

cyclo-Tetrakis(μ -2,4,6-trimethylphenyl- $\kappa C^1:\kappa C^1$)-bis(trimethylphosphane)-1 κP ,3 κP -tetracopper(I)

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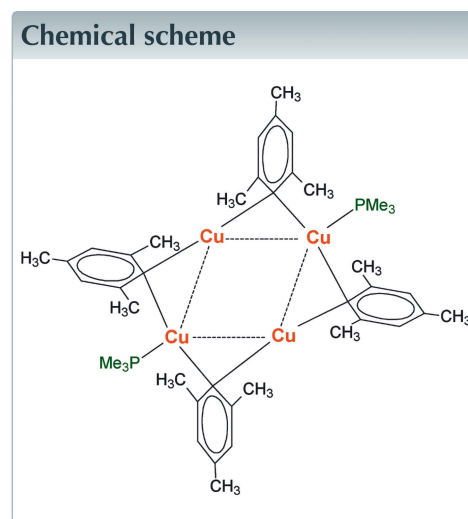
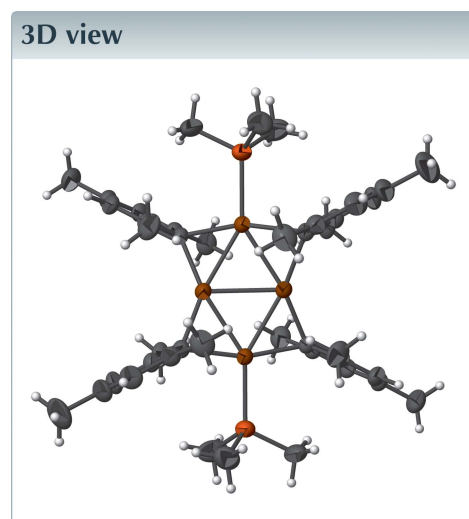
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Keywords: crystal structure; copper; phosphine; complex.

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

The title compound, $[\text{Cu}_4(\text{C}_9\text{H}_{11})_4(\text{C}_3\text{H}_9\text{P})_2]$ or $[\text{Cu}_4(\text{Mes})_4(\text{PMe}_3)_2]$ (Mes = 2,4,6-trimethylphenyl), was synthesized from copper(I) mesityl and trimethylphosphane in THF as solvent. The molecular structure of the complex has C_2 symmetry and consists of four copper(I) atoms bridged by four μ -mesityl groups, giving an eight-membered puckered $\{\text{Cu}_4\text{C}_4\}$ ring. Additionally, two copper(I) atoms at opposite corners of the Cu_4 rhomb are each linked to a terminal PMe_3 ligand. The PMe_3 -bearing copper(I) atoms exhibit a distorted trigonal-planar coordination mode whereas the remaining Cu atoms linked to two mesityl groups are nearly linearly coordinated.



Structure description

Among Cu^{I} organyls, mesitylcopper is one of the most extensively studied compounds. Since its first synthesis in 1981 (Tsuda *et al.*, 1981), mesitylcopper has found widespread application in preparative organometallic chemistry (Stollenz & Meyer, 2012). In the solid state, mesitylcopper can exist as a pentamer $(\text{CuMes})_5$ (Gambarotta *et al.*, 1983; Meyer *et al.*, 1989) or as a tetramer $(\text{CuMes})_4$ (Eriksson & Håkansson, 1997). On treatment with donor ligands L , mesitylcopper displays different reaction patterns depending on the nature of L . In the case of tetrahydrothiophene (THT), the reaction proceeds under retention of the tetranuclear cluster structure to form $[\text{Cu}_4(\text{Mes})_4(\text{THT})_2]$ (Gambarotta *et al.*, 1983; Meyer *et al.*, 1989). Treatment of mesitylcopper with PPh_3 in toluene led to a compound $[\text{CuMes}(\text{PPh}_3)_2]\cdot\text{C}_7\text{H}_8$ with a yet unknown crystal structure (Meyer *et al.*, 1989). The reaction with dppe (1,2-bis(diphenylphosphino)ethane) causes a degradation of the Cu_4Mes_4 cluster to give a cuproprate $[(\text{dppe})_2\text{Cu}][\text{CuMes}_2]$ (Leoni *et al.*, 1983).

In order to get some insight into the reactivity of mesitylcopper towards sterically less demanding phosphanes, trimethylphosphane was chosen as a ligand. Treatment of a

Table 1
Selected geometric parameters (Å, °).

