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A solvent-free modification of {2,6-bis-[(1,3-di-*tert*-butylimidazolin-2-ylidene-amino)methyl]pyridine}(hydrogen carbonato)copper(II) hexafluorido-phosphate

Peter G. Jones,* Cristian G. Hrib, Dejan Petrovic and Matthias Tamm

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
Correspondence e-mail: p.jones@tu-bs.de

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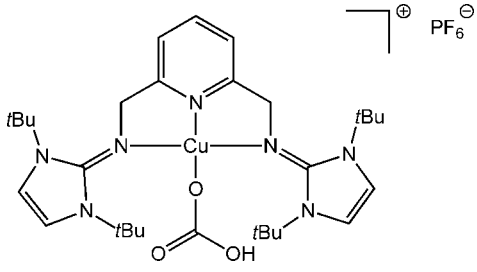
Key indicators: single-crystal X-ray study; T = 133 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.098; data-to-parameter ratio = 19.6.

A new crystal form of the title compound, $[Cu(CHO_3)(C_{29}H_{47}N_7)]PF_6$, is closely similar in cation geometry to the previously reported acetone solvate [Petrovic, Bannenberg, Randoll, Jones & Tamm (2007). *Dalton Trans.* pp. 2812–2822]. The coordination at the Cu atom is square planar, although the O atom lies 0.224 (5) Å out of the N_3 ligand plane. The cations are associated to form inversion-symmetric dimers *via* hydrogen bonding between bicarbonate units.

Related literature

For related literature, see: Darensbourg *et al.* (1996); Hossain *et al.* (1981); Ito *et al.* (1994); Jazzar *et al.* (2003); Kim *et al.* (2004); Petrovic *et al.* (2007); Steiner (2002).



Experimental

Crystal data

$[Cu(CHO_3)(C_{29}H_{47}N_7)]PF_6$
M_r = 763.26
Triclinic, $P\overline{1}$
a = 9.0309 (12) Å
b = 13.824 (2) Å
c = 15.654 (2) Å
α = 109.619 (3)°
β = 101.729 (4)°
γ = 94.164 (3)°
V = 1781.2 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.73 mm^{-1}
T = 133 (2) K
0.20 × 0.11 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.868, T_{max} = 0.944
33075 measured reflections
8789 independent reflections
6166 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.098
S = 1.01
8789 reflections
449 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9205 (16)	Cu—N2	1.9449 (17)
Cu—N1	1.9318 (17)	Cu—N3	1.9689 (18)
O1—Cu—N1	170.38 (8)	O1—Cu—N3	98.51 (7)
O1—Cu—N2	97.30 (7)	N1—Cu—N3	81.77 (8)
N1—Cu—N2	81.77 (7)	N2—Cu—N3	163.36 (7)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O2^{i}	0.88 (4)	1.73 (4)	2.599 (3)	173 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2543).

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supplementary materials

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A solvent-free modification of {2,6-bis[(1,3-di-*tert*-butylimidazolin-2-ylideneamino)methyl]pyridine}(hydrogen carbonato)copper(II) hexafluoridophosphate

P. G. Jones, C. G. Hrib, D. Petrovic and M. Tamm

Comment

As we have recently demonstrated (Petrovic *et al.*, 2007), copper(I) complexes of the highly basic pincer ligand 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine, T*L*$^{t\mathrm{Bu}}$, are extremely reactive and exhibit a pronounced tendency to form stable, square-planar copper(II) complexes. Exposure of an acetone solution of [(T*L*$^{t\mathrm{Bu}}$)Cu]PF_6 to the air readily leads to oxidation and trapping of atmospheric CO_2 to form the square-planar complex [(T*L*^{t}Bu)Cu(HCO_3-κ*O*)]PF_6 with the bicarbonate ligand adopting a rarely observed monodentate coordination mode. The compound was previously crystallized as an acetone solvate (Petrovic *et al.*, 2007). Here we report the structure of the solvent-free material. All structural features of the cation [(T*L*$^{t\mathrm{Bu}}$)Cu(HCO_3-κ*O*)]$^+$ are very similar to those of the acetone solvate. The copper center displays a slightly distorted square-planar environment; the sum of the four *cis* angles is 359.38°. The copper atom lies 0.049 (2) Å out of the plane defined by the donor atoms N1, N2 and N3. The displacement of the metal-bound oxygen atom O1 of the bicarbonate ligand, 0.224 (5) Å in the opposite direction, is considerably greater, which is presumably a consequence of minimizing the steric interaction with the bulky di-*tert*-butylimidazolin-2-ylidene moieties. As a result, the N1—Cu—O1 angle of 170.38 (8)° deviates significantly from linearity. The Cu—O1 distance of 1.9205 (16) Å is very short in comparison to the other structurally characterized copper(II) bicarbonate complexes. The angles in the bicarbonate unit are close to 120°, and the C—O distances (Table 1), with a much longer C30—O3 bond, clearly indicate that the hydrogen atom of the HCO_3 unit is bound to O_3. This was in any case confirmed by free refinement of this hydrogen position. The packing involves inversion-symmetric cation dimers bridged *via* hydrogen bonding of the bicarbonate groups (analogous to the well known "carboxylic acid dimer" type; Table 2), as observed for the acetone solvate (with two crystallographically independent formula units, each associating over an inversion centre to a dimer) and in some other transition metal bicarbonate complexes (Hossain *et al.*, 1981; Ito *et al.*, 1994; Darensbourg *et al.*, 1996; Jazzar *et al.*, 2003; Kim *et al.*, 2004).

