



# A $[\text{Cu}_3(\mu_3\text{-O})]$ –pyrazolate metallacycle with terminal nitrate ligands exhibiting point group symmetry 3

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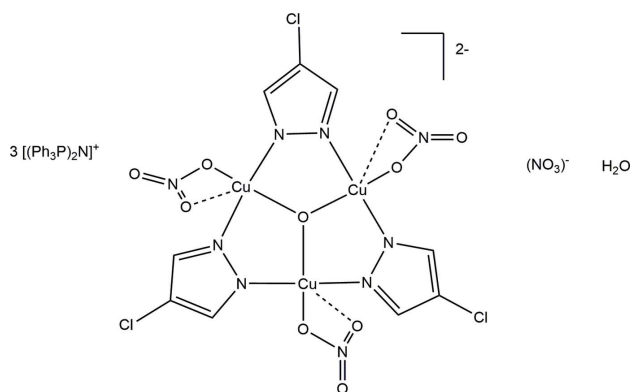
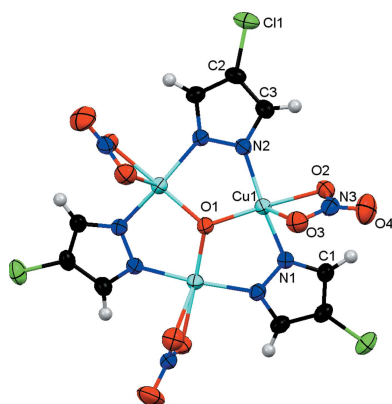
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**Keywords:** crystal structure; copper–pyrazolate complex; terminal nitrate ligands.**CCDC reference:** 1458061**Supporting information:** this article has supporting information at journals.iucr.org/e

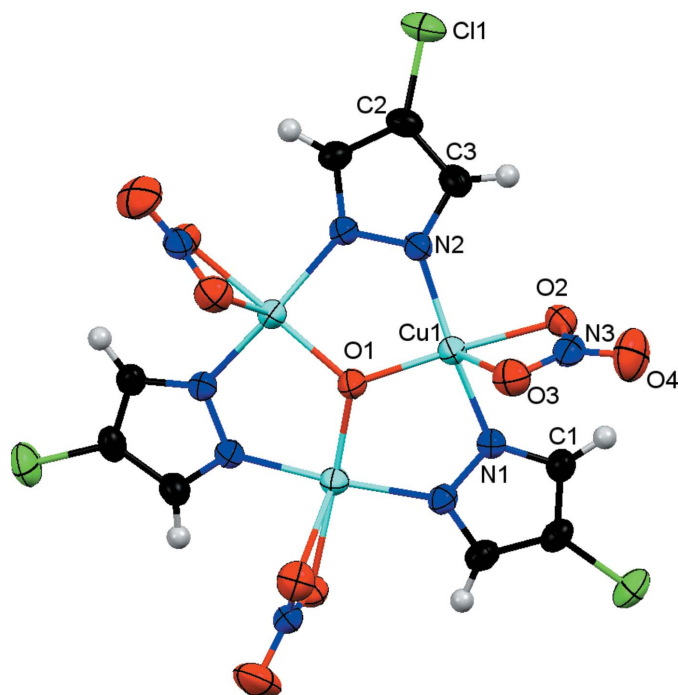
The trinuclear triangular cuprate anion of the title compound, tris[bis(tri-phenylphosphoranylidene)ammonium] tris( $\mu_2$ -4-chloropyrazolato- $\kappa^2N:N'$ )- $\mu_3$ -oxido-tris[(nitrate- $\kappa^2O,O'$ )cuprate(II)] nitrate monohydrate,  $(\text{C}_{36}\text{H}_{30}\text{P}_2\text{N})\text{[Cu}_3(\text{C}_3\text{H}_2\text{ClN}_2)_3(\text{NO}_3)_3\text{O]NO}_3\cdot\text{H}_2\text{O}$ , has point group symmetry 3., with the  $\mu_3$ -O atom located on the threefold rotation axis. The distorted square-pyramidal coordination sphere of the  $\text{Cu}^{\text{II}}$  atom is completed by two N atoms of *trans*-bridging pyrazolate groups and a chelating nitrate anion. The complex anion is slightly bent, with the nitrate and pyrazolate groups occupying positions above and below the  $\text{Cu}_3$  plane, respectively. In the crystal, weak  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, as well as  $\pi$ – $\pi$  interactions, are present.

