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[4′-(2-Bromo-5-pyridyl)-2,2′:6′,2″-terpyridine-κ^3N,N',N'']bis(triphenylphosphine-κP)copper(I) tetrafluoridoborate dichloromethane hemisolvate

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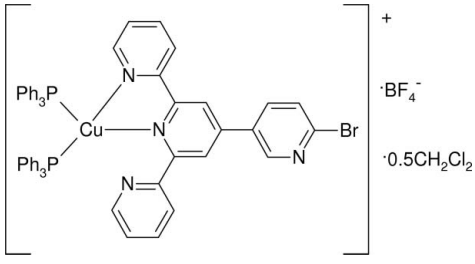
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.007 Å; some non-H atoms missing; disorder in solvent or counterion; R factor = 0.061; wR factor = 0.209; data-to-parameter ratio = 13.9.

In the title complex, $[Cu(C_{20}H_{13}BrN_4)(C_{18}H_{15}P)_2]BF_4\cdot 0.5CH_2Cl_2$, the copper(I) cation adopts a distorted tetrahedral arrangement, coordinated by two triphenylphosphine ligands and two N atoms of the potentially tridentate terpyridine ligand. One half-molecule of dichloromethane crystallizes with the complex. The chlorine atoms are disordered over two sites with occupancies fixed at 0.30 and 0.20 respectively. The N donor atom of the central pyridine interacts weakly with the copper centre at a distance of 3.071 Å.

Related literature

For general background see: Loiseau *et al.* (2002); Fitchett *et al.* (2005). For related structures see: Ainscough *et al.* (1994); Feng *et al.* (2002).



Experimental

Crystal data

$[Cu(C_{20}H_{13}BrN_4)(C_{18}H_{15}P)_2]BF_4\cdot 0.5CH_2Cl_2$
M_r = 1106.61
Triclinic, $P\overline{1}$
a = 13.8900 (5) Å
b = 13.9623 (6) Å
c = 15.2549 (5) Å
α = 72.358 (1)°
β = 83.6520 (11)°
γ = 69.821 (1)°
V = 2646.23 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.33 mm^{-1}
T = 150 (1) K
0.34 × 0.30 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker,2000)
T_{min} = 0.627, T_{max} = 0.698
22637 measured reflections
9368 independent reflections
7361 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.209
S = 1.05
9368 reflections
676 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Version 1.08; Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2424).

References

Ainscough, E. W., Brodie, A. M., Ingham, S. L. & Waters, J. M. (1994). *J. Chem. Soc. Dalton Trans*. pp. 215–220.
Bruker (2000). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.01), *SADABS* (Version 2.0) and *SHELXTL-NT* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Feng, Q., Li, D., Yin, Y.-G., Feng, X.-L. & Cai, J.-W. (2002). *Huaxue Xuebao*, **60**, 2167–2171.
Fitchett, C. M., Richardson, C. & Steel, P. J. (2005). *Org. Biomol. Chem.* **3**, 498–502.
Loiseau, F., Passalacqua, R., Campagna, S., Polson, M. I. J., Fang, Y.-Q. & Hanan, G. S. (2002). *Photochem. Photobiol. Sci.* **1**, 982–990.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Westrip, S. P. (2008). *publCIF*. In preparation.

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supporting information

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[4′-(2-Bromo-5-pyridyl)-2,2′:6′,2′′-terpyridine-κ^3N,N',N'']bis(triphenylphosphine-κP)copper(I) tetrafluoridoborate dichloromethane hemisolvate

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S1. Comment

To fully characterize a family of multi-nuclear ruthenium complexes (Loiseau *et al.*, 2002) we undertook to synthesize the the key bridging ligand 2:6:2‴:6‴tetra-2-pyridyl-4,5′:2′,2″:5″,4‴tetrapyridine. Initial attempts at the synthesis by nickel catalysed homocoupling of 4′-(2-bromo-5-pyridyl)2,2′:6′,2″terpyridine failed, presumably due to the free terpyridine unit sequestering the nickel from the catalyst (Loiseau *et al.*, 2002). The title complex, (I), Fig 1, crystallized as part of this work. The copper(I) cation adopts a distorted tetrahedral arrangement with the additional pyridine interacting weakly with the copper centre at a distance of 3.071 Å). Two other structures of copper (I) terpyridine bis-triphenylphosphine complexes were found in the literature (Ainscough *et al.*, 1994; Feng *et al.*, 2002). In both of these structures, the terpyridine ligand coordinates through all three N atoms giving a pentacoordinate complex. Despite the long N14—Cu1 distance there is an interaction, albeit somewhat weak. If there were no interaction it is likely that the N14 nitrogen of the loosely bound pyridine ring would rotate to adopt a s-*trans* arrangement, which is much more commonly seen in uncoordinated polypyridine ligands (Fitchett *et al.*, 2005).

