Crystal structure of chlorido[1-(4-nitrophenyl)thio-urea-*κS*]bis(triphenylphosphane-*κP*)copper(I)

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The mononuclear mixed-ligand title complex, [CuCl($C_7H_7N_3O_2S$)($C_{18}H_{15}P$)$_2$], displays a distorted tetrahedral coordination sphere around the Cu^I atom, with two P atoms from two triphenylphosphane molecules, one terminal S atom from a 1-(4-nitrophenyl)thiourea molecule and a chloride ion as ligands. An intramolecular N—H···Cl hydrogen bond stabilizes the molecular conformation [graph-set motif $R_2^2(6)$]. In the crystal, further N—H···Cl hydrogen bonds connect individual molecules into zigzag chains parallel to [001]. The chains are linked by weak C—H···O hydrogen-bonding interactions into a three-dimensional network.

1. Chemical context

Thiourea and thiourea derivatives constitute an interesting class of ligands, bearing a soft sulfur and a hard nitrogen donor atom in the sense of the HSAB (hard and soft acids and bases) concept. Such ligands are of relevance in biological systems because they exhibit a moderate inhibitory potency on the diphenolase activity of tyrosinase (Liu *et al.*, 2016), anti-microbial and cytotoxic activity (Bielenica *et al.*, 2015) and are developed for anti-hepatitis C virus (HCV) activity (Khatri *et al.*, 2015). Copper(I) complexes with thiourea derivatives have received significant attention for several decades due to their antibacterial activity (Chetana *et al.*, 2016), cytotoxic activity (Rauf *et al.*, 2009), catalytic and oxidation properties (Gunasekaran *et al.*, 2017). In this context, we report here on synthesis and crystal structure of the title compound, [CuCl($C_7H_7N_3O_2S$)($C_{18}H_{15}P$)$_2$], (I).
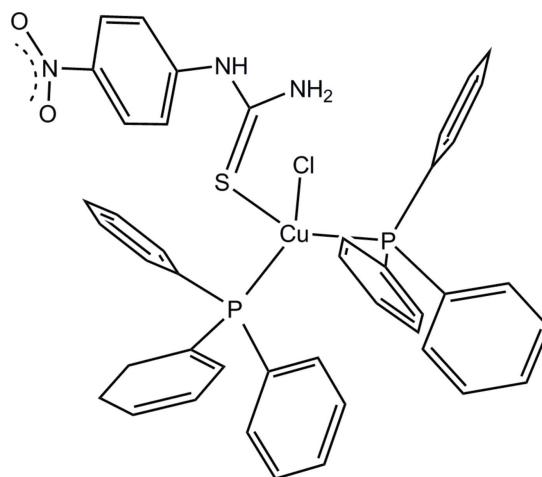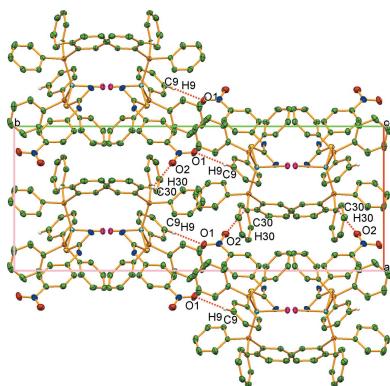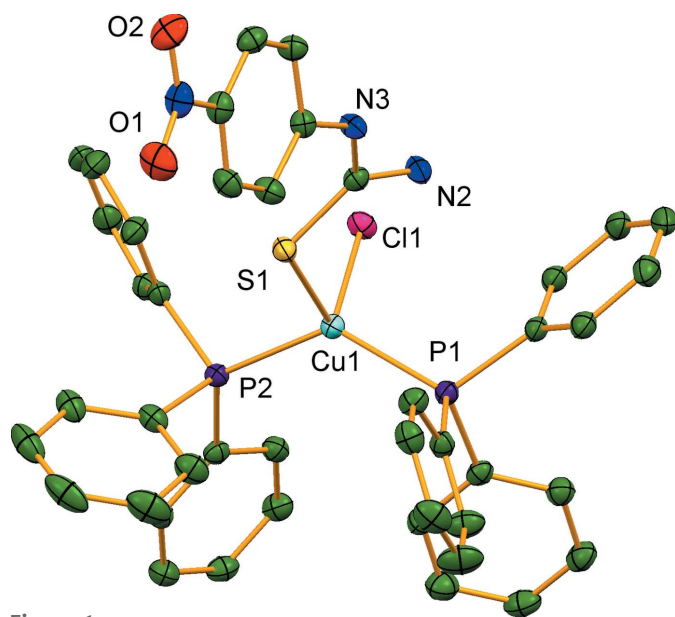
Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. All H atoms have been omitted for clarity.

2. Structural commentary

The asymmetric unit of (I) comprises of one Cu^I atom, one chloride ligand, two triphenylphosphane (PPh_3) ligands, and one 1-(4-nitrophenyl)thiourea (NPTU) ligand. The distorted tetrahedral coordination of the Cu^I atom results from binding to the chloride ligand, the P atoms of the two PPh_3 ligands and the terminal S atom of the 1-(4-nitrophenyl)thiourea ligand (Fig. 1). The distortion is evident from the angular range around the Cu^I atom [99.870 (15)–129.119 (16)°] and the disparate bond lengths (Table 1). The Cu—S distance in (I) is somewhat smaller than the values of 2.4148 (16) and

Table 1
Selected geometric parameters (Å, °).