C1—Cu1	2.006 (3)	P—Cu2	2.2967 (9)
C1—Cu2	2.095 (3)	Cu1—Cu1 ⁱ	2.5657 (7)
C10—Cu1 ⁱ	2.005 (3)	Cu1—Cu2	2.4603 (5)
C10—Cu2	2.093 (3)	Cu1—Cu2 ⁱ	2.4625 (5)
C10 ⁱ —Cu1—C1	138.26 (11)	C10—Cu2—C1	163.04 (11)
C1—Cu2—P	97.94 (8)	C10—Cu2—P	99.02 (8)

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

solution of mesitylcopper in THF with PMe_3 at room temperature led to the formation of the tetranuclear complex $[\text{Cu}_4(\text{Mes})_4(\text{PMe}_3)_2]$ (**1**).

The molecular structure of (**1**) comprises four copper(I) atoms that are linked by four μ -mesityl groups to give an eight-membered $\{\text{Cu}_4\text{C}_4\}$ ring (Fig. 1). Additionally, two copper atoms at diametrically opposite positions of the ring are each linked to a terminal PMe_3 group. The tetranuclear copper complex exhibits crystallographic C_2 symmetry with the diad axis passing through the center of the C10—C15 bond. The rhombic arrangement of the copper atoms is nearly planar, with marginal deviations of 0.0087 Å from the mean plane through the four copper atoms. The relatively small Cu···Cu distances at the edges of the rhomb [2.4603 (5)–2.4625 (5) Å] suggest cuprophilic interactions. The Cu···Cu separations between the copper atoms at opposite corners of the rhomb are 4.2013 (5) Å for $\text{Cu2} \cdots \text{Cu2}^i$ [symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$] and 2.5657 (7) Å for $\text{Cu1} \cdots \text{Cu1}^i$. Similar shaped arrangements of four Cu atoms were observed in the derivatives $[\text{Cu}_4(\text{Mes})_4(\text{THT})_2]$, $[\text{Cu}_4(o\text{-Tol})_4(\text{SMe}_2)_2]$ (Lend-

ers *et al.*, 1991) and $[\text{Cu}_4\text{Ph}_4(\text{SMe}_2)_2]$ (Olmstead & Power, 1990). Complex (**1**) exhibits two types of differently coordinated Cu atoms (Table 1). Cu1 is surrounded by two mesityl groups with Cu—C distances of 2.005 (3) and 2.006 (3) Å. In comparison with Cu_4Mes_4 , the Cu—C distances are slightly enlarged by around 0.014 Å. However, the bending of the C1—Cu1—C10ⁱ unit [138.3 (1)°] is clearly more pronounced than in $[\text{Cu}_4\text{Mes}_4]$ (164.05–165.70°). Apart from two mesityl groups, Cu2 bears a PMe_3 unit as a third ligand. The increased coordination number leads to a further enlargement of the Cu—C distances with values of 2.093 (3) and 2.095 (3) Å. The coordination around Cu2 is planar with a C—Cu—C angle of 163.0 (1)° and C—Cu—P angles of 97.9 (1)° and 99.0 (1)° (sum of the angles around Cu2: 359.9°). Comparison of the bond lengths of compound (**1**) and related $[\text{Cu}_4\text{Mes}_4L_2]$ complexes reveals that the ligand PMe_3 leads to a larger increase of the Cu—C distances for the tricoordinate copper atoms than other ligands investigated so far. In $[\text{Cu}_4\text{Mes}_4L_2]$ complexes with $L =$ piperidine, allyl methyl sulfide, 2,5-dithiahexane, tetrahydrothiophene and bis[2-[1-(dimethylamino)ethyl]phenylthiolato}magnesium, the mean Cu—C distances for the tricoordinated copper atoms are in the range 2.054–2.064 Å. In the case of the dicoordinated Cu there is no particular effect. Furthermore, there is a slight influence on the C—Cu—C angles for the dicoordinated [138.3 (1)°] and the tricoordinate copper atoms [163.0 (1)°], which are smaller than in the $[\text{Cu}_4\text{Mes}_4L_2]$ complexes mentioned above (140.3–142.8° and 165.0–170.2°, respectively).

The molecular packing reveals no special supramolecular features (Fig. 2). Most of the contacts are of the van der Waals type with some minor participation of C—H··· π interactions: C17—H17A···Cg2ⁱ with $d(\text{H} \cdots \text{Cg}2) = 2.87$ Å, C17—H17A···Cg2 = 167° [Cg2 is the centroid of the C10—C15 ring; symmetry code: (i) $-x, y, \frac{1}{2} - z$].

