Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Acetonyltriphenylphosphonium 2,3,5-triphenyltetrazolium tetrachloridocuprate(II)

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Received 21 November 2017
Accepted 17 December 2017

Edited by G. Smith, Queensland University of Technology, Australia

Keywords: crystal structure; acetonyltriphenylphosphonium cation; 2,3,5-triphenyltetrazolium cation; tetrachloridocuprate dianion; hydrogen bonds; three-dimensional structure.

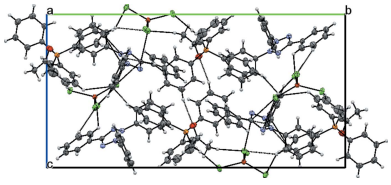
CCDC reference: 1811873

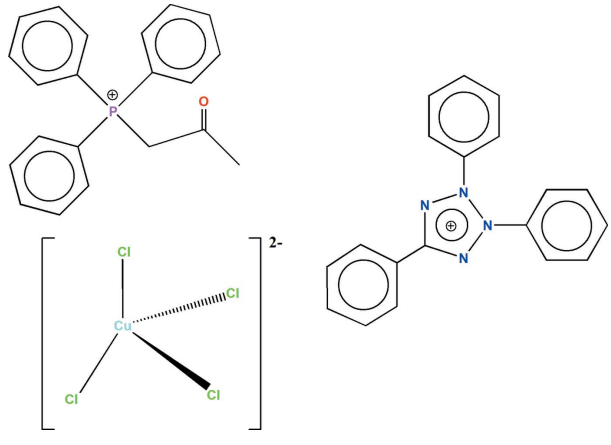
Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, $(C_{21}H_{20}OP)(C_{19}H_{15}N_4)[CuCl_4]$, was obtained by reacting $CuCl_2{\cdot}2H_2O$ with a mixture of one equivalent of acetonyltriphenylphosphonium chloride and one equivalent of 2,3,5-triphenyltetrazolium chloride in acetonitrile. In the structure, the Cu centre in the dianion is bonded to four chloride ligands and adopts a distorted tetrahedral geometry. The phosphonium cation likewise adopts the expected tetrahedral geometry. The tetrazolium ring forms dihedral angles of 77.68 (10), 26.85 (11) and 66.48 (10)° with the planes of the benzene rings of the substituent groups. In the crystal, weak C—H···Cl hydrogen-bonding interactions involving both cations and the anion give rise to a three-dimensional supramolecular structure.

1. Chemical context

Compounds containing the $[CuCl_4]^{2-}$ tetrahedral dianion with various cations have been widely studied (Wei & Willett, 2002; Elangovan *et al.*, 2007; Haddad & Al-Far, 2008; Al-Ktaifani & Rukiah, 2012; Wikaira *et al.*, 2013; Laus *et al.*, 2015). Likewise, a few compounds with an acetonyl triphenylphosphonium or 2,3,5-triphenyltetrazolium cation have also been reported (Diop *et al.*, 2013, 2015; Zhang *et al.*, 2007). To expand on the available data on both the $[CuCl_4]^{2-}$ anion as well as that on acetonyltriphenylphosphonium and 2,3,5-triphenyltetrazolium cations, we have initiated in this work the study of the interactions between $CuCl_2{\cdot}2H_2O$, acetonyl triphenylphosphonium chloride and 2,3,5-triphenyltetrazolium chloride, expecting the presence of both cations in the resulting compound. This has yielded the title complex salt, $(C_{21}H_{20}OP)^+{\cdot}(C_{19}H_{15}N_4)^+{\cdot}[CuCl_4]^{2-}$ whose crystal structure is reported herein.