Cu1—P2	2.2602 (4)	Cu1—S1	2.3782 (4)
Cu1—P1	2.2671 (4)	Cu1—Cl1	2.4023 (4)
P2—Cu1—P1	129.119 (16)	P2—Cu1—Cl1	99.870 (15)
P2—Cu1—S1	101.267 (15)	P1—Cu1—Cl1	109.823 (16)
P1—Cu1—S1	110.861 (15)	S1—Cu1—Cl1	102.637 (15)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$Cl1^i	0.88 (2)	2.35 (2)	3.1974 (14)	160 (2)
N2—H2B$\cdots$Cl1	0.88 (1)	2.42 (2)	3.2504 (15)	158 (2)
N3—H3A$\cdots$Cl1^i	0.87 (1)	2.49 (2)	3.3199 (14)	158 (2)
C9—H9$\cdots$O1^{ii}	0.95	2.57	3.303 (2)	135
C30—H30$\cdots$O2^{iii}	0.95	2.70	3.386 (2)	130

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x, -y, -z + 1$; (iii) $x + 1, y, z$.

2.3942 (15) Å reported in molecules A and B, respectively, of [CuI(PPh$_3$)$_2$(ptu)] (ptu is phenyl thiourea) (Nimthong *et al.*, 2008). The formation of an intramolecular N—H$\cdots$Cl hydrogen bond involving the primary amine functionality (N2—H2B; Table 2) creates a six-membered ring system with graph set motif $R_2^2(6)$.

3. Supramolecular features

In the crystal, neighbouring molecules are linked by further N—H$\cdots$Cl hydrogen bonds between the NPTU NH2 (N2—H2A) and NHPh (N1—H3A) moieties and the chloride ligands into zigzag chains extending parallel to [001] (Fig. 2, Table 2). The chains are connected *via* weak C9—H9$\cdots$O1 and C30—H30$\cdots$O2 hydrogen bonds (Fig. 3, Table 2), leading to the formation of a three-dimensional network (Fig. 3).
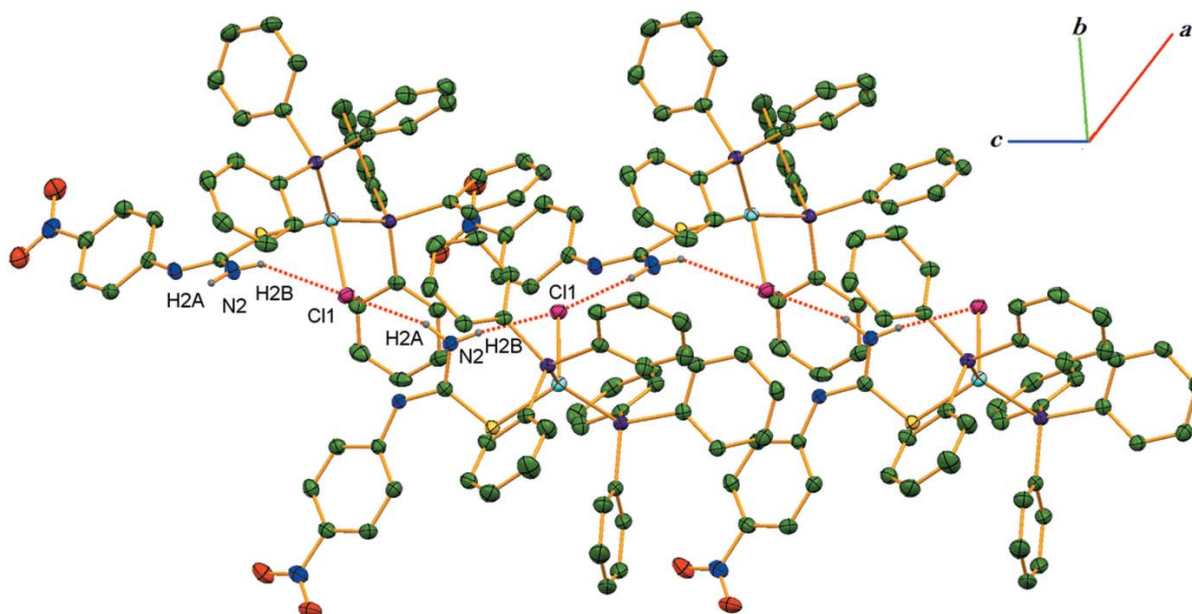

Figure 2
Part of the crystal structure of (I), showing intermolecular N—H$\cdots$Cl hydrogen bonds as dashed lines, forming a zigzag chain parallel to [001].

Table 3
Experimental details.

Crystal data

Chemical formula	$[CuCl(C_7H_7N_3O_2S)(C_{18}H_{15}P)_2]$
M_r	820.74
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	11.6986 (1), 28.7847 (4), 11.8471 (1)
β (°)	106.3394 (9)
V (Å³)	3828.28 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.82
Crystal size (mm)	$0.45 \times 0.32 \times 0.20$

Data collection

Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.746, 0.853
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37561, 10435, 8243
R_{int}	0.034
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.720

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.095, 1.10
No. of reflections	10435
No. of parameters	488
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.53, −0.70

Computer programs: *COLLECT* (Nonius, 1998), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXLE* (Hübschle *et al.*, 2011), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

4. Database survey

A search of the Cambridge Structural Database (Version 5.37, Feb 2016 with two updates; Groom *et al.*, 2016) revealed no complexes with the 1-(4-nitrophenyl)thiourea ligand, and only the crystal structure of the ligand itself has been reported (LONSEN; Xian *et al.*, 2008). A search for phenylthiourea ligands with substitutions on the phenyl ring yielded 34 hits. Of these, four hits were Cu[I] complexes, namely IYUXOP01 (Li *et al.*, 2006), TULXIJ, TULXUV (Grifasi *et al.*, 2015) and TULXUV (Nimthong *et al.*, 2008).