S2. Experimental

4′-(2-bromo-5-pyridyl)2,2′:6′,2″terpyridine (100 mg) and bis-triphenylphosphine bis-acetonitrile copper(I) tetrafloroborate (194 mg) were stirred in dichloromethane (20 ml) under argon for 1 h. After the colour had changed from colourless to yellow, the solution was evaporated to dryness, redissolved in a mimimum of dichloromethane and crystals suitable for X-ray crystallography were grown by diffusion with diethyl ether. Yield (191 mg, 70%)

S3. Refinement

One half molecule of dichloromethane crystallizes with the compound (1) with the chlorine atoms disordered over two sites with occupancies of fixed at 0.30 and 0.20 respectively. The hydrogen atoms of this hemi-solvate were not included in the refinement. All other H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic and 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2 atoms.

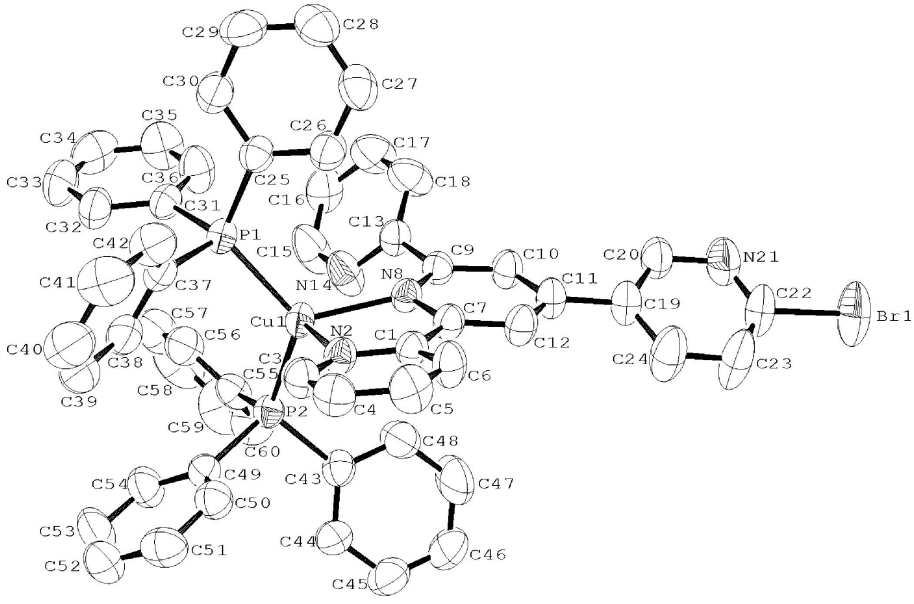

Figure 1

The molecular structure of (1), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

[4′-(2-Bromo-5-pyridyl)-2,2′:6′,2″-terpyridine-\k^3*N*,*N*′,*N*″]bis(triphenylphosphine-*κP*)copper(I) tetrafluoridoborate dichloromethane hemisolvate

Crystal data

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Triclinic, $P\overline{1}$
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c = 15.2549 (5) Å
α = 72.358 (1)°
β = 83.6520 (11)°
γ = 69.821 (1)°
V = 2646.23 (16) Å^3
Z = 2
F(000) = 1126
D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6660 reflections
θ = 2.4–29.9°
μ = 1.33 mm^{-1}
T = 150 K
Prism, yellow
0.34 × 0.30 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker,2000)
T_{min} = 0.627, T_{max} = 0.698
22637 measured reflections
9368 independent reflections
7361 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.1°, θ_{min} = 1.6°
h = −16→16
k = −16→16
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.209$
$S = 1.05$
9368 reflections
676 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
$w = 1/[\sigma^2(F_o^2) + (0.020P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.37$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.20583 (3)	0.25255 (3)	0.24907 (3)	0.04279 (18)	
P1	0.14443 (7)	0.14203 (7)	0.36391 (6)	0.0424 (2)	
P2	0.14842 (7)	0.43189 (7)	0.22730 (6)	0.0421 (2)	
Br1	0.92793 (5)	0.11921 (7)	−0.14023 (5)	0.1063 (3)	
C1	0.2577 (3)	0.1842 (3)	0.0794 (2)	0.0425 (8)	
N2	0.1746 (2)	0.2181 (2)	0.1297 (2)	0.0445 (7)	
C3	0.0854 (3)	0.2164 (3)	0.1056 (3)	0.0512 (9)	
H3	0.0271	0.2395	0.1401	0.061*	
C4	0.0758 (3)	0.1823 (3)	0.0324 (3)	0.0561 (10)	
H4	0.0127	0.1814	0.0185	0.067*	
C5	0.1597 (4)	0.1501 (4)	−0.0192 (3)	0.0620 (11)	
H5	0.1550	0.1285	−0.0700	0.074*	
C6	0.2523 (3)	0.1499 (4)	0.0052 (3)	0.0566 (10)	
H6	0.3112	0.1266	−0.0286	0.068*	
C7	0.3570 (3)	0.1824 (3)	0.1106 (2)	0.0441 (8)	
N8	0.3551 (2)	0.1939 (2)	0.19544 (19)	0.0411 (6)	
C9	0.4458 (3)	0.1841 (3)	0.2282 (2)	0.0443 (8)	
C10	0.5351 (3)	0.1692 (3)	0.1767 (3)	0.0500 (9)	
H10	0.5955	0.1638	0.2018	0.060*	
C11	0.5357 (3)	0.1621 (3)	0.0882 (3)	0.0527 (9)	
C12	0.4434 (3)	0.1683 (3)	0.0561 (3)	0.0522 (9)	
H12	0.4401	0.1630	−0.0028	0.063*	
C13	0.4479 (3)	0.1911 (3)	0.3233 (3)	0.0481 (9)	
N14	0.3784 (3)	0.2734 (4)	0.3441 (3)	0.0770 (12)	
C15	0.3831 (4)	0.2848 (5)	0.4277 (4)	0.093 (2)	