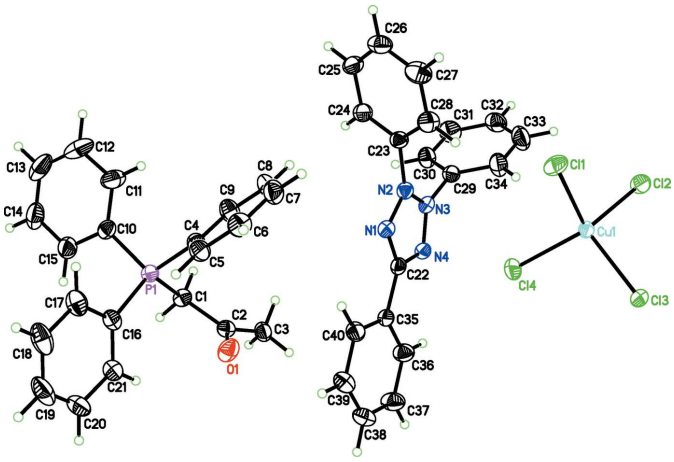


Figure 1
The molecular components of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The asymmetric unit of the title complex comprises an acetonyl triphenylphosphonium cation, a 2,3,5-triphenyltetrazolium cation and a tetrachloridocuprate dianion (Fig. 1). The environment around the Cu^{II} atom is distorted tetrahedral with distances and angles [Cu—Cl = 2.2327 (6)–2.2540 (5) Å and Cl—Cu—Cl = 97.67 (2)–135.49 (2)°] in normal ranges for the $[CuCl_4]^{2-}$ complex anion (Clay *et al.*, 1975; Laus *et al.*, 2015). The P—C distances within the acetonyl triphenylphosphonium cation are similar to those reported for the same cation (Diop *et al.*, 2013, 2015). The range for the C—P—C angles [107.07 (9)–113.36 (10)°] indicate a small variation of the geometry for this cation. Present in the cation is a C21—H···O1 interaction [3.147 (3) Å with C—H···O angle = 115°]. The N—C and N—N distances within the 2,3,5-triphenyl tetrazolium cation are consistent with a π delocalization in the tetrazolium ring, which forms dihedral angles of 77.68 (10), 26.85 (11) and 66.48 (10)° with the planes of the benzene rings of the substituent groups.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl2^{i}	0.99	2.54	3.363 (2)	141
C1—H1B···Cl2^{ii}	0.99	2.69	3.662 (2)	168
C3—H3B···Cl3^{ii}	0.98	2.74	3.714 (2)	171
C3—H3C···Cl2^{i}	0.98	2.90	3.630 (2)	132
C9—H9···Cl2^{ii}	0.95	2.97	3.917 (2)	172
C24—H24···Cl3^{ii}	0.95	2.99	3.783 (2)	142
C28—H28···Cl1	0.95	2.72	3.605 (2)	156
C30—H30···Cl3^{ii}	0.95	2.87	3.683 (2)	144
C30—H30···Cl4^{ii}	0.95	2.85	3.630 (2)	140

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

3. Supramolecular features

In the crystal, inter-species C—H···Cl hydrogen bonds between aromatic, methylene and methyl H atoms of the acetonyl triphenylphosphonium cation and the $[CuCl_4]^{2-}$ anions are present (Table 1) together with weak C—H···Cl hydrogen-bonding interactions involving phenyl H atoms of the 2,3,5-triphenyl tetrazolium cations. A three-dimensional supramolecular structure is formed (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.39; Groom *et al.*, 2016) returned hundreds and hundreds of different structures containing the $[CuCl_4]^{2-}$ dianion. To date,

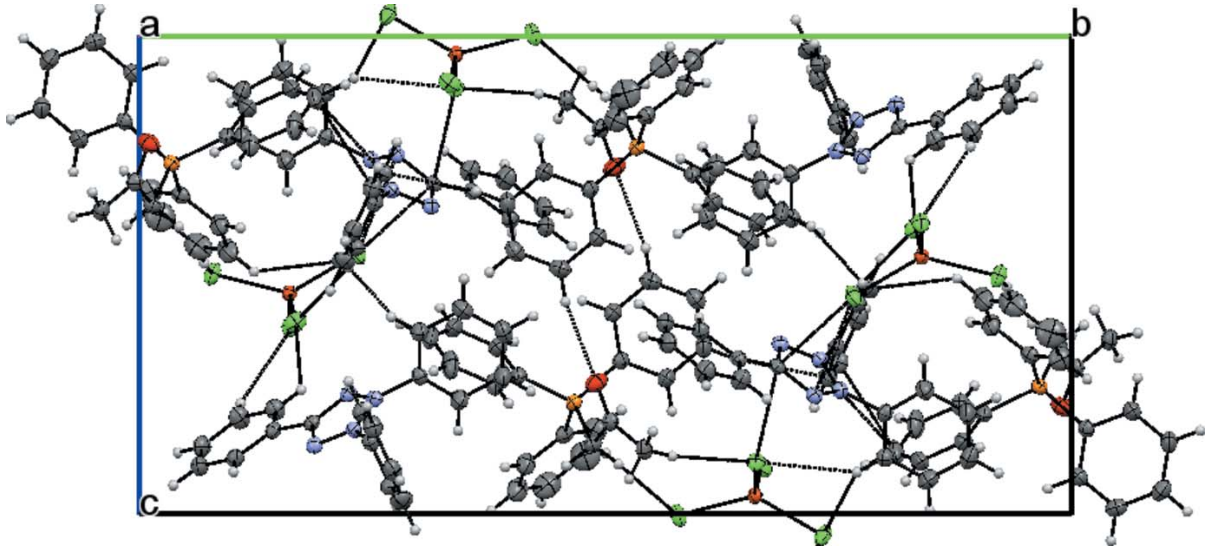


Figure 2
A view of the packing of the title compound viewed along [100], with hydrogen-bonding interactions shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. The acetonyltriphenylphosphonium cations form supramolecular dimers through pairs of centrosymmetric C—H···O interactions.

only nine structures of acetonyl triphenylphosphonium and seventeen structures of 2,3,5-triphenyltetrazolium have been deposited in the CSD. No structure including both acetonyltriphenylphosphonium and 2,3,5-triphenyltetrazolium species was found.

5. Synthesis and crystallization

All chemicals were purchased from Aldrich Company, Germany and used as received. Acetonyl triphenylphosphonium chloride and 2,3,5-triphenyl tetrazolium chloride were mixed in acetonitrile with $CuCl_2{\cdot}2H_2O$ in a 1:1:1 ratio: a yellow–orange solution was obtained. Orange crystals suitable for a single-crystal X-ray diffraction study were obtained after a slow solvent evaporation at room temperature (300 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed at calculated positions and refined as riding atoms, with C—H = 0.95 Å (aromatic), 0.99 Å (methylene) or 0.98 Å (methyl), and with U_{iso}(H) = 1.2U_{eq}(aromatic or methylene) or 1.5U_{eq}(methyl).