## 1. Chemical context

Trinuclear copper complexes with a triangular arrangement of the copper(II) cations are of importance in terms of their magnetic and redox properties (Rivera-Carrillo *et al.*, 2008). Moreover,  $\text{Cu}_3(\mu_3\text{-O/OH})$  moieties make up the active sites of several multicopper oxidase enzymes (Solomon *et al.*, 2014). Pyrazolate anions as ligands are of bidentate chelating nature and are able to bind to the  $\text{Cu}^{\text{II}}$  cations in suitable angles to form triangular complexes (Halcrow, 2009; Viciano-Chumillas *et al.*, 2010).



Nitrato and pyrazolato ligands are commonly studied ligands in  $\text{Cu}^{\text{II}}$  coordination chemistry. Simple  $\text{Cu}^{\text{II}}$  nitrate complexes are aplenty in the literature and have been studied in detail with respect to their part in the nitrogen cycle. Triangular trinuclear  $\text{Cu}^{\text{II}}$  complexes with terminal nitrate ligands, however, are scarcer (Alsalmé *et al.*, 2014). Nitrates, being good hydrogen-bonding acceptors, are able to form  $\text{Cu}_3(\mu_3\text{-OH})$  complexes, with hydrogen bonds to the  $\mu_3\text{-OH}$  group and to ancillary ligands and water molecules.



**Figure 1**  
The molecular structure of the trinuclear pyrazolotocuprate anion in the title compound showing the atom-labeling scheme for the symmetry-independent atoms. Non-H atoms are shown as displacement ellipsoids at the 30% probability level.

In this communication we describe the accidental synthesis and the structure of a trinuclear Cu–pyrazolato complex, *viz.*  $(\text{PPN})_3[\text{Cu}_3(\mu_3\text{-O})(\mu\text{-4-Clpz})_3(\text{NO}_3)_3](\text{NO}_3)\cdot\text{H}_2\text{O}$ , where PPN = bis(triphenylphosphoranylidene)ammonium; 4-Cl-pz =

**Table 1**  
Selected bond lengths (Å).

Cu1–O1	1.8816 (7)	Cu1–O2	2.059 (3)
Cu1–N2	1.952 (4)	Cu1–O3	2.483 (4)
Cu1–N1	1.960 (4)		

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

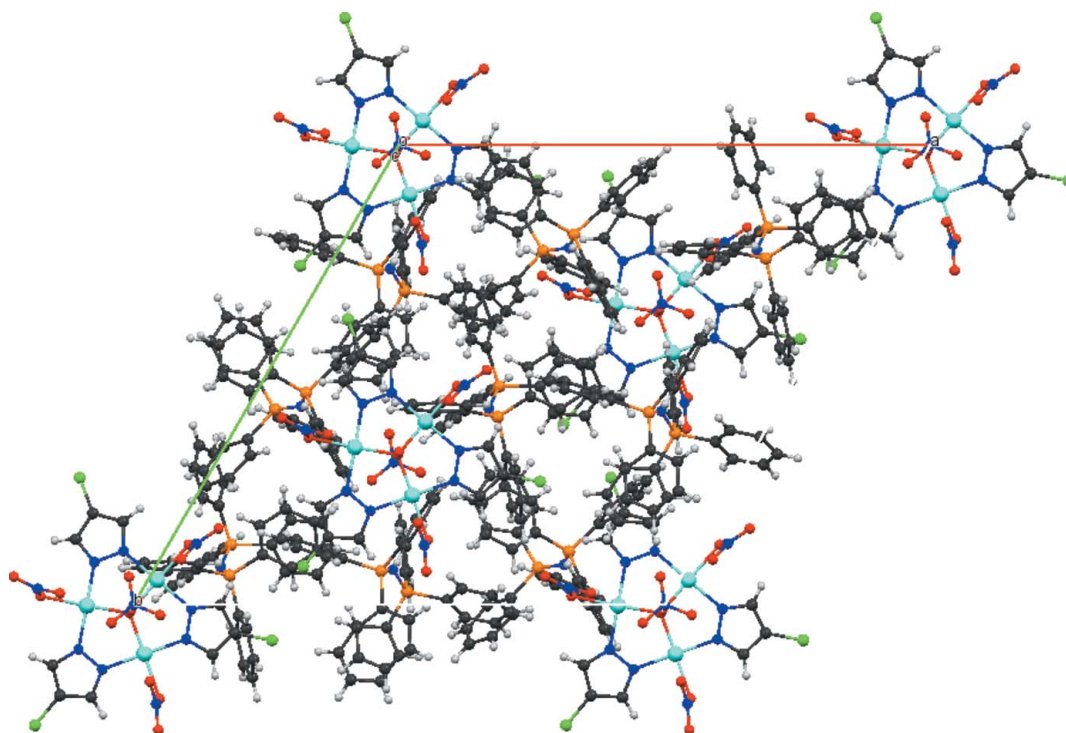
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
Cl13–H13···O3 <sup>i</sup>	0.93	2.53	3.410 (11)	157

Symmetry code: (i)  $-x + y + \frac{4}{3}, -x + \frac{2}{3}, z - \frac{1}{3}$ .