5. Synthesis and crystallization

Triphenylphosphane (0.26 g, 0.99 mmol) was dissolved in 30 ml of acetonitrile at 338 K and then copper(I) chloride (0.1 g, 1.01 mmol) was added. The mixture was stirred for 3 h and then 1-(4-nitrophenyl)thiourea, (0.2 g, 1.01 mmol) was added. The resulting reaction mixture was heated under reflux for 3 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to evaporate at room temperature. The crystalline complex, which deposited upon standing for a couple of days, was filtered off and dried *in vacuo* (0.38 g, 45% yield). M.p. 483–485 K. IR bands (KBr, cm⁻¹): 3066 (*m*), 3049 (*m*), 3017 (*m*), 2345 (*w*), 1961 (*w*),
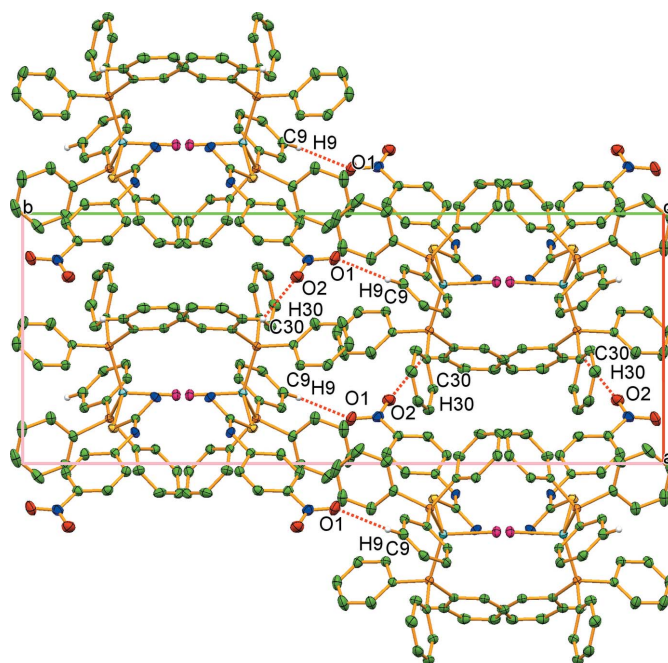

Figure 3
Part of the crystal structure of (I), showing the three-dimensional network formed by intermolecular C—H···O hydrogen bonds (shown as dashed lines).

1890 (*w*), 1814 (*w*), 1582 (*w*), 1474 (*s*), 1433 (*s*), 1307 (*w*), 1268 (*w*), 1176 (*m*), 1153 (*m*), 1088 (*s*), 1065 (*m*), 1024 (*s*), 994 (*m*), 916 (*w*), 852 (*m*), 741 (*s*), 692 (*s*).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95 Å. Nitrogen-bound H atoms were located in difference density maps and were refined with an N—H distance restraint of 0.88 (2) Å. U_{iso}(H) values were set to $1.2U_{eq}$(C/N).

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Crystal structure of chlorido[1-(4-nitrophenyl)thiourea-*κS*]bis(triphenylphosphane-*κP*)copper(I)

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Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL-3000* (Otwinowski & Minor, 1997); data reduction: *HKL-3000* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Chlorido[1-(4-nitrophenyl)thiourea-*κS*]bis(triphenylphosphane-*κP*)copper(I)

Crystal data

[CuCl($C_7H_7N_3O_2S$)($C_{18}H_{15}P$)$_2$]	$F(000) = 1696$
$M_r = 820.74$	$D_x = 1.424$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.6986 (1)$ Å	Cell parameters from 37561 reflections
$b = 28.7847 (4)$ Å	$\theta = 1.9$–$30.8°$
$c = 11.8471 (1)$ Å	$\mu = 0.82$ mm^{-1}
$\beta = 106.3394 (9)°$	$T = 100$ K
$V = 3828.28 (7)$ Å^3	Plate, yellow
$Z = 4$	$0.45 \times 0.32 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer	37561 measured reflections
Radiation source: fine focus X-ray tube	10435 independent reflections
Graphite monochromator	8243 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.034$
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)	$\theta_{max} = 30.8°$, $\theta_{min} = 1.9°$
	$h = -15 \rightarrow 16$
	$k = -31 \rightarrow 38$
$T_{min} = 0.746$, $T_{max} = 0.853$	$l = -15 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.095$	
$S = 1.10$	Hydrogen site location: inferred from neighbouring sites
10435 reflections	
488 parameters	H atoms treated by a mixture of independent and constrained refinement
3 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.4104P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}

Extinction correction: SHELXL2014
(Sheldrick, 2015),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0016 (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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.28282 (2)	0.15638 (2)	0.54942 (2)	0.01735 (6)
O1	−0.17866 (13)	0.01265 (5)	0.98751 (12)	0.0385 (3)
N1	−0.18661 (13)	0.05452 (6)	1.00307 (13)	0.0286 (3)
S1	0.14096 (4)	0.14121 (2)	0.65448 (3)	0.01970 (9)
Cl1	0.27367 (4)	0.23943 (2)	0.52868 (3)	0.02252 (9)
P1	0.46802 (4)	0.13469 (2)	0.65603 (3)	0.01731 (9)
C1	0.58276 (14)	0.13035 (6)	0.57889 (14)	0.0193 (3)
P2	0.17975 (4)	0.13535 (2)	0.36507 (3)	0.01688 (9)
N2	0.26531 (13)	0.20750 (5)	0.78940 (12)	0.0226 (3)
H2A	0.2850 (17)	0.2247 (6)	0.8536 (14)	0.027*
H2B	0.2894 (17)	0.2142 (7)	0.7271 (15)	0.027*
O2	−0.25332 (12)	0.07159 (5)	1.05564 (12)	0.0357 (3)
C2	0.70247 (15)	0.14023 (6)	0.63207 (15)	0.0242 (3)
H2	0.7269	0.1515	0.7106	0.029*
C3	0.78635 (16)	0.13360 (6)	0.57006 (17)	0.0284 (4)
H3	0.8678	0.1406	0.6062	0.034*
N3	0.12426 (13)	0.17546 (5)	0.86177 (12)	0.0205 (3)
H3A	0.1444 (17)	0.1990 (6)	0.9099 (15)	0.025*
C4	0.63253 (17)	0.10666 (7)	0.40297 (16)	0.0305 (4)
H4	0.6086	0.0949	0.3249	0.037*
C6	0.75117 (17)	0.11684 (6)	0.45616 (16)	0.0298 (4)
H6	0.8086	0.1123	0.4142	0.036*
C7	0.25157 (14)	0.13084 (5)	0.24718 (13)	0.0185 (3)
C8	0.22295 (15)	0.09615 (6)	0.16151 (14)	0.0220 (3)
H8	0.1626	0.0741	0.1620	0.026*
C9	0.28264 (15)	0.09374 (6)	0.07539 (15)	0.0256 (4)
H9	0.2639	0.0697	0.0181	0.031*
C10	0.36928 (15)	0.12618 (6)	0.07284 (14)	0.0244 (3)
H10	0.4096	0.1245	0.0137	0.029*
C11	0.39707 (15)	0.16098 (6)	0.15629 (15)	0.0244 (4)
H11	0.4555	0.1835	0.1536	0.029*
C12	0.33950 (15)	0.16309 (6)	0.24439 (14)	0.0216 (3)
H12	0.3603	0.1866	0.3028	0.026*
C13	0.05888 (14)	0.17673 (5)	0.30754 (13)	0.0190 (3)