Generally, X-ray crystallographic studies on Cu^I aryl compounds with auxiliary phosphane ligands are relatively rare. According to the CSD database (Groom *et al.*, 2016), there are two compounds of the type $[\text{RCu}(\text{PR}'_3)]$ [$R = (2,2'',4,4'',6,6''\text{-hexamethyl-1,1':3,1''-terphenyl-2'-yl})$, $R' = \text{Ph}$

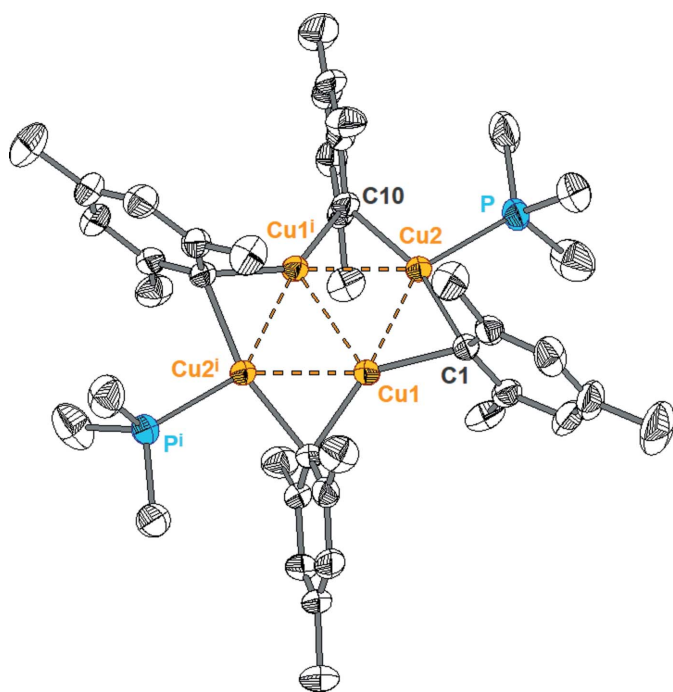


Figure 1
Molecular structure of $[\text{Cu}_4\text{Mes}_4(\text{PMe}_3)_2]$ showing the labeling scheme. Displacement ellipsoids were drawn at the 50% probability level, H atoms are omitted for clarity. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$].

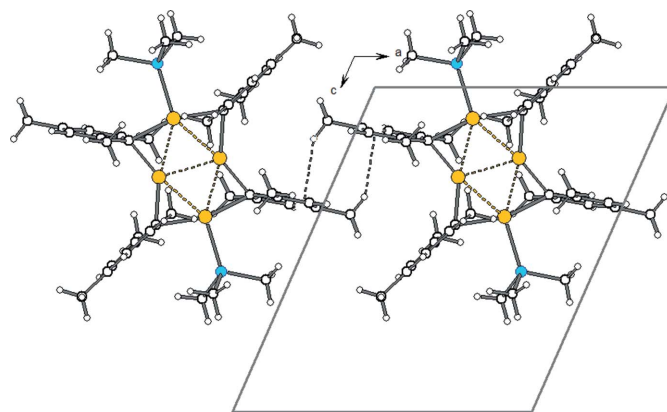


Figure 2
Partial packing diagram for **1** in a view down the crystallographic b axis. The intermolecular C—H··· π interactions are shown as gray dashed lines.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Cu ₄ (C ₉ H ₁₁) ₄ (C ₃ H ₉ P) ₂]
<i>M_r</i>	883.01
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	213
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.0750 (8), 27.5202 (18), 14.3164 (9)
β (°)	113.668 (5)
<i>V</i> (Å ³)	4357.3 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.03
Crystal size (mm)	0.51 × 0.32 × 0.19
Data collection	
Diffraction	Stoe IPDS 2
Absorption correction	Integration (<i>X-AREA</i> ; Stoe & Cie, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.508, 0.758
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	10982, 3839, 3043
<i>R_{int}</i>	0.050
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.597
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.100, 1.04
No. of reflections	3839
No. of parameters	217
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.48, -0.44

Computer programs: (*X-AREA*; Stoe & Cie, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