4-chloropyrazolate. A related  $\text{Cu}_3$ -pyrazolato complex was reported by Angaridis *et al.* (2002).

## 2. Structural commentary

The nine-membered metallacycle  $\text{Cu}_3\text{N}_6$  in the cuprate anion (Fig. 1) is strung together by a  $\mu_3\text{-O}$  group located at the center of the triangle (point group symmetry of the complete molecule 3.), forming an almost planar  $\text{Cu}_3(\mu_3\text{-O})$ -core, where the  $\mu_3\text{-O}$  atom O1 is located 0.122 (7) Å above the  $\text{Cu}_3$  plane. The distorted square-pyramidal geometry of the  $\text{Cu}^{\text{II}}$  atom is completed by the two N atoms of symmetry-related *trans*-bridging pyrazolato ligands, and a terminal nitrate ligand that is bound to the metal in a chelating fashion (Table 1). The complex is slightly bent with the nitrate and pyrazolato groups occupying positions above and below the  $\text{Cu}_3$  plane, respectively. The Cl atom of the pyrazole anion is located approximately 1.28 Å below the  $\text{Cu}_3$  plane. The non-coordinating



**Figure 2**  
The crystal packing diagram for the title compound shown down [001].

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	(C <sub>36</sub> H <sub>30</sub> P <sub>2</sub> N)[Cu <sub>3</sub> (C <sub>3</sub> H <sub>2</sub> ClN <sub>2</sub> ) <sub>3</sub> -(NO <sub>3</sub> ) <sub>3</sub> O]NO <sub>3</sub> ·H <sub>2</sub> O
<i>M<sub>r</sub></i>	2390.85
Crystal system, space group	Trigonal, <i>R</i> 3
Temperature (K)	296
<i>a</i> , <i>c</i> (Å)	23.038 (2), 18.4214 (17)
<i>V</i> (Å <sup>3</sup> )	8466.9 (17)
<i>Z</i>	3
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	0.79
Crystal size (mm)	0.23 × 0.14 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2005)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.840, 0.905
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	30414, 7675, 6428
<i>R<sub>int</sub></i>	0.033
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.625
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.034, 0.088, 1.03
No. of reflections	7675
No. of parameters	468
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.41, -0.29
Absolute structure	Flack <i>x</i> determined using 2750 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.004 (5)

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

nitrate counter-anion is located about a special position with the nitrogen atom on the threefold rotation axis.

The triphenylphosphene groups in the PPN cation are staggered around the central N atom [P–N–P angle 139.5 (2)°] and show bond lengths and angles characteristic for this unit (Beckett *et al.*, 2010).

### 3. Supramolecular features

The interstitial water O atom is also located on a threefold rotation axis which consequently results in disordered H atoms of this moiety. Although these H atoms could not be located, three O···O distances to the chelating nitrate anions of 3.367 (6) Å point to weak O–H···O hydrogen bonds in the structure. This nitrate O atom is additionally involved in weak non-classical hydrogen-bonding interactions with one of the C–H groups of the PPN cation (Table 2). The latter shows also π–π interactions [3.902 (7) Å] with one of the pyrazolate rings, leading to an overall three-dimensional network. The packing of the molecular units is shown in Fig. 2.

### 4. Synthesis and crystallization

4-Cl-pz and the hexanuclear Cu<sub>6</sub>-pyrazolato complex (PPN)[{Cu<sub>3</sub>(μ<sub>3</sub>-O)(μ-4-Cl-pz)<sub>3</sub>]<sub>2</sub>(μ-3,5-Ph<sub>2</sub>pz)<sub>3</sub>], were synthesized by published procedures (Maresca *et al.*, 1997; Mezei *et al.*, 2007). (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (2 eq.) was dissolved in 5 ml of acetonitrile and was layered over a CH<sub>2</sub>Cl<sub>2</sub> solution of the hexanuclear copper(II) complex (1 eq.). Slow mixing of the reactants and solvent evaporation over a few weeks yielded dark-blue crystals of the title compound.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were placed geometrically, with C–H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The isolated water solvent O atom, O1*W*, was refined isotropically. H atoms bound to the water oxygen atom could not be placed satisfactorily with agreeable occupancy as O1*W* resides on a threefold rotation axis, resulting in crystallographically disordered H atoms. These H atoms were not modelled but are included in the formula of the title compound.