Funding information

The authors acknowledge the Cheikh Anta Diop University of Dakar (Senegal) and the University of Notre Dame (USA) for financial support and instrumentation use.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{21}H_{20}OP)(C_{19}H_{15}N_4)[CuCl_4]$
M_r	824.03
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	10.6868 (12), 26.421 (3), 13.5628 (15)
β (°)	90.709 (1)
V (Å^3)	3829.2 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.93
Crystal size (mm)	0.29 × 0.20 × 0.16
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.850, 0.939
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	86744, 9517, 7659
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.096, 1.04
No. of reflections	9517
No. of parameters	461
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.31

Computer programs: *APEX2* , *SAINT* and *XP* (Bruker, 2015), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *CIFTAB* (Sheldrick, 2015*b*).

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supporting information

Acta Cryst. (2018). E**74**, 69-71 [https://doi.org/10.1107/S205698901701800X]

Acetonyltriphenylphosphonium 2,3,5-triphenyltetrazolium tetrachloridocuprate(II)

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Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* (Bruker, 2015); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2015b).

Acetonyltriphenylphosphonium 2,3,5-triphenyltetrazolium tetrachloridocuprate(II)

Crystal data

$(C_{21}H_{20}OP)(C_{19}H_{15}N_4)[CuCl_4]$
M_r = 824.03
Monoclinic, $P2_1/n$
a = 10.6868 (12) Å
b = 26.421 (3) Å
c = 13.5628 (15) Å
β = 90.709 (1)°
V = 3829.2 (7) Å^3
Z = 4
$F(000)$ = 1692
D_x = 1.429 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9465 reflections
θ = 2.4–28.1°
μ = 0.93 mm^{-1}
T = 120 K
Irregular fragment, orange
0.29 × 0.20 × 0.16 mm

Data collection

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.33 pixels mm^{-1}
combination of ω and φ–scans
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)
T_{min} = 0.850, T_{max} = 0.939
86744 measured reflections
9517 independent reflections
7659 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 28.3°, θ_{min} = 1.5°
h = −14→14
k = −35→35
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.096
S = 1.04
9517 reflections
461 parameters
0 restraints
Primary atom site location: real-space vector search
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 2.8241P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.18416 (2)	0.83950 (2)	0.46171 (2)	0.01990 (7)
Cl1	0.37755 (5)	0.83273 (2)	0.40187 (4)	0.03219 (12)
Cl2	0.18895 (5)	0.92209 (2)	0.50256 (4)	0.03061 (12)
Cl3	−0.00778 (4)	0.83854 (2)	0.39095 (4)	0.02588 (11)
Cl4	0.17809 (5)	0.76656 (2)	0.54465 (4)	0.03418 (13)
P1	0.62501 (5)	0.46610 (2)	0.76661 (4)	0.02193 (11)
O1	0.35961 (15)	0.49029 (6)	0.72476 (11)	0.0365 (4)
C1	0.51075 (18)	0.48642 (8)	0.85438 (14)	0.0242 (4)
H1A	0.4910	0.4578	0.8987	0.029*
H1B	0.5471	0.5139	0.8953	0.029*
C2	0.38982 (18)	0.50531 (8)	0.80594 (15)	0.0258 (4)
C3	0.3142 (2)	0.54137 (8)	0.86465 (16)	0.0299 (4)
H3A	0.2388	0.5508	0.8271	0.045*
H3B	0.3639	0.5718	0.8788	0.045*
H3C	0.2902	0.5253	0.9267	0.045*
C4	0.64250 (18)	0.51654 (8)	0.67895 (15)	0.0242 (4)
C5	0.6371 (2)	0.50811 (8)	0.57820 (15)	0.0286 (4)
H5	0.6253	0.4748	0.5534	0.034*
C6	0.6490 (2)	0.54866 (9)	0.51329 (16)	0.0344 (5)
H6	0.6462	0.5430	0.4441	0.041*
C7	0.6650 (2)	0.59706 (9)	0.54977 (18)	0.0363 (5)
H7	0.6730	0.6248	0.5056	0.044*
C8	0.6693 (2)	0.60526 (9)	0.65035 (18)	0.0372 (5)
H8	0.6805	0.6386	0.6749	0.045*
C9	0.6576 (2)	0.56546 (8)	0.71550 (17)	0.0333 (5)
H9	0.6599	0.5714	0.7846	0.040*
C10	0.76907 (18)	0.45595 (8)	0.83306 (15)	0.0262 (4)
C11	0.8699 (2)	0.48849 (10)	0.82425 (19)	0.0408 (6)
H11	0.8650	0.5172	0.7822	0.049*
C12	0.9787 (2)	0.47832 (13)	0.8783 (2)	0.0576 (8)
H12	1.0487	0.5002	0.8725	0.069*
C13	0.9863 (2)	0.43719 (12)	0.9400 (2)	0.0528 (7)
H13	1.0613	0.4307	0.9760	0.063*
C14	0.8858 (2)	0.40559 (10)	0.9494 (2)	0.0450 (6)
H14	0.8908	0.3775	0.9930	0.054*
C15	0.7763 (2)	0.41431 (9)	0.89564 (18)	0.0361 (5)