(Niemeyer, 2003), *R'* = Et (Rungthanaphatsophon *et al.*, 2016), containing nearly linear C—Cu—P units. Typically, this structural motif occurs if further molecular aggregation is prevented by sterically demanding aryl groups. The Cu—C bond lengths in [RCu(PR'₃)]-type compounds are 1.922 Å for the PPh₃ derivative (Niemeyer, 2003) and 1.930 Å in the case of the PEt₃ co-ligand. The shortening of the Cu—C distances in comparison with [Cu₄(Mes)₄(PMe₃)₂] may be attributed to the lower coordination number of the copper atoms. The same effect is also visible for the Cu—P distances of 2.189 Å (Niemeyer, 2003) and 2.200 Å (Rungthanaphatsophon *et al.*, 2016), respectively. Furthermore, there is a terphenyl copper complex of the type [RCu(PR'₃)₂] (*R'* = Et) with two phosphane units attached to copper. In this case, the copper atom exhibits a distorted trigonal-planar coordination with markedly enlarged Cu—C (1.979 Å) and Cu—P (2.250 and 2.256 Å) distances (Rungthanaphatsophon *et al.*, 2016).

The CSD database contains five entries for [Cu₄Mes₄L₂] complexes, with *L* = THT (Gambarotta *et al.*, 1983; Meyer *et al.*, 1989), piperidine (Sung *et al.*, 2015), allyl methyl sulfide or 2,5-dithiahexane (Kokoli *et al.*, 2013). There are also some heterometallic Cu₄Mes₄ complexes with bis(thiophenolato)magnesium units as ligands (Knotter *et al.*, 1990).

Synthesis and crystallization

A solution of 0.46 g (2.5 mmol) mesitylcopper (Meyer *et al.*, 1989) in 10 ml of THF was treated with 0.13 ml (1.25 mmol) of

trimethyl phosphane. The reaction mixture was stirred for one h at 293 K. The reaction product [Cu₄(Mes)₄(PMe₃)₂] (**1**) was precipitated by the addition of 30 ml of *n*-hexane. After filtration, the colorless product was washed with diethyl ether (2 × 5 ml) and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a THF solution of the product. Yield: 0.33 g (60%). C₄₂H₆₂Cu₄P₂ (883.01 g mol⁻¹). Analysis: Cu 29.0% (calc. 28.8%) IR (cm⁻¹) 2997(*w*), 2963(*m*), 2901(*m*), 2855(*w*), 2842(*w*), 2802(*w*), 2705(*w*), 1589(*w*), 1637(*w*), 1376(*w*), 1448(*w*), 1418(*m*), 1362(*w*), 1302(*w*), 1286(*m*), 1257(*w*), 1215(*w*), 1164(*w*), 1024(*w*), 939(*s*), 873(*w*), 844(*s*), 730(*s*), 710(*w*), 670(*m*), 576(*w*), 538(*m*), 484(*w*), 357(*m*), 328(*m*), 301(*m*), 275(*w*). ¹H NMR (C₆D₆): δ 0.60 (*s br*, 18H; PCH₃), 2.08 (*s*, 12H; *p*-CH₃), 2.73 (*s*, 24H; *o*-CH₃), 6.68 (*s*, 8H; CH). ¹³C{¹H} NMR (C₆D₆): δ 15.4 (*s br*; PCH₃), 21.4 (*s*; *p*-CH₃), 28.7 (*s*; *o*-CH₃), 125.6 (*s*; CH), 127.4 (*s*; CCu₂), 134.4 (*s*; *p*-CCH₃), 150.0 (*s*; *o*-CCH₃). ³¹P{¹H} NMR (C₆D₆): δ -44.6 (*s br*).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

IUCrData (2021). 6, x210594 [https://doi.org/10.1107/S2414314621005940]

cyclo-Tetrakis(μ -2,4,6-trimethylphenyl- κ C¹: κ C¹)bis(trimethylphosphane)-1 κ P,3 κ P-tetracopper(I)

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cyclo-Tetrakis(μ -2,4,6-trimethylphenyl- κ C¹: κ C¹)bis(trimethylphosphane)-1 κ P,3 κ P-tetracopper(I)

Crystal data

[Cu₄(C₉H₁₁)₄(C₃H₉P)₂]

$M_r = 883.01$

Monoclinic, $C2/c$

$a = 12.0750$ (8) Å

$b = 27.5202$ (18) Å

$c = 14.3164$ (9) Å

$\beta = 113.668$ (5)°

$V = 4357.3$ (5) Å³

$Z = 4$

$F(000) = 1840$

$D_x = 1.346$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10871 reflections

$\theta = 1.5$ – 25.6 °

$\mu = 2.03$ mm⁻¹

$T = 213$ K

Block, pale yellow

$0.51 \times 0.32 \times 0.19$ mm

Data collection

Stoe IPDS 2

diffractometer

rotation method scans

Absorption correction: integration

(X-AREA; Stoe & Cie, 2016)