H15	0.3356	0.3435	0.4426	0.111*
C16	0.4552 (4)	0.2135 (4)	0.4927 (3)	0.0720 (13)
H16	0.4558	0.2234	0.5502	0.086*
C17	0.5253 (4)	0.1286 (4)	0.4703 (3)	0.0802 (15)
H17	0.5746	0.0788	0.5125	0.096*
C18	0.5220 (4)	0.1176 (4)	0.3841 (3)	0.0754 (14)
H18	0.5699	0.0605	0.3672	0.090*
C19	0.6294 (3)	0.1514 (4)	0.0300 (3)	0.0568 (10)
C20	0.7254 (3)	0.1068 (4)	0.0688 (3)	0.0617 (11)
H20	0.7302	0.0818	0.1325	0.074*
N21	0.8130 (3)	0.0976 (4)	0.0186 (3)	0.0759 (11)
C22	0.8033 (4)	0.1336 (4)	−0.0706 (3)	0.0706 (13)
C23	0.7126 (4)	0.1801 (6)	−0.1162 (3)	0.094 (2)
H23	0.7098	0.2065	−0.1799	0.113*
C24	0.6260 (4)	0.1859 (6)	−0.0639 (3)	0.0886 (18)
H24	0.5627	0.2142	−0.0928	0.106*
C25	0.2110 (3)	−0.0005 (3)	0.3844 (3)	0.0464 (8)
C26	0.2852 (3)	−0.0364 (3)	0.3229 (3)	0.0553 (10)
H26	0.2997	0.0125	0.2710	0.066*
C27	0.3377 (4)	−0.1427 (4)	0.3369 (3)	0.0652 (12)
H27	0.3861	−0.1654	0.2939	0.078*
C28	0.3195 (4)	−0.2154 (4)	0.4136 (4)	0.0664 (12)
H28	0.3567	−0.2873	0.4238	0.080*
C29	0.2447 (4)	−0.1817 (4)	0.4767 (4)	0.0714 (13)
H29	0.2309	−0.2311	0.5286	0.086*
C30	0.1917 (4)	−0.0750 (3)	0.4616 (3)	0.0627 (11)
H30	0.1420	−0.0525	0.5038	0.075*
C31	0.1328 (3)	0.1546 (3)	0.4806 (2)	0.0470 (8)
C32	0.0418 (3)	0.1829 (4)	0.5276 (3)	0.0614 (11)
H32	−0.0196	0.1946	0.5006	0.074*
C33	0.0415 (4)	0.1939 (4)	0.6151 (3)	0.0769 (14)
H33	−0.0205	0.2146	0.6459	0.092*
C34	0.1310 (5)	0.1749 (4)	0.6562 (3)	0.0814 (15)
H34	0.1305	0.1811	0.7153	0.098*
C35	0.2224 (4)	0.1463 (5)	0.6098 (4)	0.0791 (14)
H35	0.2839	0.1337	0.6371	0.095*
C36	0.2222 (4)	0.1364 (4)	0.5239 (3)	0.0690 (12)
H36	0.2844	0.1168	0.4932	0.083*
C37	0.0140 (3)	0.1617 (3)	0.3331 (3)	0.0479 (9)
C38	−0.0562 (3)	0.2630 (4)	0.3151 (3)	0.0592 (10)
H38	−0.0376	0.3168	0.3249	0.071*
C39	−0.1537 (4)	0.2871 (4)	0.2829 (3)	0.0755 (14)
H39	−0.1998	0.3561	0.2704	0.091*
C40	−0.1806 (4)	0.2059 (5)	0.2698 (4)	0.0886 (18)
H40	−0.2463	0.2203	0.2496	0.106*
C41	−0.1129 (4)	0.1057 (5)	0.2861 (4)	0.0846 (16)
H41	−0.1322	0.0523	0.2763	0.102*
C42	−0.0139 (4)	0.0821 (4)	0.3176 (3)	0.0675 (12)