H15	0.7070	0.3920	0.9016	0.043*
C16	0.5878 (2)	0.40659 (8)	0.71009 (15)	0.0268 (4)
C17	0.6791 (2)	0.38438 (9)	0.65135 (16)	0.0355 (5)
H17	0.7554	0.4017	0.6396	0.043*
C18	0.6582 (3)	0.33723 (9)	0.61035 (18)	0.0441 (6)
H18	0.7192	0.3223	0.5691	0.053*
C19	0.5484 (3)	0.31196 (9)	0.6296 (2)	0.0500 (7)
H19	0.5346	0.2793	0.6022	0.060*
C20	0.4587 (3)	0.33336 (9)	0.6881 (2)	0.0486 (7)
H20	0.3836	0.3154	0.7008	0.058*
C21	0.4772 (2)	0.38109 (8)	0.72871 (18)	0.0355 (5)
H21	0.4148	0.3961	0.7687	0.043*
N1	0.41588 (15)	0.68767 (6)	0.64421 (12)	0.0231 (3)
N2	0.46486 (15)	0.72999 (6)	0.67689 (12)	0.0218 (3)
N3	0.38773 (14)	0.75180 (6)	0.74104 (12)	0.0219 (3)
N4	0.28719 (15)	0.72419 (6)	0.75175 (12)	0.0225 (3)
C22	0.30628 (17)	0.68472 (7)	0.69106 (14)	0.0217 (4)
C23	0.58844 (18)	0.74780 (7)	0.65044 (15)	0.0237 (4)
C24	0.68680 (19)	0.73834 (8)	0.71430 (16)	0.0280 (4)
H24	0.6733	0.7241	0.7776	0.034*
C25	0.80653 (19)	0.75032 (8)	0.68297 (17)	0.0318 (5)
H25	0.8765	0.7440	0.7251	0.038*
C26	0.8245 (2)	0.77132 (9)	0.59150 (18)	0.0349 (5)
H26	0.9067	0.7793	0.5707	0.042*
C27	0.7234 (2)	0.78090 (10)	0.52971 (17)	0.0389 (5)
H27	0.7367	0.7956	0.4668	0.047*
C28	0.6029 (2)	0.76927 (9)	0.55851 (16)	0.0315 (5)
H28	0.5329	0.7758	0.5166	0.038*
C29	0.40967 (18)	0.80011 (8)	0.78841 (15)	0.0243 (4)
C30	0.4634 (2)	0.80027 (8)	0.88116 (16)	0.0315 (5)
H30	0.4889	0.7697	0.9122	0.038*
C31	0.4789 (2)	0.84658 (9)	0.92767 (18)	0.0392 (5)
H31	0.5162	0.8481	0.9915	0.047*
C32	0.4403 (2)	0.89058 (9)	0.88143 (19)	0.0376 (5)
H32	0.4505	0.9221	0.9141	0.045*
C33	0.3869 (3)	0.88917 (9)	0.7881 (2)	0.0442 (6)
H33	0.3608	0.9197	0.7570	0.053*
C34	0.3714 (2)	0.84312 (8)	0.73976 (18)	0.0373 (5)
H34	0.3356	0.8415	0.6754	0.045*
C35	0.21638 (18)	0.64331 (7)	0.67518 (14)	0.0225 (4)
C36	0.0992 (2)	0.64553 (9)	0.71863 (17)	0.0314 (5)
H36	0.0781	0.6733	0.7596	0.038*
C37	0.0135 (2)	0.60693 (9)	0.70173 (18)	0.0371 (5)
H37	−0.0665	0.6081	0.7314	0.045*
C38	0.0449 (2)	0.56676 (9)	0.64165 (17)	0.0344 (5)
H38	−0.0146	0.5408	0.6287	0.041*
C39	0.1622 (2)	0.56409 (8)	0.60035 (16)	0.0322 (5)
H39	0.1837	0.5359	0.5605	0.039*