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## supporting information

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## A [Cu<sub>3</sub>(μ<sub>3</sub>-O)]–pyrazolate metallacycle with terminal nitrate ligands exhibiting point group symmetry 3

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### Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Tris[bis(triphenylphosphoranylidene)ammonium] tris(μ<sub>2</sub>-4-chloropyrazolato-κ<sup>2</sup>N:N')-μ<sub>3</sub>-oxido-tris[(nitrate-κ<sup>2</sup>O,O')cuprate(II)] nitrate monohydrate

### Crystal data

(C<sub>36</sub>H<sub>30</sub>P<sub>2</sub>N)[Cu<sub>3</sub>(C<sub>3</sub>H<sub>2</sub>ClN<sub>2</sub>)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>O]NO<sub>3</sub>·H<sub>2</sub>O  
*M<sub>r</sub>* = 2390.85  
 Trigonal, R3  
*a* = 23.038 (2) Å  
*c* = 18.4214 (17) Å  
*V* = 8466.9 (17) Å<sup>3</sup>  
*Z* = 3  
*F*(000) = 3687

*D<sub>x</sub>* = 1.407 Mg m<sup>-3</sup>  
 Mo *Kα* radiation, λ = 0.71073 Å  
 Cell parameters from 9882 reflections  
 θ = 2.3–26.0°  
 μ = 0.79 mm<sup>-1</sup>  
*T* = 296 K  
 Polygon, blue  
 0.23 × 0.14 × 0.13 mm

### Data collection

Bruker APEXII CCD  
 diffractometer  
 Radiation source: sealed tube  
 Graphite monochromator  
 φ and ω scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2005)  
*T<sub>min</sub>* = 0.840, *T<sub>max</sub>* = 0.905

30414 measured reflections  
 7675 independent reflections  
 6428 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.033  
 θ<sub>max</sub> = 26.4°, θ<sub>min</sub> = 2.3°  
*h* = -28→28  
*k* = -28→28  
*l* = -22→22

### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.034  
*wR*(*F*<sup>2</sup>) = 0.088  
*S* = 1.03  
 7675 reflections  
 468 parameters  
 1 restraint  
 Hydrogen site location: inferred from  
 neighbouring sites

H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0468*P*)<sup>2</sup> + 0.1352*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.41 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.29 e Å<sup>-3</sup>  
 Absolute structure: Flack *x* determined using  
 2750 quotients [(*I*<sup>+</sup>)-(*I*)]/[(*I*<sup>+</sup>)+(*I*)] (Parsons *et al.*, 2013)  
 Absolute structure parameter: 0.004 (5)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1W	0.0000	1.0000	0.3698 (7)	0.141 (4)*
Cu1	0.57819 (3)	0.31688 (3)	0.88140 (3)	0.04893 (15)
O1	0.6667	0.3333	0.8748 (4)	0.0691 (18)
O2	0.48058 (17)	0.29648 (18)	0.8736 (2)	0.0619 (9)
N1	0.54504 (18)	0.22155 (19)	0.8997 (2)	0.0504 (9)
N2	0.61014 (18)	0.41208 (18)	0.8960 (2)	0.0493 (9)
N3	0.4670 (2)	0.28251 (19)	0.8087 (3)	0.0582 (10)
C1	0.4851 (2)	0.1710 (2)	0.9186 (3)	0.0590 (12)
H1	0.4465	0.1738	0.9249	0.071*
C2	0.4893 (3)	0.1144 (2)	0.9272 (3)	0.0570 (12)
C3	0.5783 (3)	0.4455 (3)	0.9126 (3)	0.0582 (12)
H3	0.5321	0.4274	0.9141	0.070*
C11	0.42537 (8)	0.03570 (7)	0.95132 (10)	0.0859 (5)
O3	0.5141 (2)	0.2937 (2)	0.7664 (2)	0.0753 (10)
O4	0.4095 (2)	0.2572 (3)	0.7874 (3)	0.1105 (17)
P1	0.81315 (5)	0.23893 (5)	0.23155 (5)	0.0379 (2)
P2	0.78221 (5)	0.16748 (5)	0.37198 (5)	0.0392 (2)
N4	0.78666 (18)	0.21790 (18)	0.31150 (18)	0.0461 (8)
C4	0.7627 (2)	0.1937 (2)	0.4558 (2)	0.0440 (10)
C5	0.7353 (2)	0.2344 (2)	0.4544 (2)	0.0487 (11)
H5	0.7293	0.2500	0.4101	0.058*
C6	0.7165 (3)	0.2526 (3)	0.5183 (3)	0.0625 (13)
H6	0.6978	0.2803	0.5167	0.075*
C7	0.7254 (3)	0.2299 (3)	0.5829 (3)	0.0754 (17)
H7	0.7129	0.2424	0.6256	0.090*
C8	0.7527 (3)	0.1887 (3)	0.5860 (3)	0.0788 (17)
H8	0.7584	0.1732	0.6305	0.095*
C9	0.7717 (3)	0.1703 (3)	0.5224 (3)	0.0615 (13)
H9	0.7904	0.1427	0.5242	0.074*
C10	0.8593 (2)	0.1669 (2)	0.3837 (2)	0.0463 (10)
C11	0.9135 (2)	0.2251 (3)	0.4090 (3)	0.0610 (12)
H11	0.9081	0.2606	0.4241	0.073*
C12	0.9761 (3)	0.2304 (4)	0.4120 (3)	0.0801 (18)
H12	1.0128	0.2696	0.4289	0.096*
C13	0.9836 (3)	0.1783 (4)	0.3899 (3)	0.0796 (18)
H13	1.0257	0.1819	0.3922	0.095*
C14	0.9302 (3)	0.1205 (4)	0.3645 (4)	0.0833 (18)
H14	0.9363	0.0855	0.3490	0.100*
C15	0.8679 (3)	0.1139 (3)	0.3617 (3)	0.0629 (13)