C14	−0.02848 (15)	0.18109 (6)	0.36695 (14)	0.0252 (4)
H14	−0.0266	0.1612	0.4315	0.030*
C15	−0.11740 (16)	0.21401 (7)	0.33257 (16)	0.0301 (4)
H15	−0.1775	0.2161	0.3721	0.036*
C16	−0.11927 (16)	0.24407 (6)	0.24056 (15)	0.0292 (4)
H16	−0.1803	0.2668	0.2173	0.035*
C17	−0.03195 (16)	0.24083 (6)	0.18273 (15)	0.0272 (4)
H17	−0.0324	0.2616	0.1203	0.033*
C18	0.05679 (15)	0.20707 (6)	0.21616 (14)	0.0221 (3)
H18	0.1163	0.2049	0.1759	0.027*
C19	0.10921 (15)	0.07869 (6)	0.36250 (14)	0.0219 (3)
C20	0.18067 (18)	0.04382 (6)	0.42833 (16)	0.0298 (4)
H20	0.2598	0.0508	0.4730	0.036*
C21	0.1372 (2)	−0.00109 (7)	0.42928 (18)	0.0397 (5)
H21	0.1869	−0.0248	0.4727	0.048*
C22	0.0206 (2)	−0.01094 (7)	0.36626 (17)	0.0409 (5)
H22	−0.0099	−0.0415	0.3677	0.049*
C23	−0.05114 (19)	0.02317 (7)	0.30175 (16)	0.0366 (5)
H23	−0.1309	0.0161	0.2591	0.044*
C24	−0.00719 (16)	0.06825 (7)	0.29855 (15)	0.0273 (4)
H24	−0.0566	0.0916	0.2529	0.033*
C25	0.53685 (14)	0.17298 (6)	0.78059 (13)	0.0189 (3)
C26	0.54102 (14)	0.22062 (6)	0.75712 (15)	0.0228 (3)
H26	0.5135	0.2316	0.6785	0.027*
C27	0.58508 (15)	0.25178 (6)	0.84823 (16)	0.0272 (4)
H27	0.5884	0.2840	0.8317	0.033*
C28	0.62437 (15)	0.23607 (7)	0.96356 (16)	0.0291 (4)
H28	0.6532	0.2575	1.0261	0.035*
C29	0.62144 (16)	0.18898 (7)	0.98716 (15)	0.0283 (4)
H29	0.6489	0.1782	1.0660	0.034*
C30	0.57845 (15)	0.15744 (6)	0.89593 (14)	0.0229 (3)
H30	0.5776	0.1252	0.9126	0.027*
C31	0.47481 (14)	0.07718 (6)	0.72334 (13)	0.0202 (3)
C32	0.39244 (15)	0.06663 (6)	0.78530 (14)	0.0236 (3)
H32	0.3346	0.0891	0.7906	0.028*
C33	0.39449 (16)	0.02369 (6)	0.83911 (14)	0.0264 (4)
H33	0.3390	0.0171	0.8821	0.032*
C34	0.47685 (18)	−0.00944 (7)	0.83038 (16)	0.0333 (4)
H34	0.4779	−0.0389	0.8669	0.040*
C35	0.5581 (2)	0.00040 (7)	0.76808 (19)	0.0397 (5)
H35	0.6145	−0.0224	0.7616	0.048*
C36	0.55731 (18)	0.04345 (7)	0.71507 (17)	0.0316 (4)
H36	0.6135	0.0499	0.6728	0.038*
C38	0.17955 (14)	0.17619 (6)	0.77521 (13)	0.0191 (3)
C40	0.04170 (14)	0.14409 (6)	0.88460 (13)	0.0195 (3)
C41	−0.03251 (15)	0.16167 (6)	0.94837 (14)	0.0225 (3)
H41	−0.0313	0.1939	0.9654	0.027*
C42	−0.10781 (15)	0.13253 (6)	0.98702 (14)	0.0244 (4)