C40	0.24869 (19)	0.60236 (8)	0.61681 (15)	0.0276 (4)
H40	0.3294	0.6005	0.5884	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01889 (12)	0.01888 (12)	0.02188 (12)	0.00136 (8)	−0.00154 (8)	−0.00022 (9)
Cl1	0.0206 (2)	0.0399 (3)	0.0361 (3)	0.0023 (2)	0.00368 (19)	−0.0073 (2)
Cl2	0.0262 (2)	0.0225 (2)	0.0430 (3)	0.00192 (19)	−0.0028 (2)	−0.0096 (2)
Cl3	0.0214 (2)	0.0246 (2)	0.0315 (2)	−0.00047 (17)	−0.00662 (18)	0.00112 (19)
Cl4	0.0374 (3)	0.0270 (3)	0.0379 (3)	−0.0007 (2)	−0.0100 (2)	0.0112 (2)
P1	0.0215 (2)	0.0225 (2)	0.0219 (2)	−0.00009 (19)	0.00078 (18)	−0.00152 (19)
O1	0.0346 (8)	0.0422 (9)	0.0324 (8)	0.0075 (7)	−0.0091 (7)	−0.0084 (7)
C1	0.0229 (9)	0.0283 (10)	0.0214 (9)	0.0004 (8)	0.0029 (7)	−0.0025 (8)
C2	0.0239 (9)	0.0245 (10)	0.0290 (10)	−0.0021 (8)	0.0016 (8)	0.0005 (8)
C3	0.0303 (11)	0.0227 (10)	0.0366 (11)	0.0029 (8)	0.0051 (9)	0.0017 (9)
C4	0.0238 (9)	0.0230 (10)	0.0260 (10)	0.0013 (7)	0.0034 (7)	−0.0004 (8)
C5	0.0312 (11)	0.0266 (11)	0.0279 (10)	−0.0002 (8)	0.0005 (8)	−0.0029 (8)
C6	0.0367 (12)	0.0402 (13)	0.0263 (11)	−0.0003 (10)	0.0013 (9)	0.0045 (9)
C7	0.0385 (12)	0.0321 (12)	0.0385 (12)	0.0040 (10)	0.0016 (10)	0.0100 (10)
C8	0.0474 (14)	0.0222 (11)	0.0422 (13)	0.0008 (10)	0.0035 (10)	0.0010 (9)
C9	0.0450 (13)	0.0259 (11)	0.0293 (11)	0.0020 (9)	0.0020 (9)	−0.0029 (9)
C10	0.0230 (9)	0.0288 (11)	0.0268 (10)	0.0033 (8)	0.0011 (7)	−0.0032 (8)
C11	0.0267 (11)	0.0484 (15)	0.0471 (14)	−0.0069 (10)	−0.0003 (10)	0.0021 (11)
C12	0.0228 (12)	0.078 (2)	0.072 (2)	−0.0072 (13)	−0.0036 (12)	−0.0031 (17)
C13	0.0309 (13)	0.0672 (19)	0.0598 (17)	0.0169 (13)	−0.0146 (12)	−0.0122 (15)
C14	0.0468 (15)	0.0390 (14)	0.0488 (15)	0.0165 (11)	−0.0157 (12)	−0.0051 (11)
C15	0.0357 (12)	0.0309 (12)	0.0414 (13)	0.0038 (9)	−0.0095 (10)	−0.0019 (10)
C16	0.0335 (11)	0.0218 (10)	0.0249 (10)	−0.0004 (8)	−0.0032 (8)	0.0005 (8)
C17	0.0474 (13)	0.0300 (12)	0.0292 (11)	0.0033 (10)	0.0042 (10)	−0.0011 (9)
C18	0.0739 (19)	0.0283 (12)	0.0300 (12)	0.0084 (12)	0.0016 (12)	−0.0045 (9)
C19	0.078 (2)	0.0225 (12)	0.0493 (16)	−0.0013 (12)	−0.0186 (14)	−0.0061 (11)
C20	0.0479 (15)	0.0266 (12)	0.0709 (19)	−0.0099 (11)	−0.0150 (14)	−0.0003 (12)
C21	0.0342 (12)	0.0270 (11)	0.0452 (13)	−0.0009 (9)	−0.0055 (10)	0.0008 (10)
N1	0.0213 (8)	0.0232 (8)	0.0247 (8)	0.0005 (6)	−0.0019 (6)	0.0004 (6)
N2	0.0208 (8)	0.0220 (8)	0.0225 (8)	0.0013 (6)	0.0011 (6)	−0.0002 (6)
N3	0.0190 (7)	0.0237 (8)	0.0228 (8)	0.0030 (6)	−0.0006 (6)	0.0000 (6)
N4	0.0199 (8)	0.0236 (8)	0.0240 (8)	−0.0001 (6)	−0.0017 (6)	0.0026 (6)
C22	0.0205 (9)	0.0227 (9)	0.0219 (9)	0.0018 (7)	−0.0015 (7)	0.0039 (7)
C23	0.0207 (9)	0.0227 (10)	0.0277 (10)	−0.0007 (7)	0.0031 (7)	−0.0026 (8)
C24	0.0261 (10)	0.0290 (11)	0.0288 (10)	−0.0021 (8)	−0.0004 (8)	0.0015 (8)
C25	0.0226 (10)	0.0316 (11)	0.0411 (12)	−0.0017 (8)	−0.0005 (8)	−0.0031 (9)
C26	0.0296 (11)	0.0316 (12)	0.0438 (13)	−0.0066 (9)	0.0111 (9)	−0.0080 (10)
C27	0.0420 (13)	0.0451 (14)	0.0300 (11)	−0.0077 (11)	0.0124 (10)	0.0028 (10)
C28	0.0318 (11)	0.0367 (12)	0.0260 (10)	−0.0025 (9)	−0.0008 (8)	0.0019 (9)
C29	0.0227 (9)	0.0232 (10)	0.0270 (10)	0.0004 (7)	0.0027 (7)	−0.0026 (8)
C30	0.0374 (12)	0.0273 (11)	0.0298 (11)	0.0035 (9)	−0.0021 (9)	−0.0011 (9)
C31	0.0462 (14)	0.0373 (13)	0.0339 (12)	−0.0017 (11)	−0.0022 (10)	−0.0083 (10)