Experimental

The title compound was prepared according to the literature procedure (Petrovic *et al.*, 2007). Crystals could be obtained selectively as clear yellow prisms by cooling the acetone solution. The compound exhibits dichroism (the previously reported acetone solvate, obtained by evaporation of an acetone solution, is deep green or red depending on the view direction), but we have not investigated this phenomenon further.

Refinement

The bicarbonate hydrogen H1 was freely refined. Methyl H atoms were included on the basis of idealized rigid groups (C—H 0.98 Å, H—C—H 109.5°) allowed to rotate but not tip. Other hydrogen atoms were included using a riding model with C—H 0.95 (aromatic) or 0.99 (methylene) Å. U(H) values were fixed at 1.2U_{iso}(C) of the parent C atom.

Figures

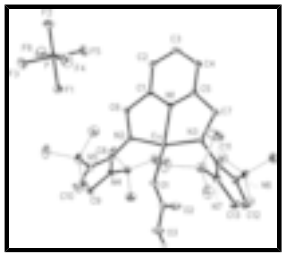


Fig. 1. The formula unit of the title compound in the crystal. Ellipsoids represent 30% probability levels. Hydrogen atoms and butyl atom labels have been omitted for clarity.

{2,6-bis[(1,3-di-*tert*-butylimidazolin-2-ylideneamino)methyl]pyridine}(hydrogen carbonato)copper(II) hexafluoridophosphate

Crystal data

$[Cu(CHO_3)(C_{29}H_{47}N_7)]PF_6$	$Z = 2$
$M_r = 763.26$	$F_{000} = 798$
Triclinic, $P\bar{1}$	$D_x = 1.423$ Mg m^{-3}
$a = 9.0309$ (12) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 13.824$ (2) Å	Cell parameters from 8159 reflections
$c = 15.654$ (2) Å	$\theta = 2$–28º
$\alpha = 109.619$ (3)º	$\mu = 0.73$ mm^{-1}
$\beta = 101.729$ (4)º	$T = 133$ (2) K
$\gamma = 94.164$ (3)º	Prism, yellow
$V = 1781.2$ (4) Å^3	0.20 × 0.11 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer	8789 independent reflections
Radiation source: fine-focus sealed tube	6166 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.053$
Detector resolution: 8.192 pixels mm^{-1}	$\theta_{max} = 28.3$º
$T = 133(2)$ K	$\theta_{min} = 1.4$º
ω and φ scans	$h = -11 \rightarrow 12$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$k = -18 \rightarrow 18$
$T_{min} = 0.868$, $T_{max} = 0.944$	$l = -20 \rightarrow 20$
33075 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 1.4465P]$ where $P = (F_o^2 + 2F_c^2)3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
8789 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
449 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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.

Least-squares planes (*x*,*y*,*z* in crystal coordinates) and deviations from them (* indicates atom used to define plane)

− 6.3861 (0.0088) *x* + 7.5326 (0.0093) *y* + 6.7527 (0.0131) *z* = 1.9001 (0.0040)

* 0.0000 (0.0000) N1 * 0.0000 (0.0000) N2 * 0.0000 (0.0000) N3 0.0486 (0.0017) Cu −0.2240 (0.0045) O1

Rms deviation of fitted atoms = 0.0000

3.0050 (0.0115) *x* + 11.4156 (0.0098) *y* − 11.5236 (0.0125) *z* = 1.4495 (0.0078)

Angle to previous plane (with approximate e.s.d.) = 89.00 (0.08)

* 0.0000 (0.0000) O1 * 0.0000 (0.0000) O2 * 0.0000 (0.0000) O3 0.0052 (0.0026) C30

Rms deviation of fitted atoms = 0.0000

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^ > 2sigma(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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.23080 (3)	0.25694 (2)	0.220239 (18)	0.01536 (8)
P	0.18744 (8)	0.18997 (5)	−0.23416 (4)	0.02368 (15)
O1	0.43029 (19)	0.31751 (13)	0.30096 (11)	0.0248 (4)
O2	0.3586 (2)	0.44446 (16)	0.40803 (13)	0.0399 (5)
O3	0.5977 (2)	0.40524 (17)	0.43152 (14)	0.0368 (5)
H1	0.607 (4)	0.458 (3)	0.484 (3)	0.066 (12)*
N1	0.0481 (2)	0.18007 (14)	0.12599 (12)	0.0153 (4)
N2	0.2354 (2)	0.33105 (14)	0.13469 (12)	0.0163 (4)
N3	0.1781 (2)	0.15538 (15)	0.27650 (13)	0.0203 (4)
N4	0.3319 (2)	0.51640 (14)	0.19051 (13)	0.0195 (4)
N5	0.4858 (2)	0.40802 (16)	0.13604 (14)	0.0221 (4)
N6	0.1977 (2)	0.23238 (15)	0.44538 (13)	0.0235 (5)