H42	−0.1569	0.1443	1.0321	0.029*
C43	−0.11000 (15)	0.08595 (6)	0.95871 (14)	0.0237 (3)
C44	−0.03983 (16)	0.06778 (6)	0.89303 (15)	0.0257 (4)
H44	−0.0438	0.0357	0.8736	0.031*
C45	0.03635 (16)	0.09711 (6)	0.85594 (14)	0.0245 (3)
H45	0.0851	0.0851	0.8108	0.029*
C5	0.54875 (15)	0.11370 (6)	0.46403 (15)	0.0261 (4)
H5	0.4672	0.1071	0.4270	0.031*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01643 (11)	0.01770 (11)	0.01733 (10)	0.00078 (7)	0.00379 (7)	−0.00070 (7)
O1	0.0449 (9)	0.0264 (8)	0.0473 (8)	−0.0121 (6)	0.0183 (7)	0.0012 (6)
N1	0.0257 (8)	0.0294 (9)	0.0295 (8)	−0.0044 (6)	0.0058 (6)	0.0061 (6)
S1	0.0188 (2)	0.0219 (2)	0.01894 (18)	−0.00284 (15)	0.00621 (14)	−0.00332 (14)
Cl1	0.0282 (2)	0.01691 (19)	0.02100 (18)	0.00003 (15)	0.00450 (15)	0.00155 (14)
P1	0.0162 (2)	0.0165 (2)	0.01874 (19)	0.00010 (15)	0.00413 (15)	0.00061 (14)
C1	0.0185 (8)	0.0165 (8)	0.0230 (8)	0.0021 (6)	0.0059 (6)	0.0031 (6)
P2	0.0168 (2)	0.0162 (2)	0.01734 (19)	−0.00007 (15)	0.00429 (14)	−0.00065 (14)
N2	0.0227 (7)	0.0255 (8)	0.0204 (7)	−0.0064 (6)	0.0075 (6)	−0.0053 (6)
O2	0.0300 (7)	0.0390 (8)	0.0435 (8)	−0.0004 (6)	0.0192 (6)	0.0092 (6)
C2	0.0221 (9)	0.0226 (9)	0.0285 (8)	−0.0008 (7)	0.0082 (7)	−0.0006 (7)
C3	0.0198 (9)	0.0265 (10)	0.0406 (10)	−0.0020 (7)	0.0114 (7)	0.0005 (7)
N3	0.0241 (7)	0.0187 (7)	0.0205 (6)	−0.0042 (6)	0.0092 (5)	−0.0037 (5)
C4	0.0322 (10)	0.0332 (10)	0.0278 (9)	0.0032 (8)	0.0110 (7)	−0.0021 (7)
C6	0.0296 (10)	0.0261 (9)	0.0395 (10)	0.0042 (8)	0.0191 (8)	0.0035 (8)
C7	0.0177 (8)	0.0185 (8)	0.0189 (7)	0.0037 (6)	0.0044 (6)	0.0020 (6)
C8	0.0216 (8)	0.0207 (8)	0.0236 (8)	−0.0011 (6)	0.0062 (6)	−0.0013 (6)
C9	0.0275 (9)	0.0255 (9)	0.0245 (8)	0.0007 (7)	0.0086 (7)	−0.0041 (7)
C10	0.0257 (9)	0.0262 (9)	0.0238 (8)	0.0059 (7)	0.0113 (7)	0.0031 (6)
C11	0.0245 (9)	0.0200 (9)	0.0310 (9)	−0.0005 (7)	0.0119 (7)	0.0026 (6)
C12	0.0219 (8)	0.0184 (8)	0.0248 (8)	−0.0002 (6)	0.0069 (6)	−0.0016 (6)
C13	0.0173 (8)	0.0170 (8)	0.0202 (7)	−0.0005 (6)	0.0010 (6)	−0.0032 (6)
C14	0.0198 (8)	0.0304 (10)	0.0257 (8)	0.0027 (7)	0.0066 (6)	0.0010 (7)
C15	0.0203 (9)	0.0369 (11)	0.0318 (9)	0.0054 (8)	0.0051 (7)	−0.0041 (8)
C16	0.0235 (9)	0.0243 (9)	0.0334 (9)	0.0075 (7)	−0.0026 (7)	−0.0058 (7)
C17	0.0297 (10)	0.0202 (9)	0.0276 (8)	0.0015 (7)	0.0011 (7)	0.0010 (7)
C18	0.0232 (9)	0.0193 (8)	0.0226 (8)	−0.0003 (6)	0.0045 (6)	−0.0008 (6)
C19	0.0281 (9)	0.0194 (8)	0.0198 (7)	−0.0040 (7)	0.0093 (6)	−0.0022 (6)
C20	0.0374 (11)	0.0218 (9)	0.0308 (9)	−0.0020 (8)	0.0109 (8)	0.0008 (7)
C21	0.0648 (15)	0.0209 (9)	0.0367 (10)	−0.0006 (9)	0.0198 (10)	0.0030 (8)
C22	0.0719 (16)	0.0245 (10)	0.0339 (10)	−0.0199 (10)	0.0271 (10)	−0.0073 (8)
C23	0.0464 (12)	0.0380 (11)	0.0286 (9)	−0.0224 (9)	0.0159 (8)	−0.0115 (8)
C24	0.0295 (9)	0.0308 (10)	0.0231 (8)	−0.0096 (8)	0.0099 (7)	−0.0050 (7)
C25	0.0141 (7)	0.0198 (8)	0.0218 (7)	0.0000 (6)	0.0035 (6)	−0.0002 (6)
C26	0.0177 (8)	0.0210 (9)	0.0286 (8)	0.0005 (6)	0.0047 (6)	−0.0003 (6)
C27	0.0177 (8)	0.0219 (9)	0.0395 (10)	−0.0013 (7)	0.0039 (7)	−0.0043 (7)