C32	0.0379 (12)	0.0277 (11)	0.0472 (14)	−0.0023 (9)	0.0065 (10)	−0.0092 (10)
C33	0.0549 (16)	0.0244 (12)	0.0531 (15)	0.0043 (11)	−0.0057 (12)	0.0016 (11)
C34	0.0471 (14)	0.0284 (12)	0.0361 (12)	0.0035 (10)	−0.0086 (10)	0.0017 (9)
C35	0.0215 (9)	0.0220 (9)	0.0239 (9)	−0.0004 (7)	−0.0022 (7)	0.0033 (7)
C36	0.0251 (10)	0.0324 (11)	0.0368 (12)	−0.0023 (9)	0.0049 (8)	−0.0037 (9)
C37	0.0284 (11)	0.0386 (13)	0.0446 (13)	−0.0076 (9)	0.0072 (9)	−0.0040 (10)
C38	0.0356 (12)	0.0298 (11)	0.0379 (12)	−0.0109 (9)	0.0009 (9)	0.0005 (9)
C39	0.0391 (12)	0.0257 (11)	0.0320 (11)	−0.0035 (9)	0.0021 (9)	−0.0016 (9)
C40	0.0275 (10)	0.0256 (10)	0.0299 (10)	0.0009 (8)	0.0047 (8)	0.0013 (8)

Geometric parameters (Å, º)

Cu1—Cl4	2.2327 (6)	C19—H19	0.9500
Cu1—Cl1	2.2368 (6)	C20—C21	1.389 (3)
Cu1—Cl2	2.2518 (6)	C20—H20	0.9500
Cu1—Cl3	2.2540 (5)	C21—H21	0.9500
P1—C16	1.792 (2)	N1—N2	1.310 (2)
P1—C10	1.794 (2)	N1—C22	1.342 (2)
P1—C4	1.797 (2)	N2—N3	1.336 (2)
P1—C1	1.7979 (19)	N2—C23	1.451 (2)
O1—C2	1.210 (3)	N3—N4	1.308 (2)
C1—C2	1.526 (3)	N3—C29	1.447 (3)
C1—H1A	0.9900	N4—C22	1.346 (3)
C1—H1B	0.9900	C22—C35	1.470 (3)
C2—C3	1.487 (3)	C23—C24	1.377 (3)
C3—H3A	0.9800	C23—C28	1.380 (3)
C3—H3B	0.9800	C24—C25	1.390 (3)
C3—H3C	0.9800	C24—H24	0.9500
C4—C5	1.385 (3)	C25—C26	1.375 (3)
C4—C9	1.393 (3)	C25—H25	0.9500
C5—C6	1.393 (3)	C26—C27	1.383 (3)
C5—H5	0.9500	C26—H26	0.9500
C6—C7	1.381 (3)	C27—C28	1.384 (3)
C6—H6	0.9500	C27—H27	0.9500
C7—C8	1.381 (3)	C28—H28	0.9500
C7—H7	0.9500	C29—C34	1.374 (3)
C8—C9	1.380 (3)	C29—C30	1.376 (3)
C8—H8	0.9500	C30—C31	1.385 (3)
C9—H9	0.9500	C30—H30	0.9500
C10—C11	1.385 (3)	C31—C32	1.382 (3)
C10—C15	1.391 (3)	C31—H31	0.9500
C11—C12	1.393 (4)	C32—C33	1.383 (4)
C11—H11	0.9500	C32—H32	0.9500
C12—C13	1.373 (4)	C33—C34	1.391 (3)
C12—H12	0.9500	C33—H33	0.9500
C13—C14	1.368 (4)	C34—H34	0.9500
C13—H13	0.9500	C35—C40	1.387 (3)
C14—C15	1.390 (3)	C35—C36	1.391 (3)

C14—H14	0.9500	C36—C37	1.388 (3)
C15—H15	0.9500	C36—H36	0.9500
C16—C21	1.387 (3)	C37—C38	1.382 (3)
C16—C17	1.396 (3)	C37—H37	0.9500
C17—C18	1.381 (3)	C38—C39	1.381 (3)
C17—H17	0.9500	C38—H38	0.9500
C18—C19	1.378 (4)	C39—C40	1.386 (3)
C18—H18	0.9500	C39—H39	0.9500
C19—C20	1.373 (4)	C40—H40	0.9500