N7	0.3711 (2)	0.13706 (15)	0.39765 (13)	0.0224 (4)
F1	0.2607 (2)	0.28868 (12)	−0.14117 (11)	0.0438 (4)
F2	0.1146 (2)	0.09254 (13)	−0.32614 (12)	0.0504 (5)
F3	0.34247 (18)	0.19827 (12)	−0.26827 (12)	0.0408 (4)
F4	0.2523 (2)	0.11459 (14)	−0.18277 (13)	0.0522 (5)
F5	0.03368 (19)	0.18281 (13)	−0.19943 (12)	0.0427 (4)
F6	0.1247 (2)	0.26685 (15)	−0.28479 (13)	0.0512 (5)
C1	0.0126 (3)	0.20213 (17)	0.04791 (15)	0.0161 (4)
C2	−0.1082 (3)	0.14157 (18)	−0.02528 (16)	0.0196 (5)
H2	−0.1332	0.1554	−0.0815	0.024*
C3	−0.1921 (3)	0.05982 (18)	−0.01428 (17)	0.0234 (5)
H3	−0.2762	0.0179	−0.0634	0.028*
C4	−0.1544 (3)	0.03885 (18)	0.06722 (16)	0.0218 (5)
H4	−0.2121	−0.0167	0.0747	0.026*
C5	−0.0304 (2)	0.10082 (17)	0.13787 (15)	0.0166 (5)
C6	0.1133 (3)	0.29510 (18)	0.04916 (15)	0.0192 (5)
H6A	0.1575	0.2755	−0.0061	0.023*
H6B	0.0522	0.3512	0.0471	0.023*
C7	0.0292 (3)	0.08814 (18)	0.22988 (16)	0.0214 (5)
H7A	−0.0440	0.1077	0.2698	0.026*
H7B	0.0412	0.0147	0.2194	0.026*
C8	0.3419 (3)	0.41321 (17)	0.15052 (15)	0.0172 (5)
C9	0.4700 (3)	0.5742 (2)	0.19914 (19)	0.0297 (6)
H9	0.4936	0.6479	0.2236	0.036*
C10	0.5630 (3)	0.5087 (2)	0.16724 (19)	0.0305 (6)
H10	0.6656	0.5275	0.1659	0.037*
C11	0.2396 (3)	0.17239 (17)	0.36715 (16)	0.0189 (5)
C12	0.3025 (3)	0.2319 (2)	0.52342 (17)	0.0315 (6)
H12	0.2992	0.2660	0.5866	0.038*
C13	0.4083 (3)	0.1757 (2)	0.49465 (17)	0.0303 (6)
H13	0.4947	0.1640	0.5339	0.036*
C14	0.1976 (3)	0.56795 (18)	0.21563 (16)	0.0225 (5)
C15	0.0870 (3)	0.5000 (2)	0.2413 (2)	0.0322 (6)
H15A	0.0386	0.4385	0.1861	0.039*
H15B	0.0082	0.5396	0.2639	0.039*
H15C	0.1432	0.4783	0.2905	0.039*
C16	0.1178 (4)	0.5944 (2)	0.1323 (2)	0.0388 (7)
H16A	0.1886	0.6431	0.1208	0.047*
H16B	0.0277	0.6264	0.1458	0.047*
H16C	0.0858	0.5307	0.0768	0.047*
C17	0.2579 (4)	0.6672 (2)	0.3017 (2)	0.0426 (7)
H17A	0.3211	0.6501	0.3519	0.051*
H17B	0.1715	0.6983	0.3227	0.051*
H17C	0.3198	0.7166	0.2855	0.051*
C18	0.5652 (3)	0.3173 (2)	0.09667 (18)	0.0261 (6)
C19	0.6273 (4)	0.3355 (3)	0.0180 (2)	0.0405 (7)
H19A	0.5428	0.3431	−0.0286	0.049*
H19B	0.6757	0.2761	−0.0119	0.049*
H19C	0.7029	0.3989	0.0442	0.049*