$T_{\min} = 0.508$, $T_{\max} = 0.758$

10982 measured reflections

3839 independent reflections

3043 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 25.1$ °, $\theta_{\min} = 1.5$ °

$h = -14 \rightarrow 13$

$k = -32 \rightarrow 31$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.100$

$S = 1.03$

3839 reflections

217 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 5.6305P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.48$ e Å⁻³

$\Delta\rho_{\min} = -0.44$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5285 (3)	0.14472 (10)	0.0734 (2)	0.0352 (6)
C2	0.5698 (3)	0.11189 (11)	0.0184 (2)	0.0406 (7)
C3	0.6133 (3)	0.12859 (13)	−0.0520 (3)	0.0535 (9)
H3	0.637972	0.106131	−0.088230	0.064*
C4	0.6210 (3)	0.17740 (14)	−0.0697 (3)	0.0567 (9)
C5	0.5825 (3)	0.21013 (13)	−0.0155 (3)	0.0542 (9)
H5	0.587281	0.243244	−0.026399	0.065*
C6	0.5369 (3)	0.19478 (11)	0.0549 (2)	0.0422 (7)
C7	0.5670 (3)	0.05827 (11)	0.0365 (3)	0.0530 (8)
H7A	0.534717	0.052614	0.086869	0.064*
H7B	0.516843	0.042475	−0.026048	0.064*
H7C	0.647534	0.045416	0.060229	0.064*
C8	0.6704 (5)	0.1944 (2)	−0.1462 (4)	0.0953 (16)
H8A	0.669255	0.229266	−0.148853	0.114*
H8B	0.751950	0.183073	−0.125860	0.114*
H8C	0.621237	0.181647	−0.212391	0.114*
C9	0.4929 (4)	0.23236 (11)	0.1078 (3)	0.0564 (9)
H9A	0.464229	0.216650	0.153714	0.068*
H9B	0.558068	0.253924	0.145463	0.068*
H9C	0.428204	0.250577	0.058072	0.068*
C10	0.2575 (3)	0.10497 (11)	0.1661 (2)	0.0362 (6)
C11	0.1633 (3)	0.13739 (12)	0.1595 (2)	0.0428 (7)
C12	0.0481 (3)	0.12024 (13)	0.1414 (3)	0.0525 (8)
H12	−0.011475	0.142360	0.138276	0.063*
C13	0.0193 (3)	0.07129 (14)	0.1277 (2)	0.0531 (9)
C14	0.1118 (3)	0.03930 (12)	0.1352 (2)	0.0490 (8)
H14	0.094931	0.006227	0.126572	0.059*
C15	0.2281 (3)	0.05497 (11)	0.1551 (2)	0.0390 (6)
C16	0.1869 (3)	0.19137 (12)	0.1699 (3)	0.0605 (9)
H16A	0.269829	0.197512	0.182150	0.073*
H16B	0.135141	0.207348	0.108126	0.073*
H16C	0.170640	0.203603	0.225913	0.073*
C17	−0.1068 (3)	0.05407 (19)	0.1057 (3)	0.0798 (13)
H17A	−0.110277	0.019351	0.098586	0.096*
H17B	−0.128522	0.063189	0.160898	0.096*
H17C	−0.162240	0.068660	0.043644	0.096*
C18	0.3221 (3)	0.01757 (11)	0.1617 (3)	0.0517 (8)
H18A	0.397928	0.033449	0.175720	0.062*
H18B	0.331256	−0.005010	0.215374	0.062*
H18C	0.297023	0.000460	0.098044	0.062*
C19	0.0817 (4)	0.1129 (2)	−0.0945 (3)	0.0864 (15)
H19A	0.073605	0.083645	−0.061181	0.104*
H19B	0.052908	0.139998	−0.068566	0.104*
H19C	0.035169	0.109988	−0.166632	0.104*
C20	0.2658 (4)	0.07802 (15)	−0.1540 (3)	0.0816 (13)