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H15	0.8315	0.0743	0.3451	0.075*
C16	0.7162 (2)	0.0829 (2)	0.3546 (2)	0.0467 (10)
C17	0.6790 (2)	0.0681 (3)	0.2917 (3)	0.0569 (12)
H17	0.6875	0.1021	0.2589	0.068*
C18	0.6291 (3)	0.0032 (3)	0.2771 (3)	0.0732 (15)
H18	0.6053	-0.0064	0.2338	0.088*
C19	0.6146 (3)	-0.0466 (3)	0.3259 (4)	0.0771 (17)
H19	0.5810	-0.0902	0.3158	0.093*
C20	0.6493 (3)	-0.0327 (3)	0.3896 (4)	0.0807 (18)
H20	0.6381	-0.0665	0.4236	0.097*
C21	0.7012 (3)	0.0315 (3)	0.4039 (3)	0.0737 (16)
H21	0.7260	0.0403	0.4465	0.088*
C22	0.8529 (2)	0.1956 (2)	0.1928 (2)	0.0414 (9)
C23	0.8160 (2)	0.1331 (2)	0.1628 (3)	0.0532 (11)
H23	0.7698	0.1141	0.1578	0.064*
C24	0.8467 (3)	0.0979 (3)	0.1398 (3)	0.0678 (14)
H24	0.8214	0.0559	0.1185	0.081*
C25	0.9149 (3)	0.1251 (3)	0.1483 (3)	0.0666 (14)
H25	0.9355	0.1010	0.1339	0.080*
C26	0.9520 (3)	0.1870 (3)	0.1778 (3)	0.0630 (13)
H26	0.9980	0.2055	0.1828	0.076*
C27	0.9219 (2)	0.2228 (2)	0.2003 (3)	0.0505 (10)
H27	0.9477	0.2652	0.2204	0.061*
C28	0.7444 (2)	0.2268 (2)	0.1749 (2)	0.0415 (9)
C29	0.6909 (2)	0.2287 (2)	0.2075 (3)	0.0526 (11)
H29	0.6902	0.2334	0.2575	0.063*
C30	0.6394 (2)	0.2237 (3)	0.1659 (3)	0.0674 (14)
H30	0.6037	0.2250	0.1880	0.081*
C31	0.6397 (3)	0.2167 (3)	0.0916 (3)	0.0738 (16)
H31	0.6048	0.2140	0.0636	0.089*
C32	0.6910 (3)	0.2138 (3)	0.0599 (3)	0.0698 (15)
H32	0.6906	0.2081	0.0098	0.084*
C33	0.7439 (3)	0.2192 (3)	0.1000 (2)	0.0578 (12)
H33	0.7791	0.2176	0.0772	0.069*
C34	0.8736 (2)	0.3267 (2)	0.2287 (3)	0.0468 (10)
C35	0.8897 (3)	0.3652 (3)	0.2894 (4)	0.0845 (19)
H35	0.8686	0.3462	0.3331	0.101*
C36	0.9372 (5)	0.4322 (3)	0.2866 (5)	0.123 (3)
H36	0.9495	0.4580	0.3287	0.147*
C37	0.9664 (4)	0.4611 (3)	0.2211 (5)	0.106 (3)
H37	0.9980	0.5065	0.2190	0.127*
C38	0.9497 (3)	0.4245 (3)	0.1612 (4)	0.0813 (18)
H38	0.9697	0.4445	0.1173	0.098*
C39	0.9028 (3)	0.3568 (2)	0.1633 (3)	0.0632 (13)
H39	0.8908	0.3316	0.1208	0.076*
N5	0.6667	0.3333	0.3566 (5)	0.069 (2)
O5	0.6275 (3)	0.2721 (2)	0.3545 (3)	0.1083 (16)