C20	0.6955 (3)	0.3160 (2)	0.1756 (2)	0.0344 (6)
H20A	0.7660	0.3818	0.1998	0.041*
H20B	0.7508	0.2583	0.1516	0.041*
H20C	0.6534	0.3073	0.2260	0.041*
C21	0.4611 (3)	0.2128 (2)	0.0560 (2)	0.0334 (6)
H21A	0.4231	0.1988	0.1057	0.040*
H21B	0.5187	0.1579	0.0285	0.040*
H21C	0.3744	0.2144	0.0076	0.040*
C22	0.0600 (3)	0.2867 (2)	0.45535 (17)	0.0274 (6)
C23	−0.0643 (3)	0.2122 (2)	0.4646 (2)	0.0367 (7)
H23A	−0.0925	0.1497	0.4079	0.044*
H23B	−0.1544	0.2464	0.4729	0.044*
H23C	−0.0255	0.1929	0.5188	0.044*
C24	0.0022 (3)	0.3225 (2)	0.37383 (18)	0.0309 (6)
H24A	0.0861	0.3662	0.3669	0.037*
H24B	−0.0813	0.3626	0.3861	0.037*
H24C	−0.0352	0.2618	0.3162	0.037*
C25	0.1057 (4)	0.3842 (2)	0.54454 (18)	0.0353 (7)
H25A	0.1336	0.3637	0.5991	0.042*
H25B	0.0193	0.4230	0.5498	0.042*
H25C	0.1933	0.4281	0.5416	0.042*
C26	0.4527 (3)	0.05894 (19)	0.33900 (18)	0.0271 (6)
C27	0.5864 (3)	0.0373 (2)	0.4033 (2)	0.0367 (7)
H27A	0.6544	0.1025	0.4420	0.044*
H27B	0.6432	−0.0107	0.3656	0.044*
H27C	0.5475	0.0060	0.4436	0.044*
C28	0.5182 (4)	0.1009 (2)	0.2734 (2)	0.0413 (7)
H28A	0.4342	0.1107	0.2279	0.050*
H28B	0.5780	0.0512	0.2403	0.050*
H28C	0.5843	0.1676	0.3098	0.050*
C29	0.3417 (4)	−0.0418 (2)	0.2847 (3)	0.0529 (9)
H29A	0.3010	−0.0664	0.3285	0.063*
H29B	0.3954	−0.0945	0.2495	0.063*
H29C	0.2573	−0.0293	0.2413	0.063*
C30	0.4539 (3)	0.39054 (19)	0.37901 (17)	0.0235 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.01664 (14)	0.01417 (14)	0.01280 (13)	−0.00348 (11)	0.00252 (10)	0.00351 (10)
P	0.0280 (3)	0.0187 (3)	0.0246 (3)	−0.0005 (3)	0.0085 (3)	0.0079 (3)
O1	0.0226 (9)	0.0255 (9)	0.0184 (8)	−0.0075 (8)	−0.0006 (7)	0.0033 (7)
O2	0.0253 (10)	0.0459 (12)	0.0284 (10)	0.0048 (9)	−0.0034 (8)	−0.0062 (9)
O3	0.0237 (10)	0.0412 (12)	0.0266 (10)	0.0006 (9)	−0.0050 (8)	−0.0042 (9)
N1	0.0147 (9)	0.0141 (9)	0.0154 (9)	0.0002 (8)	0.0049 (7)	0.0026 (7)
N2	0.0164 (9)	0.0152 (9)	0.0160 (9)	−0.0029 (8)	0.0020 (8)	0.0061 (8)
N3	0.0241 (10)	0.0185 (10)	0.0158 (9)	−0.0056 (9)	0.0024 (8)	0.0063 (8)
N4	0.0203 (10)	0.0148 (9)	0.0224 (10)	−0.0011 (8)	0.0052 (8)	0.0062 (8)

N5	0.0171 (10)	0.0221 (10)	0.0297 (11)	0.0017 (9)	0.0076 (8)	0.0120 (9)
N6	0.0318 (12)	0.0220 (11)	0.0184 (10)	0.0032 (9)	0.0075 (9)	0.0090 (8)
N7	0.0283 (11)	0.0188 (10)	0.0194 (10)	0.0002 (9)	0.0040 (9)	0.0077 (8)
F1	0.0565 (11)	0.0339 (9)	0.0293 (8)	−0.0152 (8)	0.0116 (8)	0.0004 (7)
F2	0.0455 (10)	0.0424 (10)	0.0413 (10)	−0.0112 (9)	0.0121 (8)	−0.0101 (8)
F3	0.0379 (9)	0.0306 (9)	0.0543 (10)	−0.0012 (7)	0.0242 (8)	0.0096 (8)
F4	0.0572 (12)	0.0454 (11)	0.0690 (13)	0.0096 (9)	0.0119 (10)	0.0413 (10)
F5	0.0389 (9)	0.0346 (9)	0.0542 (11)	−0.0020 (8)	0.0263 (8)	0.0083 (8)
F6	0.0643 (12)	0.0567 (12)	0.0515 (11)	0.0241 (10)	0.0203 (10)	0.0370 (10)
C1	0.0168 (11)	0.0146 (11)	0.0159 (11)	0.0049 (9)	0.0067 (9)	0.0021 (9)
C2	0.0181 (11)	0.0196 (12)	0.0170 (11)	0.0038 (10)	0.0022 (9)	0.0023 (9)
C3	0.0171 (11)	0.0202 (12)	0.0235 (12)	−0.0017 (10)	−0.0011 (10)	0.0004 (10)
C4	0.0186 (12)	0.0155 (11)	0.0274 (13)	−0.0008 (10)	0.0064 (10)	0.0030 (10)
C5	0.0149 (11)	0.0147 (11)	0.0194 (11)	0.0025 (9)	0.0074 (9)	0.0031 (9)
C6	0.0203 (11)	0.0190 (11)	0.0175 (11)	−0.0018 (10)	0.0030 (9)	0.0076 (9)
C7	0.0210 (12)	0.0194 (12)	0.0218 (12)	−0.0050 (10)	0.0032 (10)	0.0078 (10)
C8	0.0193 (11)	0.0171 (11)	0.0165 (11)	0.0011 (9)	0.0043 (9)	0.0080 (9)
C9	0.0272 (13)	0.0205 (13)	0.0383 (15)	−0.0078 (11)	0.0033 (12)	0.0116 (11)
C10	0.0193 (12)	0.0277 (14)	0.0461 (16)	−0.0062 (11)	0.0080 (12)	0.0171 (13)
C11	0.0231 (12)	0.0136 (11)	0.0194 (11)	−0.0044 (10)	0.0051 (10)	0.0068 (9)
C12	0.0472 (17)	0.0291 (14)	0.0159 (12)	0.0080 (13)	0.0027 (12)	0.0075 (11)
C13	0.0400 (16)	0.0268 (14)	0.0206 (13)	0.0052 (12)	−0.0020 (11)	0.0095 (11)
C14	0.0270 (13)	0.0180 (12)	0.0226 (12)	0.0056 (10)	0.0076 (10)	0.0063 (10)
C15	0.0300 (14)	0.0318 (15)	0.0403 (16)	0.0102 (12)	0.0203 (12)	0.0120 (13)
C16	0.0461 (18)	0.0456 (18)	0.0350 (16)	0.0259 (15)	0.0150 (14)	0.0207 (14)
C17	0.0467 (18)	0.0300 (15)	0.0390 (17)	0.0025 (14)	0.0121 (14)	−0.0032 (13)
C18	0.0234 (12)	0.0337 (14)	0.0296 (13)	0.0111 (11)	0.0135 (11)	0.0166 (12)
C19	0.0439 (17)	0.0520 (19)	0.0454 (17)	0.0229 (15)	0.0285 (15)	0.0289 (16)
C20	0.0236 (13)	0.0438 (17)	0.0433 (16)	0.0109 (13)	0.0106 (12)	0.0226 (14)
C21	0.0311 (15)	0.0272 (14)	0.0388 (16)	0.0127 (12)	0.0119 (12)	0.0044 (12)
C22	0.0360 (15)	0.0257 (13)	0.0226 (13)	0.0042 (12)	0.0132 (11)	0.0077 (11)
C23	0.0405 (16)	0.0358 (16)	0.0383 (16)	0.0017 (13)	0.0216 (13)	0.0126 (13)
C24	0.0352 (15)	0.0304 (14)	0.0317 (14)	0.0107 (12)	0.0117 (12)	0.0138 (12)
C25	0.0501 (18)	0.0285 (15)	0.0279 (14)	0.0092 (14)	0.0170 (13)	0.0060 (12)
C26	0.0323 (14)	0.0202 (12)	0.0277 (13)	0.0062 (11)	0.0071 (11)	0.0069 (11)
C27	0.0353 (15)	0.0422 (17)	0.0435 (17)	0.0148 (14)	0.0155 (13)	0.0237 (14)
C28	0.0520 (19)	0.0480 (19)	0.0382 (16)	0.0233 (16)	0.0230 (15)	0.0232 (15)
C29	0.0393 (18)	0.0242 (15)	0.073 (2)	0.0037 (14)	0.0066 (17)	−0.0056 (15)
C30	0.0229 (12)	0.0238 (13)	0.0218 (12)	−0.0032 (11)	0.0040 (10)	0.0079 (10)