H42	0.0327	0.0135	0.3279	0.081*	
C43	0.2107 (3)	0.5033 (3)	0.1301 (3)	0.0493 (9)	
C44	0.1596 (4)	0.5978 (3)	0.0671 (3)	0.0603 (11)	
H44	0.0897	0.6302	0.0748	0.072*	
C45	0.2102 (4)	0.6449 (4)	−0.0066 (3)	0.0719 (13)	
H45	0.1741	0.7088	−0.0479	0.086*	
C46	0.3115 (5)	0.5999 (4)	−0.0199 (4)	0.0875 (16)	
H46	0.3454	0.6324	−0.0697	0.105*	
C47	0.3642 (5)	0.5046 (5)	0.0416 (6)	0.122 (3)	
H47	0.4336	0.4719	0.0319	0.146*	
C48	0.3150 (4)	0.4572 (4)	0.1173 (5)	0.097 (2)	
H48	0.3518	0.3945	0.1596	0.116*	
C49	0.0116 (3)	0.5008 (3)	0.1992 (3)	0.0460 (8)	
C50	−0.0272 (3)	0.4842 (3)	0.1281 (3)	0.0564 (10)	
H50	0.0159	0.4392	0.0955	0.068*	
C51	−0.1297 (4)	0.5335 (4)	0.1045 (3)	0.0687 (12)	
H51	−0.1548	0.5233	0.0552	0.082*	
C52	−0.1947 (4)	0.5982 (4)	0.1549 (4)	0.0745 (13)	
H52	−0.2637	0.6316	0.1396	0.089*	
C53	−0.1570 (4)	0.6124 (4)	0.2264 (4)	0.0788 (14)	
H53	−0.2012	0.6537	0.2614	0.095*	
C54	−0.0542 (3)	0.5666 (4)	0.2483 (3)	0.0645 (11)	
H54	−0.0290	0.5798	0.2959	0.077*	
C55	0.1621 (3)	0.4779 (3)	0.3233 (3)	0.0533 (10)	
C56	0.1300 (4)	0.4313 (4)	0.4090 (3)	0.0671 (12)	
H56	0.1031	0.3768	0.4164	0.080*	
C57	0.1369 (5)	0.4640 (5)	0.4846 (4)	0.0859 (16)	
H57	0.1153	0.4311	0.5422	0.103*	
C58	0.1750 (6)	0.5437 (7)	0.4745 (5)	0.114 (3)	
H58	0.1799	0.5655	0.5252	0.137*	
C59	0.2066 (6)	0.5925 (6)	0.3891 (6)	0.115 (2)	
H59	0.2325	0.6475	0.3823	0.138*	
C60	0.2000 (4)	0.5602 (4)	0.3137 (4)	0.0809 (15)	
H60	0.2212	0.5938	0.2561	0.097*	
F1	0.6777 (3)	0.8864 (3)	0.1912 (2)	0.1053 (11)	
F2	0.5358 (3)	0.9296 (3)	0.2740 (3)	0.1141 (12)	
F3	0.6069 (4)	0.7686 (4)	0.2744 (5)	0.195 (3)	
F4	0.5314 (5)	0.8907 (7)	0.1460 (3)	0.210 (3)	
B1	0.5864 (5)	0.8693 (5)	0.2184 (4)	0.0722 (15)	
Cl1	0.5274 (16)	0.480 (2)	0.2408 (12)	0.357 (16)	0.30
Cl2	0.5825 (17)	0.5107 (10)	0.3935 (10)	0.198 (6)	0.30
Cl3	0.5682 (8)	0.5078 (11)	0.2081 (10)	0.135 (4)	0.20
Cl4	0.572 (2)	0.458 (2)	0.394 (2)	0.253 (16)	0.20
C1S	0.538 (2)	0.5698 (13)	0.2990 (17)	0.179 (11)	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0430 (3)	0.0470 (3)	0.0407 (3)	−0.0171 (2)	0.00886 (19)	−0.0164 (2)
P1	0.0416 (5)	0.0477 (5)	0.0399 (5)	−0.0176 (4)	0.0068 (4)	−0.0144 (4)
P2	0.0424 (5)	0.0432 (5)	0.0417 (5)	−0.0145 (4)	0.0020 (4)	−0.0140 (4)
Br1	0.0707 (4)	0.1666 (7)	0.1063 (5)	−0.0550 (4)	0.0471 (3)	−0.0720 (5)
C1	0.0425 (19)	0.050 (2)	0.0368 (18)	−0.0154 (16)	0.0010 (15)	−0.0143 (15)
N2	0.0435 (17)	0.0546 (18)	0.0385 (15)	−0.0180 (14)	0.0016 (13)	−0.0164 (14)
C3	0.045 (2)	0.062 (2)	0.048 (2)	−0.0187 (18)	0.0017 (17)	−0.0188 (18)
C4	0.049 (2)	0.068 (3)	0.056 (2)	−0.021 (2)	−0.0093 (18)	−0.019 (2)