H20A	0.270385	0.046047	-0.125855	0.098*
H20B	0.200305	0.079321	-0.220072	0.098*
H20C	0.340315	0.085374	-0.160120	0.098*
C21	0.2352 (4)	0.17798 (14)	-0.1387 (3)	0.0667 (10)
H21A	0.221783	0.204870	-0.101793	0.080*
H21B	0.310611	0.182363	-0.145271	0.080*
H21C	0.170601	0.176310	-0.205223	0.080*
P	0.24013 (8)	0.12219 (3)	-0.07038 (6)	0.0456 (2)
Cu1	0.58712 (3)	0.12496 (2)	0.22033 (2)	0.03340 (13)
Cu2	0.37473 (3)	0.12434 (2)	0.09729 (2)	0.03274 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0323 (15)	0.0399 (15)	0.0349 (14)	-0.0001 (12)	0.0150 (12)	0.0030 (12)
C2	0.0351 (17)	0.0472 (16)	0.0426 (16)	-0.0017 (13)	0.0190 (14)	-0.0047 (13)
C3	0.050 (2)	0.073 (2)	0.0488 (19)	-0.0064 (17)	0.0318 (17)	-0.0115 (17)
C4	0.054 (2)	0.077 (2)	0.0462 (19)	-0.0117 (18)	0.0282 (17)	0.0040 (17)
C5	0.057 (2)	0.0540 (19)	0.053 (2)	-0.0120 (16)	0.0234 (17)	0.0129 (16)
C6	0.0404 (17)	0.0453 (16)	0.0400 (16)	-0.0012 (13)	0.0152 (14)	0.0047 (13)
C7	0.049 (2)	0.0495 (18)	0.072 (2)	-0.0015 (15)	0.0367 (18)	-0.0122 (16)
C8	0.106 (4)	0.126 (4)	0.078 (3)	-0.030 (3)	0.063 (3)	0.006 (3)
C9	0.073 (2)	0.0370 (16)	0.067 (2)	0.0041 (16)	0.0358 (19)	0.0051 (16)
C10	0.0283 (15)	0.0459 (16)	0.0339 (14)	-0.0003 (12)	0.0119 (12)	-0.0013 (12)
C11	0.0336 (16)	0.0562 (17)	0.0378 (16)	0.0050 (14)	0.0137 (13)	-0.0015 (14)
C12	0.0307 (17)	0.081 (2)	0.0451 (18)	0.0086 (16)	0.0150 (14)	-0.0009 (16)
C13	0.0315 (17)	0.086 (3)	0.0418 (18)	-0.0104 (16)	0.0144 (14)	-0.0045 (17)
C14	0.0411 (18)	0.063 (2)	0.0443 (17)	-0.0192 (16)	0.0184 (14)	-0.0052 (15)
C15	0.0355 (16)	0.0478 (16)	0.0348 (15)	-0.0065 (13)	0.0151 (13)	-0.0042 (13)
C16	0.046 (2)	0.057 (2)	0.078 (3)	0.0148 (17)	0.0246 (18)	-0.0009 (18)
C17	0.041 (2)	0.129 (4)	0.070 (3)	-0.025 (2)	0.023 (2)	-0.012 (2)
C18	0.052 (2)	0.0406 (16)	0.065 (2)	-0.0060 (14)	0.0261 (17)	-0.0058 (15)
C19	0.044 (2)	0.164 (5)	0.041 (2)	-0.016 (3)	0.0063 (17)	0.015 (2)
C20	0.076 (3)	0.081 (3)	0.066 (3)	0.007 (2)	0.005 (2)	-0.025 (2)
C21	0.072 (3)	0.073 (2)	0.054 (2)	0.013 (2)	0.024 (2)	0.0139 (18)
P	0.0392 (5)	0.0616 (5)	0.0320 (4)	-0.0034 (4)	0.0103 (3)	0.0025 (3)
Cu1	0.0285 (2)	0.0388 (2)	0.0322 (2)	0.00097 (13)	0.01154 (16)	0.00234 (13)
Cu2	0.0284 (2)	0.0384 (2)	0.0314 (2)	-0.00060 (13)	0.01196 (15)	0.00072 (13)

Geometric parameters (Å, °)

C1—C2	1.415 (4)	C13—C14	1.392 (5)
C1—C6	1.414 (4)	C13—C17	1.502 (5)
C1—Cu1	2.006 (3)	C14—H14	0.9300
C1—Cu2	2.095 (3)	C14—C15	1.385 (4)
C2—C3	1.388 (4)	C15—C18	1.507 (4)
C2—C7	1.501 (4)	C16—H16A	0.9600
C3—H3	0.9300	C16—H16B	0.9600