Geometric parameters (Å, °)

Cu—O1	1.9205 (16)	C13—H13	0.9500
Cu—N1	1.9318 (17)	C14—C15	1.523 (3)
Cu—N2	1.9449 (17)	C14—C16	1.527 (3)
Cu—N3	1.9689 (18)	C14—C17	1.531 (4)
P—F2	1.5824 (17)	C15—H15A	0.9800
P—F4	1.5925 (17)	C15—H15B	0.9800
P—F6	1.5967 (17)	C15—H15C	0.9800

P—F5	1.5989 (17)	C16—H16A	0.9800
P—F1	1.6007 (16)	C16—H16B	0.9800
P—F3	1.6063 (17)	C16—H16C	0.9800
O1—C30	1.262 (3)	C17—H17A	0.9800
O2—C30	1.236 (3)	C17—H17B	0.9800
O3—C30	1.349 (3)	C17—H17C	0.9800
O3—H1	0.88 (4)	C18—C21	1.522 (4)
N1—C1	1.340 (3)	C18—C20	1.530 (3)
N1—C5	1.347 (3)	C18—C19	1.538 (3)
N2—C8	1.353 (3)	C19—H19A	0.9800
N2—C6	1.459 (3)	C19—H19B	0.9800
N3—C11	1.347 (3)	C19—H19C	0.9800
N3—C7	1.473 (3)	C20—H20A	0.9800
N4—C8	1.370 (3)	C20—H20B	0.9800
N4—C9	1.388 (3)	C20—H20C	0.9800
N4—C14	1.505 (3)	C21—H21A	0.9800
N5—C8	1.367 (3)	C21—H21B	0.9800
N5—C10	1.388 (3)	C21—H21C	0.9800
N5—C18	1.503 (3)	C22—C24	1.529 (3)
N6—C11	1.372 (3)	C22—C23	1.529 (3)
N6—C12	1.387 (3)	C22—C25	1.535 (4)
N6—C22	1.507 (3)	C23—H23A	0.9800
N7—C11	1.373 (3)	C23—H23B	0.9800
N7—C13	1.388 (3)	C23—H23C	0.9800
N7—C26	1.509 (3)	C24—H24A	0.9800
C1—C2	1.385 (3)	C24—H24B	0.9800
C1—C6	1.512 (3)	C24—H24C	0.9800
C2—C3	1.393 (3)	C25—H25A	0.9800
C2—H2	0.9500	C25—H25B	0.9800
C3—C4	1.383 (3)	C25—H25C	0.9800
C3—H3	0.9500	C26—C27	1.524 (4)
C4—C5	1.390 (3)	C26—C29	1.524 (4)
C4—H4	0.9500	C26—C28	1.529 (4)
C5—C7	1.504 (3)	C27—H27A	0.9800
C6—H6A	0.9900	C27—H27B	0.9800
C6—H6B	0.9900	C27—H27C	0.9800
C7—H7A	0.9900	C28—H28A	0.9800
C7—H7B	0.9900	C28—H28B	0.9800
C9—C10	1.324 (4)	C28—H28C	0.9800
C9—H9	0.9500	C29—H29A	0.9800
C10—H10	0.9500	C29—H29B	0.9800
C12—C13	1.329 (4)	C29—H29C	0.9800
C12—H12	0.9500		
O1—Cu—N1	170.38 (8)	C16—C14—C17	110.4 (2)
O1—Cu—N2	97.30 (7)	C14—C15—H15A	109.5
N1—Cu—N2	81.77 (7)	C14—C15—H15B	109.5
O1—Cu—N3	98.51 (7)	H15A—C15—H15B	109.5
N1—Cu—N3	81.77 (8)	C14—C15—H15C	109.5
N2—Cu—N3	163.36 (7)	H15A—C15—H15C	109.5