C5	0.067 (3)	0.077 (3)	0.055 (2)	−0.023 (2)	−0.004 (2)	−0.037 (2)
C6	0.051 (2)	0.077 (3)	0.049 (2)	−0.020 (2)	0.0080 (18)	−0.033 (2)
C7	0.0419 (19)	0.054 (2)	0.0382 (18)	−0.0168 (16)	0.0023 (15)	−0.0160 (16)
N8	0.0414 (16)	0.0501 (16)	0.0341 (14)	−0.0162 (13)	0.0010 (12)	−0.0141 (13)
C9	0.0401 (19)	0.051 (2)	0.0398 (18)	−0.0117 (16)	0.0002 (15)	−0.0141 (16)
C10	0.040 (2)	0.069 (2)	0.046 (2)	−0.0213 (18)	0.0035 (16)	−0.0202 (19)
C11	0.041 (2)	0.068 (2)	0.052 (2)	−0.0188 (18)	0.0099 (17)	−0.0246 (19)
C12	0.051 (2)	0.071 (3)	0.0404 (19)	−0.0231 (19)	0.0051 (16)	−0.0229 (19)
C13	0.043 (2)	0.063 (2)	0.0420 (19)	−0.0186 (17)	0.0001 (16)	−0.0193 (18)
N14	0.057 (2)	0.105 (3)	0.060 (2)	0.007 (2)	−0.0119 (18)	−0.045 (2)
C15	0.069 (3)	0.129 (5)	0.069 (3)	0.015 (3)	−0.016 (3)	−0.061 (3)
C16	0.066 (3)	0.110 (4)	0.049 (2)	−0.028 (3)	−0.005 (2)	−0.036 (3)
C17	0.085 (4)	0.086 (3)	0.059 (3)	−0.006 (3)	−0.027 (3)	−0.021 (3)
C18	0.081 (3)	0.070 (3)	0.062 (3)	0.004 (2)	−0.025 (2)	−0.025 (2)
C19	0.047 (2)	0.079 (3)	0.055 (2)	−0.025 (2)	0.0132 (18)	−0.032 (2)
C20	0.045 (2)	0.080 (3)	0.056 (2)	−0.017 (2)	0.0085 (18)	−0.022 (2)
N21	0.052 (2)	0.098 (3)	0.079 (3)	−0.023 (2)	0.016 (2)	−0.035 (2)
C22	0.058 (3)	0.107 (4)	0.065 (3)	−0.039 (3)	0.027 (2)	−0.045 (3)
C23	0.069 (3)	0.182 (6)	0.052 (3)	−0.061 (4)	0.021 (2)	−0.047 (3)
C24	0.052 (3)	0.163 (6)	0.055 (3)	−0.039 (3)	0.005 (2)	−0.037 (3)
C25	0.050 (2)	0.047 (2)	0.047 (2)	−0.0210 (17)	0.0045 (16)	−0.0153 (16)
C26	0.061 (2)	0.055 (2)	0.051 (2)	−0.0209 (19)	0.0088 (19)	−0.0172 (19)
C27	0.065 (3)	0.061 (3)	0.075 (3)	−0.019 (2)	0.012 (2)	−0.035 (2)
C28	0.065 (3)	0.050 (2)	0.087 (3)	−0.017 (2)	−0.002 (2)	−0.025 (2)
C29	0.081 (3)	0.051 (2)	0.075 (3)	−0.028 (2)	−0.003 (3)	0.000 (2)
C30	0.066 (3)	0.060 (3)	0.061 (3)	−0.024 (2)	0.015 (2)	−0.017 (2)
C31	0.052 (2)	0.051 (2)	0.0407 (19)	−0.0201 (17)	0.0067 (16)	−0.0157 (16)
C32	0.056 (2)	0.076 (3)	0.052 (2)	−0.023 (2)	0.0119 (19)	−0.021 (2)
C33	0.081 (3)	0.095 (4)	0.055 (3)	−0.027 (3)	0.023 (2)	−0.032 (3)
C34	0.123 (5)	0.082 (3)	0.049 (3)	−0.039 (3)	0.005 (3)	−0.029 (2)
C35	0.075 (3)	0.104 (4)	0.070 (3)	−0.028 (3)	−0.008 (3)	−0.042 (3)
C36	0.058 (3)	0.094 (3)	0.065 (3)	−0.022 (2)	0.005 (2)	−0.042 (3)
C37	0.047 (2)	0.057 (2)	0.0415 (19)	−0.0252 (18)	0.0051 (16)	−0.0085 (17)
C38	0.054 (2)	0.066 (3)	0.056 (2)	−0.026 (2)	0.0071 (19)	−0.010 (2)
C39	0.053 (3)	0.085 (3)	0.070 (3)	−0.018 (2)	−0.002 (2)	−0.001 (3)
C40	0.064 (3)	0.114 (5)	0.081 (4)	−0.045 (3)	−0.021 (3)	0.007 (3)
C41	0.084 (4)	0.094 (4)	0.088 (4)	−0.048 (3)	−0.026 (3)	−0.013 (3)