C28	0.0202 (9)	0.0338 (10)	0.0327 (9)	−0.0024 (7)	0.0061 (7)	−0.0119 (8)
C29	0.0237 (9)	0.0380 (11)	0.0227 (8)	−0.0008 (8)	0.0054 (7)	−0.0041 (7)
C30	0.0181 (8)	0.0256 (9)	0.0248 (8)	0.0005 (7)	0.0058 (6)	0.0001 (6)
C31	0.0199 (8)	0.0171 (8)	0.0216 (7)	−0.0008 (6)	0.0024 (6)	0.0002 (6)
C32	0.0221 (8)	0.0217 (9)	0.0274 (8)	0.0007 (7)	0.0077 (7)	0.0034 (6)
C33	0.0302 (9)	0.0241 (9)	0.0243 (8)	−0.0057 (7)	0.0066 (7)	0.0022 (7)
C34	0.0477 (12)	0.0200 (9)	0.0321 (9)	−0.0004 (8)	0.0112 (8)	0.0052 (7)
C35	0.0518 (13)	0.0247 (10)	0.0483 (12)	0.0136 (9)	0.0232 (10)	0.0101 (8)
C36	0.0371 (11)	0.0241 (9)	0.0385 (10)	0.0062 (8)	0.0188 (8)	0.0055 (7)
C38	0.0186 (8)	0.0187 (8)	0.0199 (7)	0.0017 (6)	0.0053 (6)	0.0015 (6)
C40	0.0203 (8)	0.0198 (8)	0.0180 (7)	−0.0016 (6)	0.0046 (6)	0.0018 (6)
C41	0.0247 (9)	0.0197 (8)	0.0240 (8)	0.0015 (7)	0.0085 (6)	0.0006 (6)
C42	0.0235 (9)	0.0267 (9)	0.0250 (8)	0.0026 (7)	0.0099 (7)	0.0027 (6)
C43	0.0226 (9)	0.0243 (9)	0.0237 (8)	−0.0029 (7)	0.0058 (6)	0.0039 (6)
C44	0.0305 (9)	0.0202 (9)	0.0266 (8)	−0.0048 (7)	0.0083 (7)	−0.0017 (6)
C45	0.0303 (9)	0.0214 (9)	0.0236 (8)	−0.0009 (7)	0.0104 (7)	−0.0030 (6)
C5	0.0212 (9)	0.0312 (10)	0.0255 (8)	0.0024 (7)	0.0059 (6)	−0.0008 (7)

Geometric parameters (Å, º)

Cu1—P2	2.2602 (4)	C16—H16	0.9500
Cu1—P1	2.2671 (4)	C17—C18	1.395 (2)
Cu1—S1	2.3782 (4)	C17—H17	0.9500
Cu1—Cl1	2.4023 (4)	C18—H18	0.9500
O1—N1	1.227 (2)	C19—C24	1.392 (2)
N1—O2	1.230 (2)	C19—C20	1.396 (3)
N1—C43	1.471 (2)	C20—C21	1.391 (3)
S1—C38	1.7031 (16)	C20—H20	0.9500
P1—C1	1.8283 (16)	C21—C22	1.387 (3)
P1—C31	1.8296 (16)	C21—H21	0.9500
P1—C25	1.8362 (16)	C22—C23	1.375 (3)
C1—C5	1.391 (2)	C22—H22	0.9500
C1—C2	1.394 (2)	C23—C24	1.400 (3)
P2—C19	1.8241 (17)	C23—H23	0.9500
P2—C7	1.8258 (15)	C24—H24	0.9500
P2—C13	1.8278 (16)	C25—C30	1.389 (2)
N2—C38	1.324 (2)	C25—C26	1.403 (2)
N2—H2A	0.882 (15)	C26—C27	1.387 (2)
N2—H2B	0.882 (14)	C26—H26	0.9500
C2—C3	1.394 (2)	C27—C28	1.389 (3)
C2—H2	0.9500	C27—H27	0.9500
C3—C6	1.382 (3)	C28—C29	1.386 (3)
C3—H3	0.9500	C28—H28	0.9500
N3—C38	1.3578 (19)	C29—C30	1.393 (2)
N3—C40	1.403 (2)	C29—H29	0.9500
N3—H3A	0.874 (14)	C30—H30	0.9500
C4—C6	1.385 (3)	C31—C36	1.392 (2)
C4—C5	1.387 (2)	C31—C32	1.399 (2)