F2—P—F4	89.86 (11)	H15B—C15—H15C	109.5
F2—P—F6	90.87 (11)	C14—C16—H16A	109.5
F4—P—F6	179.11 (11)	C14—C16—H16B	109.5
F2—P—F5	90.27 (9)	H16A—C16—H16B	109.5
F4—P—F5	89.88 (10)	C14—C16—H16C	109.5
F6—P—F5	90.62 (10)	H16A—C16—H16C	109.5
F2—P—F1	179.82 (13)	H16B—C16—H16C	109.5
F4—P—F1	90.27 (10)	C14—C17—H17A	109.5
F6—P—F1	89.00 (10)	C14—C17—H17B	109.5
F5—P—F1	89.62 (9)	H17A—C17—H17B	109.5
F2—P—F3	90.28 (9)	C14—C17—H17C	109.5
F4—P—F3	90.25 (10)	H17A—C17—H17C	109.5
F6—P—F3	89.25 (10)	H17B—C17—H17C	109.5
F5—P—F3	179.44 (10)	N5—C18—C21	113.9 (2)
F1—P—F3	89.83 (9)	N5—C18—C20	107.6 (2)
C30—O1—Cu	123.98 (17)	C21—C18—C20	109.1 (2)
C30—O3—H1	108 (2)	N5—C18—C19	106.8 (2)
C1—N1—C5	122.78 (18)	C21—C18—C19	108.3 (2)
C1—N1—Cu	118.34 (14)	C20—C18—C19	111.1 (2)
C5—N1—Cu	118.62 (15)	C18—C19—H19A	109.5
C8—N2—C6	119.15 (17)	C18—C19—H19B	109.5
C8—N2—Cu	124.25 (14)	H19A—C19—H19B	109.5
C6—N2—Cu	116.59 (13)	C18—C19—H19C	109.5
C11—N3—C7	119.26 (18)	H19A—C19—H19C	109.5
C11—N3—Cu	120.79 (14)	H19B—C19—H19C	109.5
C7—N3—Cu	115.19 (14)	C18—C20—H20A	109.5
C8—N4—C9	108.4 (2)	C18—C20—H20B	109.5
C8—N4—C14	130.01 (18)	H20A—C20—H20B	109.5
C9—N4—C14	121.4 (2)	C18—C20—H20C	109.5
C8—N5—C10	108.1 (2)	H20A—C20—H20C	109.5
C8—N5—C18	131.80 (19)	H20B—C20—H20C	109.5
C10—N5—C18	120.1 (2)	C18—C21—H21A	109.5
C11—N6—C12	108.3 (2)	C18—C21—H21B	109.5
C11—N6—C22	130.7 (2)	H21A—C21—H21B	109.5
C12—N6—C22	120.9 (2)	C18—C21—H21C	109.5
C11—N7—C13	108.1 (2)	H21A—C21—H21C	109.5
C11—N7—C26	127.30 (19)	H21B—C21—H21C	109.5
C13—N7—C26	124.1 (2)	N6—C22—C24	112.6 (2)
N1—C1—C2	120.0 (2)	N6—C22—C23	107.7 (2)
N1—C1—C6	114.48 (18)	C24—C22—C23	111.3 (2)
C2—C1—C6	125.5 (2)	N6—C22—C25	108.5 (2)
C1—C2—C3	118.3 (2)	C24—C22—C25	107.2 (2)
C1—C2—H2	120.8	C23—C22—C25	109.5 (2)
C3—C2—H2	120.8	C22—C23—H23A	109.5
C4—C3—C2	120.8 (2)	C22—C23—H23B	109.5
C4—C3—H3	119.6	H23A—C23—H23B	109.5
C2—C3—H3	119.6	C22—C23—H23C	109.5
C3—C4—C5	118.6 (2)	H23A—C23—H23C	109.5
C3—C4—H4	120.7	H23B—C23—H23C	109.5