C42	0.068 (3)	0.073 (3)	0.065 (3)	−0.032 (2)	−0.010 (2)	−0.011 (2)
C43	0.049 (2)	0.049 (2)	0.056 (2)	−0.0223 (17)	0.0070 (17)	−0.0179 (18)
C44	0.058 (2)	0.054 (2)	0.060 (2)	−0.019 (2)	0.002 (2)	−0.004 (2)
C45	0.078 (3)	0.069 (3)	0.063 (3)	−0.032 (3)	0.001 (2)	−0.003 (2)
C46	0.092 (4)	0.072 (3)	0.084 (4)	−0.035 (3)	0.029 (3)	−0.002 (3)
C47	0.058 (3)	0.094 (4)	0.171 (7)	−0.018 (3)	0.045 (4)	0.000 (4)
C48	0.054 (3)	0.067 (3)	0.127 (5)	−0.015 (2)	0.019 (3)	0.020 (3)
C49	0.045 (2)	0.0449 (19)	0.047 (2)	−0.0159 (16)	0.0026 (16)	−0.0111 (16)
C50	0.055 (2)	0.059 (2)	0.054 (2)	−0.0156 (19)	−0.0010 (19)	−0.0178 (19)
C51	0.066 (3)	0.071 (3)	0.069 (3)	−0.025 (2)	−0.018 (2)	−0.010 (2)
C52	0.050 (3)	0.075 (3)	0.086 (3)	−0.012 (2)	−0.004 (2)	−0.015 (3)
C53	0.052 (3)	0.084 (3)	0.089 (4)	0.001 (2)	0.003 (2)	−0.037 (3)
C54	0.056 (3)	0.070 (3)	0.063 (3)	−0.007 (2)	0.002 (2)	−0.029 (2)
C55	0.050 (2)	0.053 (2)	0.057 (2)	−0.0073 (18)	−0.0081 (18)	−0.0253 (19)
C56	0.074 (3)	0.070 (3)	0.054 (3)	−0.013 (2)	−0.001 (2)	−0.026 (2)
C57	0.086 (4)	0.105 (4)	0.060 (3)	−0.003 (3)	−0.005 (3)	−0.044 (3)
C58	0.109 (5)	0.132 (6)	0.115 (6)	0.002 (4)	−0.028 (4)	−0.093 (5)
C59	0.132 (6)	0.125 (5)	0.135 (6)	−0.057 (5)	−0.007 (5)	−0.083 (5)
C60	0.093 (4)	0.082 (3)	0.091 (4)	−0.044 (3)	0.002 (3)	−0.041 (3)
F1	0.095 (2)	0.166 (3)	0.081 (2)	−0.066 (2)	0.0291 (17)	−0.056 (2)
F2	0.109 (3)	0.126 (3)	0.115 (3)	−0.034 (2)	0.037 (2)	−0.063 (2)
F3	0.139 (4)	0.091 (3)	0.313 (8)	−0.025 (3)	0.088 (5)	−0.045 (4)
F4	0.169 (5)	0.441 (11)	0.108 (3)	−0.177 (6)	0.006 (3)	−0.116 (5)
B1	0.075 (4)	0.082 (4)	0.062 (3)	−0.025 (3)	0.016 (3)	−0.030 (3)
Cl1	0.31 (2)	0.76 (5)	0.216 (14)	−0.42 (3)	0.076 (14)	−0.20 (2)
Cl2	0.311 (19)	0.125 (9)	0.140 (10)	−0.073 (10)	−0.049 (11)	0.004 (8)
Cl3	0.090 (6)	0.201 (11)	0.159 (11)	−0.066 (7)	0.003 (6)	−0.096 (9)
Cl4	0.27 (2)	0.20 (2)	0.20 (2)	−0.12 (2)	−0.069 (17)	0.14 (2)
C1S	0.27 (3)	0.078 (9)	0.20 (2)	−0.092 (13)	0.14 (2)	−0.066 (12)