Cl4—Cu1—Cl1	98.43 (2)	C20—C19—H19	119.6
Cl4—Cu1—Cl2	135.49 (2)	C18—C19—H19	119.6
Cl1—Cu1—Cl2	98.54 (2)	C19—C20—C21	120.4 (3)
Cl4—Cu1—Cl3	99.95 (2)	C19—C20—H20	119.8
Cl1—Cu1—Cl3	133.21 (2)	C21—C20—H20	119.8
Cl2—Cu1—Cl3	97.67 (2)	C16—C21—C20	119.0 (2)
C16—P1—C10	105.55 (10)	C16—C21—H21	120.5
C16—P1—C4	113.08 (9)	C20—C21—H21	120.5
C10—P1—C4	110.33 (10)	N2—N1—C22	103.71 (16)
C16—P1—C1	113.36 (10)	N1—N2—N3	109.96 (15)
C10—P1—C1	107.31 (9)	N1—N2—C23	123.66 (16)
C4—P1—C1	107.07 (9)	N3—N2—C23	126.28 (16)
C2—C1—P1	113.02 (14)	N4—N3—N2	110.24 (15)
C2—C1—H1A	109.0	N4—N3—C29	124.84 (16)
P1—C1—H1A	109.0	N2—N3—C29	124.86 (16)
C2—C1—H1B	109.0	N3—N4—C22	103.49 (15)
P1—C1—H1B	109.0	N1—C22—N4	112.61 (17)
H1A—C1—H1B	107.8	N1—C22—C35	123.14 (18)
O1—C2—C3	123.83 (19)	N4—C22—C35	124.23 (17)
O1—C2—C1	119.95 (18)	C24—C23—C28	123.34 (19)
C3—C2—C1	116.22 (17)	C24—C23—N2	118.41 (18)
C2—C3—H3A	109.5	C28—C23—N2	117.98 (18)
C2—C3—H3B	109.5	C23—C24—C25	117.7 (2)
H3A—C3—H3B	109.5	C23—C24—H24	121.1
C2—C3—H3C	109.5	C25—C24—H24	121.1
H3A—C3—H3C	109.5	C26—C25—C24	120.5 (2)
H3B—C3—H3C	109.5	C26—C25—H25	119.8
C5—C4—C9	120.24 (19)	C24—C25—H25	119.8
C5—C4—P1	122.00 (16)	C25—C26—C27	120.3 (2)
C9—C4—P1	117.72 (15)	C25—C26—H26	119.9
C4—C5—C6	119.8 (2)	C27—C26—H26	119.9
C4—C5—H5	120.1	C26—C27—C28	120.7 (2)
C6—C5—H5	120.1	C26—C27—H27	119.6
C7—C6—C5	119.8 (2)	C28—C27—H27	119.6
C7—C6—H6	120.1	C23—C28—C27	117.5 (2)
C5—C6—H6	120.1	C23—C28—H28	121.3
C6—C7—C8	120.1 (2)	C27—C28—H28	121.3
C6—C7—H7	120.0	C34—C29—C30	123.7 (2)

C8—C7—H7	120.0	C34—C29—N3	118.08 (18)
C9—C8—C7	120.7 (2)	C30—C29—N3	118.17 (18)
C9—C8—H8	119.6	C29—C30—C31	117.7 (2)
C7—C8—H8	119.6	C29—C30—H30	121.1
C8—C9—C4	119.3 (2)	C31—C30—H30	121.1
C8—C9—H9	120.3	C32—C31—C30	120.2 (2)
C4—C9—H9	120.3	C32—C31—H31	119.9
C11—C10—C15	120.4 (2)	C30—C31—H31	119.9
C11—C10—P1	121.84 (17)	C31—C32—C33	120.7 (2)
C15—C10—P1	117.74 (16)	C31—C32—H32	119.7
C10—C11—C12	118.7 (3)	C33—C32—H32	119.7
C10—C11—H11	120.7	C32—C33—C34	120.0 (2)
C12—C11—H11	120.7	C32—C33—H33	120.0
C13—C12—C11	121.1 (3)	C34—C33—H33	120.0
C13—C12—H12	119.5	C29—C34—C33	117.6 (2)
C11—C12—H12	119.5	C29—C34—H34	121.2
C14—C13—C12	120.0 (2)	C33—C34—H34	121.2
C14—C13—H13	120.0	C40—C35—C36	120.41 (19)
C12—C13—H13	120.0	C40—C35—C22	119.82 (18)
C13—C14—C15	120.4 (3)	C36—C35—C22	119.77 (18)
C13—C14—H14	119.8	C37—C36—C35	119.6 (2)
C15—C14—H14	119.8	C37—C36—H36	120.2
C14—C15—C10	119.4 (2)	C35—C36—H36	120.2
C14—C15—H15	120.3	C38—C37—C36	119.8 (2)
C10—C15—H15	120.3	C38—C37—H37	120.1
C21—C16—C17	120.2 (2)	C36—C37—H37	120.1
C21—C16—P1	122.23 (17)	C39—C38—C37	120.4 (2)
C17—C16—P1	117.39 (17)	C39—C38—H38	119.8
C18—C17—C16	119.9 (2)	C37—C38—H38	119.8
C18—C17—H17	120.1	C38—C39—C40	120.3 (2)
C16—C17—H17	120.1	C38—C39—H39	119.9
C19—C18—C17	119.6 (3)	C40—C39—H39	119.9
C19—C18—H18	120.2	C39—C40—C35	119.39 (19)
C17—C18—H18	120.2	C39—C40—H40	120.3
C20—C19—C18	120.8 (2)	C35—C40—H40	120.3