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Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0436 (3)	0.0458 (3)	0.0582 (3)	0.0230 (3)	0.0029 (3)	0.0017 (3)
O1	0.044 (2)	0.044 (2)	0.119 (6)	0.0220 (10)	0.000	0.000
O2	0.058 (2)	0.069 (2)	0.065 (2)	0.0356 (18)	0.0048 (17)	-0.0040 (18)
N1	0.044 (2)	0.046 (2)	0.060 (2)	0.0217 (18)	0.0012 (17)	-0.0010 (17)
N2	0.049 (2)	0.048 (2)	0.054 (2)	0.0268 (19)	0.0061 (17)	0.0045 (17)
N3	0.054 (3)	0.048 (2)	0.073 (3)	0.025 (2)	-0.011 (2)	0.007 (2)
C1	0.047 (3)	0.053 (3)	0.069 (3)	0.019 (2)	0.005 (2)	-0.002 (2)
C2	0.059 (3)	0.045 (3)	0.051 (3)	0.014 (2)	-0.001 (2)	0.005 (2)
C3	0.060 (3)	0.061 (3)	0.062 (3)	0.037 (3)	0.011 (2)	0.014 (2)
C11	0.0748 (10)	0.0513 (8)	0.0996 (11)	0.0075 (7)	0.0071 (8)	0.0112 (7)
O3	0.084 (3)	0.078 (3)	0.064 (2)	0.040 (2)	0.008 (2)	0.0030 (19)
O4	0.068 (3)	0.129 (4)	0.118 (4)	0.037 (3)	-0.030 (3)	0.004 (3)
P1	0.0386 (6)	0.0401 (6)	0.0386 (5)	0.0224 (5)	0.0019 (4)	0.0017 (4)
P2	0.0378 (5)	0.0423 (6)	0.0376 (5)	0.0200 (5)	-0.0016 (4)	0.0010 (4)
N4	0.053 (2)	0.055 (2)	0.0393 (18)	0.0341 (19)	0.0026 (16)	0.0058 (16)
C4	0.038 (2)	0.044 (2)	0.040 (2)	0.0136 (19)	-0.0028 (17)	-0.0008 (18)
C5	0.046 (2)	0.050 (3)	0.046 (3)	0.021 (2)	0.0003 (19)	-0.0051 (19)
C6	0.055 (3)	0.063 (3)	0.064 (3)	0.025 (3)	0.010 (2)	-0.008 (3)
C7	0.068 (4)	0.094 (4)	0.054 (3)	0.033 (3)	0.009 (3)	-0.020 (3)
C8	0.083 (4)	0.100 (5)	0.036 (3)	0.033 (4)	0.001 (2)	0.007 (3)
C9	0.071 (3)	0.076 (3)	0.043 (3)	0.041 (3)	-0.003 (2)	0.003 (2)
C10	0.041 (2)	0.057 (3)	0.044 (2)	0.027 (2)	0.0013 (18)	0.008 (2)
C11	0.048 (3)	0.065 (3)	0.066 (3)	0.026 (3)	-0.007 (2)	-0.005 (3)
C12	0.042 (3)	0.103 (5)	0.078 (4)	0.023 (3)	-0.008 (3)	0.005 (3)
C13	0.057 (4)	0.120 (6)	0.077 (4)	0.056 (4)	0.006 (3)	0.027 (4)
C14	0.081 (4)	0.098 (5)	0.099 (5)	0.066 (4)	0.006 (4)	0.009 (4)
C15	0.059 (3)	0.061 (3)	0.080 (3)	0.038 (3)	0.004 (3)	0.008 (3)
C16	0.040 (2)	0.046 (2)	0.054 (3)	0.022 (2)	0.0006 (19)	0.000 (2)
C17	0.048 (3)	0.059 (3)	0.056 (3)	0.022 (2)	-0.009 (2)	-0.003 (2)
C18	0.055 (3)	0.079 (4)	0.071 (3)	0.023 (3)	-0.013 (3)	-0.020 (3)
C19	0.051 (3)	0.055 (3)	0.105 (5)	0.011 (3)	-0.001 (3)	-0.022 (3)
C20	0.073 (4)	0.048 (3)	0.103 (5)	0.017 (3)	-0.004 (3)	0.009 (3)
C21	0.069 (3)	0.055 (3)	0.077 (4)	0.016 (3)	-0.015 (3)	0.011 (3)
C22	0.041 (2)	0.046 (2)	0.042 (2)	0.026 (2)	0.0018 (17)	0.0011 (18)
C23	0.044 (2)	0.046 (3)	0.067 (3)	0.021 (2)	0.002 (2)	-0.006 (2)
C24	0.067 (3)	0.050 (3)	0.090 (4)	0.032 (3)	0.005 (3)	-0.016 (3)
C25	0.069 (4)	0.063 (3)	0.087 (4)	0.047 (3)	0.020 (3)	0.005 (3)
C26	0.045 (3)	0.068 (3)	0.085 (4)	0.035 (3)	0.012 (2)	0.008 (3)
C27	0.042 (2)	0.047 (3)	0.065 (3)	0.025 (2)	0.002 (2)	-0.001 (2)
C28	0.044 (2)	0.042 (2)	0.043 (2)	0.0243 (19)	0.0007 (17)	0.0019 (17)
C29	0.053 (3)	0.062 (3)	0.052 (3)	0.036 (2)	0.002 (2)	0.000 (2)
C30	0.049 (3)	0.077 (4)	0.086 (4)	0.038 (3)	-0.006 (3)	-0.004 (3)
C31	0.069 (4)	0.079 (4)	0.082 (4)	0.044 (3)	-0.026 (3)	-0.001 (3)
C32	0.080 (4)	0.088 (4)	0.049 (3)	0.047 (3)	-0.013 (3)	0.004 (3)
C33	0.064 (3)	0.076 (3)	0.045 (3)	0.043 (3)	0.001 (2)	0.006 (2)

