1	123.1 (2)
C17—N3—CU1	128.05 (16)	C15—C14—C13	119.0 (2)
C13—N3—CU1	113.10 (16)	C15—C14—H14	120.5
N1—C1—C2	122.1 (2)	C13—C14—H14	120.5
N1—C1—C13	116.0 (2)	C16—C15—C14	118.8 (2)
C2—C1—C13	121.9 (2)	C16—C15—H15	120.6
C3—C2—C1	119.7 (2)	C14—C15—H15	120.6
C3—C2—H2	120.2	C15—C16—C17	119.3 (3)
C1—C2—H2	120.2	C15—C16—H16	120.3
C2—C3—C9	120.0 (2)	C17—C16—H16	120.3
C2—C3—H3	120.0	N3—C17—C16	122.3 (2)
C9—C3—H3	120.0	N3—C17—H17	118.9
C5—C4—C11	120.5 (2)	C16—C17—H17	118.9
C5—C4—H4	119.8	C19—C18—H18A	109.5
C11—C4—H4	119.8	C19—C18—H18B	109.5

C4—C5—C6	121.2 (2)	H18A—C18—H18B	109.5
C4—C5—H5	119.4	C19—C18—H18C	109.5
C6—C5—H5	119.4	H18A—C18—H18C	109.5
C7—C6—C5	120.5 (3)	H18B—C18—H18C	109.5
C7—C6—H6	119.7	N4—C19—C18	179.3 (4)
C5—C6—H6	119.7		

C10—N1—C1—C2	−1.3 (3)	C5—C4—C11—N2	−178.8 (2)
CU1—N1—C1—C2	172.05 (17)	C5—C4—C11—C12	0.9 (4)
C10—N1—C1—C13	176.41 (19)	C10—C8—C12—C7	−178.0 (2)
CU1—N1—C1—C13	−10.3 (2)	C10—C8—C12—C11	2.5 (3)
N1—C1—C2—C3	0.3 (4)	C6—C7—C12—C8	−179.6 (2)
C13—C1—C2—C3	−177.2 (2)	C6—C7—C12—C11	0.0 (4)
C1—C2—C3—C9	0.8 (3)	N2—C11—C12—C8	−1.6 (4)
C11—C4—C5—C6	0.0 (4)	C4—C11—C12—C8	178.7 (2)
C4—C5—C6—C7	−0.9 (4)	N2—C11—C12—C7	178.8 (2)
C5—C6—C7—C12	0.9 (4)	C4—C11—C12—C7	−0.9 (3)
C11—N2—C9—C3	−178.1 (2)	C17—N3—C13—C14	1.1 (4)
C11—N2—C9—C10	1.9 (3)	CU1—N3—C13—C14	−176.30 (18)
C2—C3—C9—N2	179.2 (2)	C17—N3—C13—C1	−177.1 (2)
C2—C3—C9—C10	−0.9 (3)	CU1—N3—C13—C1	5.5 (2)
C1—N1—C10—C8	−177.9 (2)	N1—C1—C13—N3	3.0 (3)
CU1—N1—C10—C8	9.5 (3)	C2—C1—C13—N3	−179.3 (2)
C1—N1—C10—C9	1.1 (3)	N1—C1—C13—C14	−175.2 (2)
CU1—N1—C10—C9	−171.43 (15)	C2—C1—C13—C14	2.5 (4)
C12—C8—C10—N1	177.8 (2)	N3—C13—C14—C15	−0.4 (4)
C12—C8—C10—C9	−1.3 (3)	C1—C13—C14—C15	177.7 (2)
N2—C9—C10—N1	179.9 (2)	C13—C14—C15—C16	−0.6 (4)
C3—C9—C10—N1	−0.1 (3)	C14—C15—C16—C17	0.8 (4)
N2—C9—C10—C8	−1.0 (3)	C13—N3—C17—C16	−1.0 (4)
C3—C9—C10—C8	179.0 (2)	CU1—N3—C17—C16	176.0 (2)
C9—N2—C11—C4	179.1 (2)	C15—C16—C17—N3	0.0 (4)
C9—N2—C11—C12	−0.6 (3)		

Symmetry codes: (i) x, $-y+1/2$, $-z+1/2$; (ii) $-x+3/2$, $-y$, z.