Geometric parameters (Å, º)

Cu1—N8	2.121 (3)	C32—C33	1.389 (7)
Cu1—N2	2.142 (3)	C32—H32	0.9300
Cu1—P1	2.2621 (10)	C33—C34	1.362 (8)
Cu1—P2	2.2788 (10)	C33—H33	0.9300
P1—C31	1.826 (4)	C34—C35	1.376 (8)
P1—C25	1.824 (4)	C34—H34	0.9300
P1—C37	1.829 (4)	C35—C36	1.360 (7)
P2—C55	1.819 (4)	C35—H35	0.9300
P2—C43	1.832 (4)	C36—H36	0.9300
P2—C49	1.841 (4)	C37—C38	1.377 (6)
Br1—C22	1.910 (4)	C37—C42	1.386 (6)
C1—N2	1.339 (5)	C38—C39	1.387 (6)
C1—C6	1.374 (5)	C38—H38	0.9300
C1—C7	1.498 (5)	C39—C40	1.382 (8)
N2—C3	1.340 (5)	C39—H39	0.9300
C3—C4	1.375 (6)	C40—C41	1.355 (8)

C3—H3	0.9300	C40—H40	0.9300
C4—C5	1.352 (6)	C41—C42	1.403 (7)
C4—H4	0.9300	C41—H41	0.9300
C5—C6	1.376 (6)	C42—H42	0.9300
C5—H5	0.9300	C43—C44	1.380 (6)
C6—H6	0.9300	C43—C48	1.386 (6)
C7—N8	1.347 (5)	C44—C45	1.374 (6)
C7—C12	1.374 (5)	C44—H44	0.9300
N8—C9	1.355 (5)	C45—C46	1.349 (7)
C9—C10	1.380 (5)	C45—H45	0.9300
C9—C13	1.488 (5)	C46—C47	1.382 (9)
C10—C11	1.383 (5)	C46—H46	0.9300
C10—H10	0.9300	C47—C48	1.383 (8)
C11—C12	1.387 (6)	C47—H47	0.9300
C11—C19	1.481 (5)	C48—H48	0.9300
C12—H12	0.9300	C49—C50	1.374 (6)
C13—N14	1.319 (5)	C49—C54	1.388 (6)
C13—C18	1.371 (6)	C50—C51	1.384 (6)
N14—C15	1.345 (6)	C50—H50	0.9300
C15—C16	1.382 (7)	C51—C52	1.388 (7)
C15—H15	0.9300	C51—H51	0.9300
C16—C17	1.358 (7)	C52—C53	1.354 (7)
C16—H16	0.9300	C52—H52	0.9300
C17—C18	1.377 (7)	C53—C54	1.381 (7)
C17—H17	0.9300	C53—H53	0.9300
C18—H18	0.9300	C54—H54	0.9300
C19—C24	1.366 (7)	C55—C56	1.374 (6)
C19—C20	1.376 (6)	C55—C60	1.385 (6)
C20—N21	1.353 (6)	C56—C57	1.386 (7)
C20—H20	0.9300	C56—H56	0.9300
N21—C22	1.304 (6)	C57—C58	1.352 (10)
C22—C23	1.359 (7)	C57—H57	0.9300
C23—C24	1.360 (7)	C58—C59	1.376 (11)
C23—H23	0.9300	C58—H58	0.9300
C24—H24	0.9300	C59—C60	1.379 (8)
C25—C26	1.382 (5)	C59—H59	0.9300
C25—C30	1.386 (6)	C60—H60	0.9300
C26—C27	1.370 (6)	F1—B1	1.368 (7)
C26—H26	0.9300	F2—B1	1.346 (6)
C27—C28	1.362 (7)	F3—B1	1.355 (8)
C27—H27	0.9300	F4—B1	1.313 (8)
C28—C29	1.394 (7)	Cl1—Cl3	0.835 (16)
C28—H28	0.9300	Cl1—C1S	1.79 (3)
C29—C30	1.374 (6)	Cl1—Cl4	2.39 (4)
C29—H29	0.9300	Cl2—Cl4	0.79 (3)
C30—H30	0.9300	Cl2—C1S	1.51 (3)
C31—C32	1.376 (6)	Cl3—C1S	1.79 (2)
C31—C36	1.379 (6)	Cl4—C1S	1.74 (3)

N8—Cu1—N2	77.85 (11)	C31—C32—C33	120.2 (4)
N8—Cu1—P1	119.66 (8)	C31—C32—H32	119.9
N2—Cu1—P1	102.16 (8)	C33—C32—H32	119.9
N8—Cu1—P2	113.91 (8)	C34—C33—C32	120.6 (5)
N2—Cu1—P2	109.81 (9)	C34—C33—H33	119.7
P1—Cu1—P2	121.80 (4)	C32—C33—H33	119.7
C31—P1—C25	101.36 (17)	C33—C34—C35	119.6 (4)
C31—P1—C37	104.69 (18)	C33—C34—H34	120.2
C25—P1—C37	104.55 (18)	C35—C34—H34	120.2
C31—P1—Cu1	120.24 (12)	C36—C35—C34	119.6 (5)
C25—P1—Cu1	116.95 (12)	C36—C35—H35	120.2
C37—P1—Cu1	107.44 (12)	C34—C35—H35	120.2
C55—P2—C43	104.72 (19)	C35—C36—C31	122.2 (5)
C55—P2—C49	102.07 (17)	C35—C36—H36	118.9
C43—P2—C49	102.12 (17)	C31—C36—H36	118.9
C55—P2—Cu1	116.80 (13)	C38—C37—C42	118.7 (4)
C43—P2—Cu1	113.20 (13)	C38—C37—P1	118.2 (3)
C49—P2—Cu1	116.11 (12)	C42—C37—P1	122.8 (3)
N2—C1—C6	121.6 (3)	C37—C38—C39	122.0 (4)
N2—C1—C7	116.2 (3)	C37—C38—H38	119.0
C6—C1—C7	122.2 (3)	C39—C38—H38	119.0
C1—N2—C3	117.6 (3)	C40—C39—C38	118.3 (5)
C1—N2—Cu1	114.3 (2)	C40—C39—H39	120.9
C3—N2—Cu1	127.8 (3)	C38—C39—H39	120.9
N2—C3—C4	123.2 (4)	C41—C40—C39	121.0 (5)
N2—C3—H3	118.4	C41—C40—H40	119.5
C4—C3—H3	118.4	C39—C40—H40	119.5
C5—C4—C3	119.0 (4)	C40—C41—C42	120.4 (5)
C5—C4—H4	120.5	C40—C41—H41	119.8
C3—C4—H4	120.5	C42—C41—H41	119.8
C4—C5—C6	118.7 (4)	C37—C42—C41	119.5 (5)
C4—C5—H5	120.7	C37—C42—H42	120.2
C6—C5—H5	120.7	C41—C42—H42	120.2
C1—C6—C5	120.0 (4)	C44—C43—C48	118.2 (4)
C1—C6—H6	120.0	C44—C43—P2	124.1 (3)
C5—C6—H6	120.0	C48—C43—P2	117.7 (3)
N8—C7—C12	123.3 (3)	C45—C44—C43	121.1 (4)
N8—C7—C1	115.3 (3)	C45—C44—H44	119.4
C12—C7—C1	121.4 (3)	C43—C44—H44	119.4
C7—N8—C9	116.4 (3)	C46—C45—C44	121.0 (5)
C7—N8—Cu1	114.5 (2)	C46—C45—H45	119.5
C9—N8—Cu1	128.1 (2)	C44—C45—H45	119.5
N8—C9—C10	122.7 (3)	C45—C46—C47	119.0 (5)
N8—C9—C13	118.0 (3)	C45—C46—H46	120.5
C10—C9—C13	119.2 (3)	C47—C46—H46	120.5
C9—C10—C11	120.6 (3)	C46—C47—C48	120.9 (5)
C9—C10—H10	119.7	C46—C47—H47	119.6