C4—H4	0.9500	C32—C33	1.388 (2)
C6—H6	0.9500	C32—H32	0.9500
C7—C12	1.393 (2)	C33—C34	1.380 (3)
C7—C8	1.396 (2)	C33—H33	0.9500
C8—C9	1.391 (2)	C34—C35	1.387 (3)
C8—H8	0.9500	C34—H34	0.9500
C9—C10	1.385 (2)	C35—C36	1.388 (3)
C9—H9	0.9500	C35—H35	0.9500
C10—C11	1.381 (2)	C36—H36	0.9500
C10—H10	0.9500	C40—C45	1.391 (2)
C11—C12	1.394 (2)	C40—C41	1.396 (2)
C11—H11	0.9500	C41—C42	1.384 (2)
C12—H12	0.9500	C41—H41	0.9500
C13—C18	1.386 (2)	C42—C43	1.380 (2)
C13—C14	1.400 (2)	C42—H42	0.9500
C14—C15	1.381 (3)	C43—C44	1.383 (2)
C14—H14	0.9500	C44—C45	1.386 (2)
C15—C16	1.387 (3)	C44—H44	0.9500
C15—H15	0.9500	C45—H45	0.9500
C16—C17	1.384 (3)	C5—H5	0.9500
P2—Cu1—P1	129.119 (16)	C24—C19—C20	119.30 (16)
P2—Cu1—S1	101.267 (15)	C24—C19—P2	124.80 (14)
P1—Cu1—S1	110.861 (15)	C20—C19—P2	115.88 (13)
P2—Cu1—Cl1	99.870 (15)	C21—C20—C19	120.67 (19)
P1—Cu1—Cl1	109.823 (16)	C21—C20—H20	119.7
S1—Cu1—Cl1	102.637 (15)	C19—C20—H20	119.7
O1—N1—O2	123.66 (15)	C22—C21—C20	119.5 (2)
O1—N1—C43	118.11 (15)	C22—C21—H21	120.3
O2—N1—C43	118.21 (15)	C20—C21—H21	120.3
C38—S1—Cu1	105.77 (6)	C23—C22—C21	120.47 (18)
C1—P1—C31	102.01 (7)	C23—C22—H22	119.8
C1—P1—C25	103.01 (7)	C21—C22—H22	119.8
C31—P1—C25	103.74 (7)	C22—C23—C24	120.35 (19)
C1—P1—Cu1	117.47 (5)	C22—C23—H23	119.8
C31—P1—Cu1	114.17 (5)	C24—C23—H23	119.8
C25—P1—Cu1	114.62 (5)	C19—C24—C23	119.72 (18)
C5—C1—C2	119.14 (15)	C19—C24—H24	120.1
C5—C1—P1	117.67 (12)	C23—C24—H24	120.1
C2—C1—P1	123.07 (12)	C30—C25—C26	119.18 (15)
C19—P2—C7	103.12 (7)	C30—C25—P1	123.38 (13)
C19—P2—C13	106.11 (8)	C26—C25—P1	117.34 (12)
C7—P2—C13	103.61 (7)	C27—C26—C25	120.28 (16)
C19—P2—Cu1	111.81 (5)	C27—C26—H26	119.9
C7—P2—Cu1	121.54 (5)	C25—C26—H26	119.9
C13—P2—Cu1	109.40 (5)	C26—C27—C28	120.18 (17)
C38—N2—H2A	119.8 (13)	C26—C27—H27	119.9
C38—N2—H2B	116.9 (13)	C28—C27—H27	119.9

H2A—N2—H2B	122.0 (18)	C29—C28—C27	119.78 (16)
C1—C2—C3	120.03 (16)	C29—C28—H28	120.1
C1—C2—H2	120.0	C27—C28—H28	120.1
C3—C2—H2	120.0	C28—C29—C30	120.32 (17)
C6—C3—C2	120.11 (17)	C28—C29—H29	119.8
C6—C3—H3	119.9	C30—C29—H29	119.8
C2—C3—H3	119.9	C25—C30—C29	120.23 (16)
C38—N3—C40	130.96 (14)	C25—C30—H30	119.9
C38—N3—H3A	112.4 (13)	C29—C30—H30	119.9
C40—N3—H3A	116.6 (13)	C36—C31—C32	118.63 (15)
C6—C4—C5	119.77 (17)	C36—C31—P1	123.13 (13)
C6—C4—H4	120.1	C32—C31—P1	118.24 (12)
C5—C4—H4	120.1	C33—C32—C31	120.59 (16)
C3—C6—C4	120.21 (16)	C33—C32—H32	119.7
C3—C6—H6	119.9	C31—C32—H32	119.7
C4—C6—H6	119.9	C34—C33—C32	120.21 (16)
C12—C7—C8	119.15 (14)	C34—C33—H33	119.9
C12—C7—P2	118.20 (12)	C32—C33—H33	119.9
C8—C7—P2	122.64 (12)	C33—C34—C35	119.76 (17)
C9—C8—C7	120.13 (16)	C33—C34—H34	120.1
C9—C8—H8	119.9	C35—C34—H34	120.1
C7—C8—H8	119.9	C34—C35—C36	120.32 (18)
C10—C9—C8	120.27 (16)	C34—C35—H35	119.8
C10—C9—H9	119.9	C36—C35—H35	119.8
C8—C9—H9	119.9	C35—C36—C31	120.48 (17)
C11—C10—C9	120.01 (15)	C35—C36—H36	119.8
C11—C10—H10	120.0	C31—C36—H36	119.8
C9—C10—H10	120.0	N2—C38—N3	114.81 (14)
C10—C11—C12	120.12 (16)	N2—C38—S1	121.44 (12)
C10—C11—H11	119.9	N3—C38—S1	123.72 (12)
C12—C11—H11	119.9	C45—C40—C41	119.48 (15)
C7—C12—C11	120.30 (15)	C45—C40—N3	124.38 (15)
C7—C12—H12	119.9	C41—C40—N3	115.95 (15)
C11—C12—H12	119.9	C42—C41—C40	120.65 (16)
C18—C13—C14	118.77 (15)	C42—C41—H41	119.7
C18—C13—P2	122.95 (12)	C40—C41—H41	119.7
C14—C13—P2	117.94 (12)	C43—C42—C41	118.56 (15)
C15—C14—C13	120.59 (16)	C43—C42—H42	120.7
C15—C14—H14	119.7	C41—C42—H42	120.7
C13—C14—H14	119.7	C42—C43—C44	122.06 (16)
C14—C15—C16	120.25 (16)	C42—C43—N1	118.82 (15)
C14—C15—H15	119.9	C44—C43—N1	119.09 (16)
C16—C15—H15	119.9	C43—C44—C45	118.96 (16)
C17—C16—C15	119.76 (16)	C43—C44—H44	120.5
C17—C16—H16	120.1	C45—C44—H44	120.5
C15—C16—H16	120.1	C44—C45—C40	120.24 (15)
C16—C17—C18	120.02 (16)	C44—C45—H45	119.9
C16—C17—H17	120.0	C40—C45—H45	119.9