C5—C4—H4	120.7	C22—C24—H24A	109.5
N1—C5—C4	119.5 (2)	C22—C24—H24B	109.5
N1—C5—C7	114.50 (18)	H24A—C24—H24B	109.5
C4—C5—C7	126.0 (2)	C22—C24—H24C	109.5
N2—C6—C1	108.48 (17)	H24A—C24—H24C	109.5
N2—C6—H6A	110.0	H24B—C24—H24C	109.5
C1—C6—H6A	110.0	C22—C25—H25A	109.5
N2—C6—H6B	110.0	C22—C25—H25B	109.5
C1—C6—H6B	110.0	H25A—C25—H25B	109.5
H6A—C6—H6B	108.4	C22—C25—H25C	109.5
N3—C7—C5	108.76 (17)	H25A—C25—H25C	109.5
N3—C7—H7A	109.9	H25B—C25—H25C	109.5
C5—C7—H7A	109.9	N7—C26—C27	109.0 (2)
N3—C7—H7B	109.9	N7—C26—C29	108.9 (2)
C5—C7—H7B	109.9	C27—C26—C29	108.8 (2)
H7A—C7—H7B	108.3	N7—C26—C28	111.3 (2)
N2—C8—N5	125.8 (2)	C27—C26—C28	107.5 (2)
N2—C8—N4	127.2 (2)	C29—C26—C28	111.3 (2)
N5—C8—N4	106.83 (18)	C26—C27—H27A	109.5
C10—C9—N4	108.0 (2)	C26—C27—H27B	109.5
C10—C9—H9	126.0	H27A—C27—H27B	109.5
N4—C9—H9	126.0	C26—C27—H27C	109.5
C9—C10—N5	108.7 (2)	H27A—C27—H27C	109.5
C9—C10—H10	125.7	H27B—C27—H27C	109.5
N5—C10—H10	125.7	C26—C28—H28A	109.5
N3—C11—N6	129.5 (2)	C26—C28—H28B	109.5
N3—C11—N7	123.5 (2)	H28A—C28—H28B	109.5
N6—C11—N7	106.83 (19)	C26—C28—H28C	109.5
C13—C12—N6	108.3 (2)	H28A—C28—H28C	109.5
C13—C12—H12	125.8	H28B—C28—H28C	109.5
N6—C12—H12	125.8	C26—C29—H29A	109.5
C12—C13—N7	108.4 (2)	C26—C29—H29B	109.5
C12—C13—H13	125.8	H29A—C29—H29B	109.5
N7—C13—H13	125.8	C26—C29—H29C	109.5
N4—C14—C15	112.5 (2)	H29A—C29—H29C	109.5
N4—C14—C16	107.5 (2)	H29B—C29—H29C	109.5
C15—C14—C16	111.1 (2)	O2—C30—O1	125.7 (2)
N4—C14—C17	108.3 (2)	O2—C30—O3	121.2 (2)
C15—C14—C17	107.1 (2)	O1—C30—O3	113.1 (2)
N2—Cu—O1—C30	100.16 (19)	C9—N4—C8—N5	0.8 (2)
N3—Cu—O1—C30	−85.02 (19)	C14—N4—C8—N5	175.5 (2)
N2—Cu—N1—C1	4.54 (17)	C8—N4—C9—C10	−1.2 (3)
N3—Cu—N1—C1	−173.00 (18)	C14—N4—C9—C10	−176.4 (2)
N2—Cu—N1—C5	178.79 (18)	N4—C9—C10—N5	1.1 (3)
N3—Cu—N1—C5	1.25 (17)	C8—N5—C10—C9	−0.6 (3)
O1—Cu—N2—C8	−11.7 (2)	C18—N5—C10—C9	−179.5 (2)
N1—Cu—N2—C8	177.9 (2)	C7—N3—C11—N6	−73.3 (3)
N3—Cu—N2—C8	−173.5 (3)	Cu—N3—C11—N6	81.1 (3)
O1—Cu—N2—C6	169.28 (16)	C7—N3—C11—N7	113.1 (3)