C34	0.046 (2)	0.038 (2)	0.059 (3)	0.023 (2)	0.004 (2)	-0.0018 (19)
C35	0.089 (4)	0.055 (3)	0.077 (4)	0.011 (3)	0.013 (3)	-0.009 (3)
C36	0.157 (8)	0.054 (4)	0.106 (6)	0.015 (4)	0.015 (5)	-0.025 (4)
C37	0.084 (5)	0.045 (3)	0.166 (8)	0.015 (3)	0.029 (5)	0.000 (4)
C38	0.074 (4)	0.055 (3)	0.118 (5)	0.035 (3)	0.035 (4)	0.021 (4)
C39	0.064 (3)	0.049 (3)	0.074 (3)	0.026 (3)	0.017 (3)	0.009 (2)
N5	0.065 (3)	0.065 (3)	0.077 (5)	0.0327 (16)	0.000	0.000
O5	0.090 (3)	0.074 (3)	0.150 (5)	0.032 (3)	0.020 (3)	0.000 (3)

*Geometric parameters (Å, °)*

Cu1—O1	1.8816 (7)	C10—C15	1.393 (7)
Cu1—N2	1.952 (4)	C11—C12	1.385 (8)
Cu1—N1	1.960 (4)	C12—C13	1.360 (9)
Cu1—O2	2.059 (3)	C13—C14	1.366 (9)
Cu1—O3	2.483 (4)	C14—C15	1.367 (8)
O1—Cu1 <sup>i</sup>	1.8816 (7)	C16—C17	1.379 (6)
O1—Cu1 <sup>ii</sup>	1.8816 (7)	C16—C21	1.391 (7)
O2—N3	1.237 (5)	C17—C18	1.382 (7)
N1—C1	1.334 (6)	C18—C19	1.362 (9)
N1—N2 <sup>i</sup>	1.345 (5)	C19—C20	1.365 (9)
N2—C3	1.337 (6)	C20—C21	1.386 (8)
N2—N1 <sup>ii</sup>	1.345 (5)	C22—C23	1.371 (6)
N3—O4	1.215 (6)	C22—C27	1.393 (6)
N3—O3	1.253 (6)	C23—C24	1.382 (7)
C1—C2	1.364 (7)	C24—C25	1.379 (8)
C2—C3 <sup>i</sup>	1.368 (7)	C25—C26	1.356 (8)
C2—C11	1.727 (5)	C26—C27	1.381 (6)
C3—C2 <sup>ii</sup>	1.368 (7)	C28—C33	1.389 (6)
P1—N4	1.575 (4)	C28—C29	1.391 (6)
P1—C34	1.794 (4)	C29—C30	1.368 (7)
P1—C28	1.799 (4)	C30—C31	1.379 (8)
P1—C22	1.805 (4)	C31—C32	1.350 (8)
P2—N4	1.576 (4)	C32—C33	1.378 (7)
P2—C10	1.795 (4)	C34—C35	1.358 (7)
P2—C4	1.795 (4)	C34—C39	1.386 (7)
P2—C16	1.802 (4)	C35—C36	1.376 (9)
C4—C5	1.366 (6)	C36—C37	1.379 (11)
C4—C9	1.397 (6)	C37—C38	1.323 (10)
C5—C6	1.391 (7)	C38—C39	1.384 (8)
C6—C7	1.356 (8)	N5—O5 <sup>i</sup>	1.238 (5)
C7—C8	1.379 (9)	N5—O5	1.238 (5)
C8—C9	1.388 (8)	N5—O5 <sup>ii</sup>	1.238 (5)
C10—C11	1.378 (7)		
O1—Cu1—N2	91.18 (12)	C8—C9—C4	119.5 (5)
O1—Cu1—N1	90.73 (12)	C11—C10—C15	119.6 (4)
N2—Cu1—N1	162.20 (16)	C11—C10—P2	117.0 (4)