C3—C4	1.377 (5)	C16—H16C	0.9600
C4—C5	1.385 (5)	C17—H17A	0.9600
C4—C8	1.516 (5)	C17—H17B	0.9600
C5—H5	0.9300	C17—H17C	0.9600
C5—C6	1.395 (4)	C18—H18A	0.9600
C6—C9	1.500 (4)	C18—H18B	0.9600
C7—H7A	0.9600	C18—H18C	0.9600
C7—H7B	0.9600	C19—H19A	0.9600
C7—H7C	0.9600	C19—H19B	0.9600
C8—H8A	0.9600	C19—H19C	0.9600
C8—H8B	0.9600	C19—P	1.820 (4)
C8—H8C	0.9600	C20—H20A	0.9600
C9—H9A	0.9600	C20—H20B	0.9600
C9—H9B	0.9600	C20—H20C	0.9600
C9—H9C	0.9600	C20—P	1.818 (4)
C10—C11	1.419 (4)	C21—H21A	0.9600
C10—C15	1.414 (4)	C21—H21B	0.9600
C10—Cu1 ⁱ	2.005 (3)	C21—H21C	0.9600
C10—Cu2	2.093 (3)	C21—P	1.808 (4)
C11—C12	1.390 (5)	P—Cu2	2.2967 (9)
C11—C16	1.509 (5)	Cu1—Cu1 ⁱ	2.5657 (7)
C12—H12	0.9300	Cu1—Cu2	2.4603 (5)
C12—C13	1.386 (5)	Cu1—Cu2 ⁱ	2.4625 (5)
C2—C1—Cu1	110.9 (2)	C11—C16—H16B	109.5
C2—C1—Cu2	117.0 (2)	C11—C16—H16C	109.5
C6—C1—C2	116.7 (3)	H16A—C16—H16B	109.5
C6—C1—Cu1	116.0 (2)	H16A—C16—H16C	109.5
C6—C1—Cu2	115.2 (2)	H16B—C16—H16C	109.5
Cu1—C1—Cu2	73.70 (9)	C13—C17—H17A	109.5
C1—C2—C7	119.6 (3)	C13—C17—H17B	109.5
C3—C2—C1	120.9 (3)	C13—C17—H17C	109.5
C3—C2—C7	119.5 (3)	H17A—C17—H17B	109.5
C2—C3—H3	119.0	H17A—C17—H17C	109.5
C4—C3—C2	122.0 (3)	H17B—C17—H17C	109.5
C4—C3—H3	119.0	C15—C18—H18A	109.5
C3—C4—C5	117.9 (3)	C15—C18—H18B	109.5
C3—C4—C8	120.7 (4)	C15—C18—H18C	109.5
C5—C4—C8	121.4 (4)	H18A—C18—H18B	109.5
C4—C5—H5	119.1	H18A—C18—H18C	109.5
C4—C5—C6	121.8 (3)	H18B—C18—H18C	109.5
C6—C5—H5	119.1	H19A—C19—H19B	109.5
C1—C6—C9	120.7 (3)	H19A—C19—H19C	109.5
C5—C6—C1	120.7 (3)	H19B—C19—H19C	109.5
C5—C6—C9	118.6 (3)	P—C19—H19A	109.5
C2—C7—H7A	109.5	P—C19—H19B	109.5
C2—C7—H7B	109.5	P—C19—H19C	109.5
C2—C7—H7C	109.5	H20A—C20—H20B	109.5