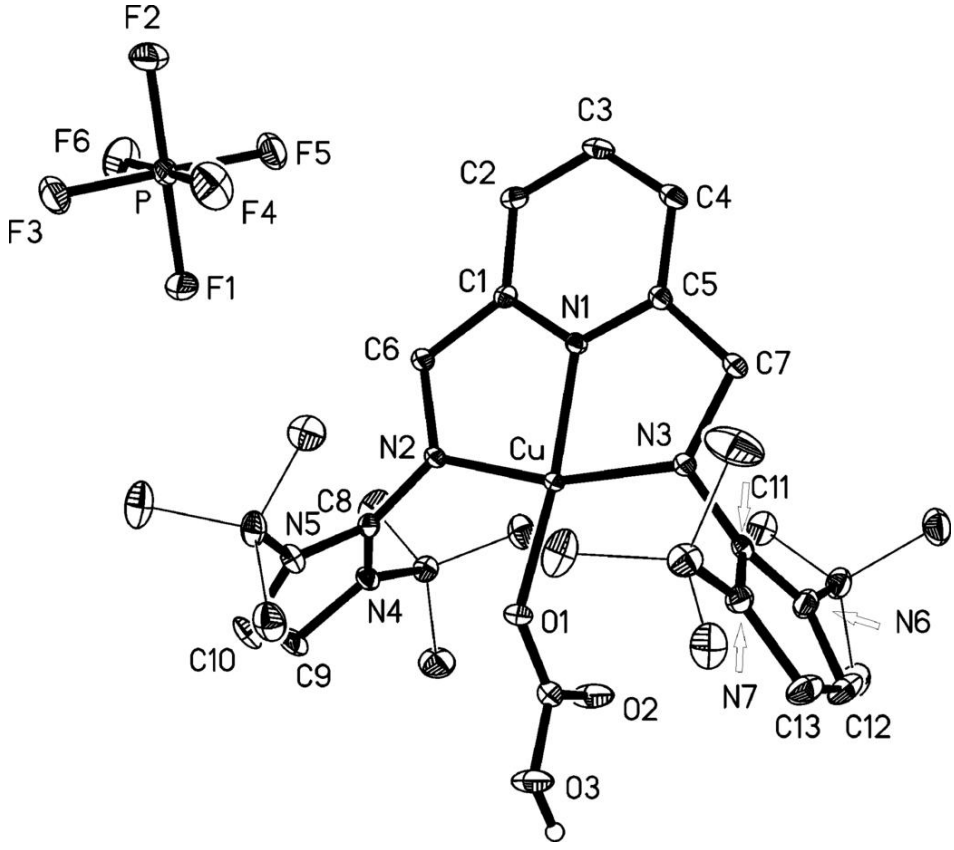
N1—Cu—N2—C6	−1.06 (16)	Cu—N3—C11—N7	−92.5 (2)
N3—Cu—N2—C6	7.5 (4)	C12—N6—C11—N3	−175.5 (2)
O1—Cu—N3—C11	26.8 (2)	C22—N6—C11—N3	8.9 (4)
N1—Cu—N3—C11	−162.9 (2)	C12—N6—C11—N7	−1.0 (2)
N2—Cu—N3—C11	−171.4 (3)	C22—N6—C11—N7	−176.6 (2)
O1—Cu—N3—C7	−177.78 (16)	C13—N7—C11—N3	175.0 (2)
N1—Cu—N3—C7	−7.50 (17)	C26—N7—C11—N3	−12.3 (3)
N2—Cu—N3—C7	−16.0 (4)	C13—N7—C11—N6	0.1 (2)
C5—N1—C1—C2	−0.7 (3)	C26—N7—C11—N6	172.8 (2)
Cu—N1—C1—C2	173.27 (17)	C11—N6—C12—C13	1.6 (3)
C5—N1—C1—C6	179.1 (2)	C22—N6—C12—C13	177.7 (2)
Cu—N1—C1—C6	−6.9 (3)	N6—C12—C13—N7	−1.5 (3)
N1—C1—C2—C3	1.3 (3)	C11—N7—C13—C12	0.8 (3)
C6—C1—C2—C3	−178.5 (2)	C26—N7—C13—C12	−172.1 (2)
C1—C2—C3—C4	−0.8 (4)	C8—N4—C14—C15	30.4 (3)
C2—C3—C4—C5	−0.3 (4)	C9—N4—C14—C15	−155.5 (2)
C1—N1—C5—C4	−0.5 (3)	C8—N4—C14—C16	−92.2 (3)
Cu—N1—C5—C4	−174.45 (17)	C9—N4—C14—C16	81.9 (3)
C1—N1—C5—C7	179.1 (2)	C8—N4—C14—C17	148.5 (2)
Cu—N1—C5—C7	5.1 (3)	C9—N4—C14—C17	−37.3 (3)
C3—C4—C5—N1	1.0 (3)	C8—N5—C18—C21	7.6 (4)
C3—C4—C5—C7	−178.5 (2)	C10—N5—C18—C21	−173.8 (2)
C8—N2—C6—C1	179.0 (2)	C8—N5—C18—C20	−113.5 (3)
Cu—N2—C6—C1	−2.0 (2)	C10—N5—C18—C20	65.0 (3)
N1—C1—C6—N2	5.5 (3)	C8—N5—C18—C19	127.2 (3)
C2—C1—C6—N2	−174.7 (2)	C10—N5—C18—C19	−54.3 (3)
C11—N3—C7—C5	167.3 (2)	C11—N6—C22—C24	−31.5 (3)
Cu—N3—C7—C5	11.6 (2)	C12—N6—C22—C24	153.4 (2)
N1—C5—C7—N3	−10.5 (3)	C11—N6—C22—C23	91.6 (3)
C4—C5—C7—N3	169.0 (2)	C12—N6—C22—C23	−83.5 (3)
C6—N2—C8—N5	−100.3 (3)	C11—N6—C22—C25	−149.9 (2)
Cu—N2—C8—N5	80.8 (3)	C12—N6—C22—C25	35.0 (3)
C6—N2—C8—N4	85.3 (3)	C11—N7—C26—C27	−175.7 (2)
Cu—N2—C8—N4	−93.7 (3)	C13—N7—C26—C27	−4.1 (3)
C10—N5—C8—N2	−175.5 (2)	C11—N7—C26—C29	−57.1 (3)
C18—N5—C8—N2	3.2 (4)	C13—N7—C26—C29	114.4 (3)
C10—N5—C8—N4	−0.2 (2)	C11—N7—C26—C28	66.0 (3)
C18—N5—C8—N4	178.5 (2)	C13—N7—C26—C28	−122.5 (3)
C9—N4—C8—N2	176.1 (2)	Cu—O1—C30—O2	−12.5 (3)
C14—N4—C8—N2	−9.2 (4)	Cu—O1—C30—O3	166.73 (15)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2^{i}	0.88 (4)	1.73 (4)	2.599 (3)	173 (4)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Fig. 1


F2
F6
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P
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C5
C6
C7
N2
Cu
N3
C11
C8
N5
N4
O1
N6
C10
C9
O2
N7
C13
C12
O3