C16—P1—C1—C2	−73.90 (17)	C22—N1—N2—C23	176.44 (17)
C10—P1—C1—C2	169.96 (14)	N1—N2—N3—N4	0.2 (2)
C4—P1—C1—C2	51.51 (17)	C23—N2—N3—N4	−176.19 (17)
P1—C1—C2—O1	25.5 (3)	N1—N2—N3—C29	−177.26 (16)
P1—C1—C2—C3	−155.48 (15)	C23—N2—N3—C29	6.4 (3)
C16—P1—C4—C5	−4.8 (2)	N2—N3—N4—C22	−0.21 (19)
C10—P1—C4—C5	113.14 (18)	C29—N3—N4—C22	177.20 (17)
C1—P1—C4—C5	−130.39 (17)	N2—N1—C22—N4	−0.1 (2)
C16—P1—C4—C9	173.01 (17)	N2—N1—C22—C35	178.44 (17)
C10—P1—C4—C9	−69.04 (19)	N3—N4—C22—N1	0.2 (2)
C1—P1—C4—C9	47.43 (19)	N3—N4—C22—C35	−178.33 (17)
C9—C4—C5—C6	1.1 (3)	N1—N2—C23—C24	−97.3 (2)

P1—C4—C5—C6	178.89 (16)	N3—N2—C23—C24	78.6 (3)
C4—C5—C6—C7	−0.6 (3)	N1—N2—C23—C28	77.0 (2)
C5—C6—C7—C8	0.1 (4)	N3—N2—C23—C28	−107.2 (2)
C6—C7—C8—C9	−0.1 (4)	C28—C23—C24—C25	−1.2 (3)
C7—C8—C9—C4	0.6 (4)	N2—C23—C24—C25	172.68 (18)
C5—C4—C9—C8	−1.1 (3)	C23—C24—C25—C26	0.6 (3)
P1—C4—C9—C8	−178.98 (18)	C24—C25—C26—C27	0.2 (3)
C16—P1—C10—C11	130.83 (19)	C25—C26—C27—C28	−0.4 (4)
C4—P1—C10—C11	8.3 (2)	C24—C23—C28—C27	1.0 (3)
C1—P1—C10—C11	−108.0 (2)	N2—C23—C28—C27	−172.92 (19)
C16—P1—C10—C15	−50.06 (19)	C26—C27—C28—C23	−0.2 (4)
C4—P1—C10—C15	−172.54 (17)	N4—N3—C29—C34	−90.4 (2)
C1—P1—C10—C15	71.13 (19)	N2—N3—C29—C34	86.6 (2)
C15—C10—C11—C12	0.7 (4)	N4—N3—C29—C30	87.2 (2)
P1—C10—C11—C12	179.8 (2)	N2—N3—C29—C30	−95.8 (2)
C10—C11—C12—C13	−0.5 (4)	C34—C29—C30—C31	0.2 (3)
C11—C12—C13—C14	−0.4 (5)	N3—C29—C30—C31	−177.20 (19)
C12—C13—C14—C15	1.1 (4)	C29—C30—C31—C32	0.5 (4)
C13—C14—C15—C10	−1.0 (4)	C30—C31—C32—C33	−0.6 (4)
C11—C10—C15—C14	0.0 (3)	C31—C32—C33—C34	0.1 (4)
P1—C10—C15—C14	−179.11 (18)	C30—C29—C34—C33	−0.8 (4)
C10—P1—C16—C21	121.13 (19)	N3—C29—C34—C33	176.7 (2)
C4—P1—C16—C21	−118.17 (18)	C32—C33—C34—C29	0.6 (4)
C1—P1—C16—C21	4.0 (2)	N1—C22—C35—C40	6.5 (3)
C10—P1—C16—C17	−54.18 (19)	N4—C22—C35—C40	−175.14 (18)
C4—P1—C16—C17	66.53 (19)	N1—C22—C35—C36	−173.36 (19)
C1—P1—C16—C17	−171.35 (16)	N4—C22—C35—C36	5.0 (3)
C21—C16—C17—C18	1.1 (3)	C40—C35—C36—C37	−1.3 (3)
P1—C16—C17—C18	176.46 (18)	C22—C35—C36—C37	178.6 (2)
C16—C17—C18—C19	−1.5 (4)	C35—C36—C37—C38	−0.3 (4)
C17—C18—C19—C20	0.9 (4)	C36—C37—C38—C39	1.7 (4)
C18—C19—C20—C21	0.1 (4)	C37—C38—C39—C40	−1.6 (4)
C17—C16—C21—C20	−0.1 (3)	C38—C39—C40—C35	0.0 (3)
P1—C16—C21—C20	−175.23 (19)	C36—C35—C40—C39	1.4 (3)
C19—C20—C21—C16	−0.5 (4)	C22—C35—C40—C39	−178.46 (19)
C22—N1—N2—N3	−0.02 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···Cl2^{i}	0.99	2.54	3.363 (2)	141
C1—H1*B*···Cl2^{ii}	0.99	2.69	3.662 (2)	168
C3—H3*B*···Cl3^{ii}	0.98	2.74	3.714 (2)	171
C3—H3*C*···Cl2^{i}	0.98	2.90	3.630 (2)	132
C9—H9···Cl2^{ii}	0.95	2.97	3.917 (2)	172
C24—H24···Cl3^{ii}	0.95	2.99	3.783 (2)	142
C28—H28···Cl1	0.95	2.72	3.605 (2)	156

C30—H30···Cl3^{ii}	0.95	2.87	3.683 (2)	144
C30—H30···Cl4^{ii}	0.95	2.85	3.630 (2)	140

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