H7A—C7—H7B	109.5	H20A—C20—H20C	109.5
H7A—C7—H7C	109.5	H20B—C20—H20C	109.5
H7B—C7—H7C	109.5	P—C20—H20A	109.5
C4—C8—H8A	109.5	P—C20—H20B	109.5
C4—C8—H8B	109.5	P—C20—H20C	109.5
C4—C8—H8C	109.5	H21A—C21—H21B	109.5
H8A—C8—H8B	109.5	H21A—C21—H21C	109.5
H8A—C8—H8C	109.5	H21B—C21—H21C	109.5
H8B—C8—H8C	109.5	P—C21—H21A	109.5
C6—C9—H9A	109.5	P—C21—H21B	109.5
C6—C9—H9B	109.5	P—C21—H21C	109.5
C6—C9—H9C	109.5	C19—P—Cu2	116.81 (13)
H9A—C9—H9B	109.5	C20—P—C19	103.0 (2)
H9A—C9—H9C	109.5	C20—P—Cu2	117.98 (14)
H9B—C9—H9C	109.5	C21—P—C19	102.3 (2)
C11—C10—Cu1 ⁱ	110.2 (2)	C21—P—C20	100.9 (2)
C11—C10—Cu2	119.0 (2)	C21—P—Cu2	113.53 (14)
C15—C10—C11	116.5 (3)	C1—Cu1—Cu1 ⁱ	110.85 (8)
C15—C10—Cu1 ⁱ	117.9 (2)	C1—Cu1—Cu2	54.80 (8)
C15—C10—Cu2	112.5 (2)	C1—Cu1—Cu2 ⁱ	161.89 (8)
Cu1 ⁱ —C10—Cu2	73.85 (9)	C10 ⁱ —Cu1—C1	138.26 (11)
C10—C11—C16	119.9 (3)	C10 ⁱ —Cu1—Cu1 ⁱ	110.89 (8)
C12—C11—C10	120.9 (3)	C10 ⁱ —Cu1—Cu2 ⁱ	54.72 (8)
C12—C11—C16	119.2 (3)	C10 ⁱ —Cu1—Cu2	161.12 (8)
C11—C12—H12	118.9	Cu2 ⁱ —Cu1—Cu1 ⁱ	58.546 (15)
C13—C12—C11	122.2 (3)	Cu2—Cu1—Cu1 ⁱ	58.630 (15)
C13—C12—H12	118.9	Cu2—Cu1—Cu2 ⁱ	117.169 (16)
C12—C13—C14	117.1 (3)	C1—Cu2—P	97.94 (8)
C12—C13—C17	120.8 (4)	C1—Cu2—Cu1	51.50 (8)
C14—C13—C17	122.1 (4)	C1—Cu2—Cu1 ⁱ	111.73 (8)
C13—C14—H14	118.8	C10—Cu2—C1	163.04 (11)
C15—C14—C13	122.3 (3)	C10—Cu2—P	99.02 (8)
C15—C14—H14	118.8	C10—Cu2—Cu1	111.87 (8)
C10—C15—C18	120.6 (3)	C10—Cu2—Cu1 ⁱ	51.43 (8)
C14—C15—C10	121.0 (3)	P—Cu2—Cu1 ⁱ	149.44 (3)
C14—C15—C18	118.4 (3)	P—Cu2—Cu1	147.71 (3)
C11—C16—H16A	109.5	Cu1—Cu2—Cu1 ⁱ	62.824 (16)
C1—C2—C3—C4	1.5 (5)	C15—C10—C11—C12	-1.1 (4)
C2—C1—C6—C5	0.8 (4)	C15—C10—C11—C16	-179.7 (3)
C2—C1—C6—C9	178.6 (3)	C16—C11—C12—C13	177.8 (3)
C2—C3—C4—C5	-0.7 (6)	C17—C13—C14—C15	179.8 (3)
C2—C3—C4—C8	179.3 (4)	Cu1—C1—C2—C3	-137.4 (3)
C3—C4—C5—C6	-0.2 (5)	Cu1—C1—C2—C7	42.3 (3)
C4—C5—C6—C1	0.1 (5)	Cu1—C1—C6—C5	134.4 (3)
C4—C5—C6—C9	-177.8 (3)	Cu1—C1—C6—C9	-47.8 (4)
C6—C1—C2—C3	-1.6 (4)	Cu1 ⁱ —C10—C11—C12	-139.0 (3)
C6—C1—C2—C7	178.2 (3)	Cu1 ⁱ —C10—C11—C16	42.5 (3)

C7—C2—C3—C4	-178.2 (3)	Cu1 ⁱ —C10—C15—C14	136.9 (3)
C8—C4—C5—C6	179.9 (4)	Cu1 ⁱ —C10—C15—C18	-45.0 (4)
C10—C11—C12—C13	-0.7 (5)	Cu2—C1—C2—C3	140.8 (3)
C11—C10—C15—C14	2.3 (4)	Cu2—C1—C2—C7	-39.4 (4)
C11—C10—C15—C18	-179.6 (3)	Cu2—C1—C6—C5	-142.2 (3)
C11—C12—C13—C14	1.4 (5)	Cu2—C1—C6—C9	35.6 (4)
C11—C12—C13—C17	-178.5 (3)	Cu2—C10—C11—C12	138.7 (3)
C12—C13—C14—C15	-0.2 (5)	Cu2—C10—C11—C16	-39.8 (4)
C13—C14—C15—C10	-1.8 (5)	Cu2—C10—C15—C14	-140.1 (2)
C13—C14—C15—C18	-179.9 (3)	Cu2—C10—C15—C18	38.0 (3)

Symmetry code: (i) $-x+1, y, -z+1/2$.