C18—C17—H17	120.0	C4—C5—C1	120.72 (16)
C13—C18—C17	120.58 (16)	C4—C5—H5	119.6
C13—C18—H18	119.7	C1—C5—H5	119.6
C17—C18—H18	119.7		
C31—P1—C1—C5	88.90 (14)	C22—C23—C24—C19	−1.0 (3)
C25—P1—C1—C5	−163.75 (13)	C1—P1—C25—C30	−107.34 (14)
Cu1—P1—C1—C5	−36.73 (15)	C31—P1—C25—C30	−1.30 (16)
C31—P1—C1—C2	−87.15 (15)	Cu1—P1—C25—C30	123.85 (13)
C25—P1—C1—C2	20.21 (16)	C1—P1—C25—C26	76.16 (13)
Cu1—P1—C1—C2	147.23 (12)	C31—P1—C25—C26	−177.80 (12)
C5—C1—C2—C3	0.3 (3)	Cu1—P1—C25—C26	−52.65 (13)
P1—C1—C2—C3	176.27 (13)	C30—C25—C26—C27	−0.6 (2)
C1—C2—C3—C6	−0.6 (3)	P1—C25—C26—C27	176.02 (13)
C2—C3—C6—C4	0.1 (3)	C25—C26—C27—C28	−0.6 (2)
C5—C4—C6—C3	0.6 (3)	C26—C27—C28—C29	1.2 (3)
C19—P2—C7—C12	−163.25 (13)	C27—C28—C29—C30	−0.5 (3)
C13—P2—C7—C12	86.29 (14)	C26—C25—C30—C29	1.3 (2)
Cu1—P2—C7—C12	−37.05 (15)	P1—C25—C30—C29	−175.13 (13)
C19—P2—C7—C8	15.84 (15)	C28—C29—C30—C25	−0.8 (3)
C13—P2—C7—C8	−94.63 (14)	C1—P1—C31—C36	3.32 (17)
Cu1—P2—C7—C8	142.04 (12)	C25—P1—C31—C36	−103.47 (15)
C12—C7—C8—C9	0.6 (2)	Cu1—P1—C31—C36	131.09 (14)
P2—C7—C8—C9	−178.45 (13)	C1—P1—C31—C32	−176.22 (13)
C7—C8—C9—C10	−1.1 (3)	C25—P1—C31—C32	76.99 (14)
C8—C9—C10—C11	0.3 (3)	Cu1—P1—C31—C32	−48.45 (14)
C9—C10—C11—C12	1.1 (3)	C36—C31—C32—C33	1.1 (3)
C8—C7—C12—C11	0.7 (2)	P1—C31—C32—C33	−179.30 (13)
P2—C7—C12—C11	179.84 (13)	C31—C32—C33—C34	−1.1 (3)
C10—C11—C12—C7	−1.6 (3)	C32—C33—C34—C35	0.3 (3)
C19—P2—C13—C18	−127.51 (14)	C33—C34—C35—C36	0.3 (3)
C7—P2—C13—C18	−19.27 (15)	C34—C35—C36—C31	−0.3 (3)
Cu1—P2—C13—C18	111.71 (13)	C32—C31—C36—C35	−0.5 (3)
C19—P2—C13—C14	59.38 (14)	P1—C31—C36—C35	179.99 (16)
C7—P2—C13—C14	167.63 (13)	C40—N3—C38—N2	−170.95 (16)
Cu1—P2—C13—C14	−61.39 (14)	C40—N3—C38—S1	10.9 (3)
C18—C13—C14—C15	2.1 (3)	Cu1—S1—C38—N2	6.43 (15)
P2—C13—C14—C15	175.53 (14)	Cu1—S1—C38—N3	−175.53 (12)
C13—C14—C15—C16	−1.8 (3)	C38—N3—C40—C45	29.7 (3)
C14—C15—C16—C17	0.3 (3)	C38—N3—C40—C41	−155.33 (17)
C15—C16—C17—C18	0.7 (3)	C45—C40—C41—C42	2.5 (3)
C14—C13—C18—C17	−1.1 (2)	N3—C40—C41—C42	−172.74 (15)
P2—C13—C18—C17	−174.11 (13)	C40—C41—C42—C43	−1.6 (3)
C16—C17—C18—C13	−0.3 (3)	C41—C42—C43—C44	−0.2 (3)
C7—P2—C19—C24	−92.07 (15)	C41—C42—C43—N1	177.84 (15)
C13—P2—C19—C24	16.52 (16)	O1—N1—C43—C42	−172.69 (16)
Cu1—P2—C19—C24	135.72 (13)	O2—N1—C43—C42	5.9 (2)
C7—P2—C19—C20	86.40 (13)	O1—N1—C43—C44	5.4 (2)

C13—P2—C19—C20	−165.01 (12)	O2—N1—C43—C44	−176.00 (16)
Cu1—P2—C19—C20	−45.80 (14)	C42—C43—C44—C45	1.0 (3)
C24—C19—C20—C21	0.8 (3)	N1—C43—C44—C45	−177.05 (15)
P2—C19—C20—C21	−177.76 (14)	C43—C44—C45—C40	0.0 (3)
C19—C20—C21—C22	−1.5 (3)	C41—C40—C45—C44	−1.7 (3)
C20—C21—C22—C23	1.0 (3)	N3—C40—C45—C44	173.11 (16)
C21—C22—C23—C24	0.2 (3)	C6—C4—C5—C1	−0.8 (3)
C20—C19—C24—C23	0.4 (2)	C2—C1—C5—C4	0.4 (3)
P2—C19—C24—C23	178.87 (13)	P1—C1—C5—C4	−175.79 (14)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···Cl1[i]	0.88 (2)	2.35 (2)	3.1974 (14)	160 (2)
N2—H2B···Cl1	0.88 (1)	2.42 (2)	3.2504 (15)	158 (2)
N3—H3A···Cl1[i]	0.87 (1)	2.49 (2)	3.3199 (14)	158 (2)
C9—H9···O1[ii]	0.95	2.57	3.303 (2)	135
C30—H30···O2[iii]	0.95	2.70	3.386 (2)	130

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