C11—C10—H10	119.7	C48—C47—H47	119.6
C10—C11—C12	116.5 (3)	C43—C48—C47	119.8 (5)
C10—C11—C19	121.5 (4)	C43—C48—H48	120.1
C12—C11—C19	122.0 (4)	C47—C48—H48	120.1
C7—C12—C11	120.4 (3)	C50—C49—C54	118.9 (4)
C7—C12—H12	119.8	C50—C49—P2	118.5 (3)
C11—C12—H12	119.8	C54—C49—P2	122.7 (3)
N14—C13—C18	122.4 (4)	C49—C50—C51	120.9 (4)
N14—C13—C9	116.7 (3)	C49—C50—H50	119.6
C18—C13—C9	120.8 (4)	C51—C50—H50	119.6
C13—N14—C15	117.6 (4)	C50—C51—C52	119.6 (4)
N14—C15—C16	123.1 (5)	C50—C51—H51	120.2
N14—C15—H15	118.4	C52—C51—H51	120.2
C16—C15—H15	118.4	C53—C52—C51	119.5 (4)
C17—C16—C15	118.2 (4)	C53—C52—H52	120.2
C17—C16—H16	120.9	C51—C52—H52	120.2
C15—C16—H16	120.9	C52—C53—C54	121.2 (5)
C16—C17—C18	118.9 (4)	C52—C53—H53	119.4
C16—C17—H17	120.5	C54—C53—H53	119.4
C18—C17—H17	120.5	C53—C54—C49	119.9 (4)
C13—C18—C17	119.7 (4)	C53—C54—H54	120.1
C13—C18—H18	120.2	C49—C54—H54	120.1
C17—C18—H18	120.2	C56—C55—C60	118.4 (4)
C24—C19—C20	116.4 (4)	C56—C55—P2	118.4 (3)
C24—C19—C11	122.6 (4)	C60—C55—P2	123.2 (4)
C20—C19—C11	121.0 (4)	C55—C56—C57	121.2 (5)
N21—C20—C19	123.1 (4)	C55—C56—H56	119.4
N21—C20—H20	118.4	C57—C56—H56	119.4
C19—C20—H20	118.4	C58—C57—C56	119.9 (6)
C22—N21—C20	116.8 (4)	C58—C57—H57	120.0
N21—C22—C23	125.0 (4)	C56—C57—H57	120.0
N21—C22—Br1	116.1 (4)	C57—C58—C59	120.0 (5)
C23—C22—Br1	118.8 (4)	C57—C58—H58	120.0
C22—C23—C24	116.7 (5)	C59—C58—H58	120.0
C22—C23—H23	121.6	C58—C59—C60	120.4 (6)
C24—C23—H23	121.6	C58—C59—H59	119.8
C23—C24—C19	121.9 (5)	C60—C59—H59	119.8
C23—C24—H24	119.1	C59—C60—C55	120.2 (6)
C19—C24—H24	119.1	C59—C60—H60	119.9
C26—C25—C30	118.1 (4)	C55—C60—H60	119.9
C26—C25—P1	119.7 (3)	F4—B1—F2	110.9 (6)
C30—C25—P1	122.2 (3)	F4—B1—F3	114.6 (7)
C27—C26—C25	121.2 (4)	F2—B1—F3	103.3 (5)
C27—C26—H26	119.4	F4—B1—F1	109.8 (5)
C25—C26—H26	119.4	F2—B1—F1	109.9 (5)
C28—C27—C26	120.4 (4)	F3—B1—F1	108.1 (5)
C28—C27—H27	119.8	Cl3—Cl1—C1S	76.2 (18)
C26—C27—H27	119.8	Cl3—Cl1—Cl4	103.8 (16)

C27—C28—C29	119.8 (4)	C1S—Cl1—Cl4	46.5 (10)
C27—C28—H28	120.1	Cl4—Cl2—C1S	93 (3)
C29—C28—H28	120.1	Cl1—Cl3—C1S	76.9 (19)
C30—C29—C28	119.4 (4)	Cl2—Cl4—C1S	60 (2)
C30—C29—H29	120.3	Cl2—Cl4—Cl1	107 (3)
C28—C29—H29	120.3	C1S—Cl4—Cl1	48.5 (11)
C29—C30—C25	121.1 (4)	Cl2—C1S—Cl1	111.1 (13)
C29—C30—H30	119.4	Cl2—C1S—Cl4	27.1 (12)
C25—C30—H30	119.4	Cl1—C1S—Cl4	85.0 (16)
C32—C31—C36	117.9 (4)	Cl2—C1S—Cl3	121.0 (14)
C32—C31—P1	124.9 (3)	Cl1—C1S—Cl3	27.0 (6)
C36—C31—P1	117.2 (3)	Cl4—C1S—Cl3	100.4 (16)