O1—Cu1—O2	172.2 (2)	C15—C10—P2	123.2 (4)
N2—Cu1—O2	91.22 (15)	C10—C11—C12	119.8 (5)
N1—Cu1—O2	89.25 (14)	C13—C12—C11	119.8 (6)
Cu1—O1—Cu1 <sup>i</sup>	119.59 (5)	C12—C13—C14	120.8 (5)
Cu1—O1—Cu1 <sup>ii</sup>	119.59 (5)	C13—C14—C15	120.4 (6)
Cu1 <sup>i</sup> —O1—Cu1 <sup>ii</sup>	119.59 (5)	C14—C15—C10	119.6 (6)
N3—O2—Cu1	103.4 (3)	C17—C16—C21	118.6 (4)
C1—N1—N2 <sup>i</sup>	108.1 (4)	C17—C16—P2	120.0 (4)
C1—N1—Cu1	132.6 (3)	C21—C16—P2	121.4 (4)
N2 <sup>i</sup> —N1—Cu1	119.3 (3)	C16—C17—C18	120.6 (5)
C3—N2—N1 <sup>ii</sup>	108.3 (4)	C19—C18—C17	120.3 (5)
C3—N2—Cu1	132.1 (3)	C18—C19—C20	120.1 (5)
N1 <sup>ii</sup> —N2—Cu1	118.9 (3)	C19—C20—C21	120.4 (6)
O4—N3—O2	120.7 (5)	C20—C21—C16	119.9 (5)
O4—N3—O3	121.5 (5)	C23—C22—C27	118.8 (4)
O2—N3—O3	117.9 (4)	C23—C22—P1	121.4 (3)
N1—C1—C2	109.1 (4)	C27—C22—P1	119.4 (3)
C1—C2—C3 <sup>i</sup>	105.8 (4)	C22—C23—C24	120.6 (4)
C1—C2—C11	127.0 (4)	C25—C24—C23	120.0 (5)
C3 <sup>i</sup> —C2—C11	127.2 (4)	C26—C25—C24	119.9 (5)
N2—C3—C2 <sup>ii</sup>	108.6 (4)	C25—C26—C27	120.6 (5)
N4—P1—C34	109.7 (2)	C26—C27—C22	120.1 (5)
N4—P1—C28	108.61 (19)	C33—C28—C29	118.8 (4)
C34—P1—C28	106.6 (2)	C33—C28—P1	123.1 (3)
N4—P1—C22	115.14 (19)	C29—C28—P1	118.1 (3)
C34—P1—C22	106.8 (2)	C30—C29—C28	120.1 (5)
C28—P1—C22	109.62 (19)	C29—C30—C31	120.6 (5)
N4—P2—C10	113.0 (2)	C32—C31—C30	119.5 (5)
N4—P2—C4	107.2 (2)	C31—C32—C33	121.3 (5)
C10—P2—C4	108.3 (2)	C32—C33—C28	119.7 (5)
N4—P2—C16	112.4 (2)	C35—C34—C39	118.9 (5)
C10—P2—C16	108.4 (2)	C35—C34—P1	121.2 (4)
C4—P2—C16	107.4 (2)	C39—C34—P1	119.9 (4)
P1—N4—P2	139.5 (2)	C34—C35—C36	120.4 (6)
C5—C4—C9	119.3 (4)	C35—C36—C37	119.7 (7)
C5—C4—P2	119.6 (3)	C38—C37—C36	120.5 (6)
C9—C4—P2	121.0 (4)	C37—C38—C39	120.6 (6)
C4—C5—C6	120.8 (5)	C38—C39—C34	119.8 (5)
C7—C6—C5	119.7 (5)	O5 <sup>i</sup> —N5—O5	119.91 (5)
C6—C7—C8	120.7 (5)	O5 <sup>i</sup> —N5—O5 <sup>ii</sup>	119.90 (6)
C7—C8—C9	119.8 (5)	O5—N5—O5 <sup>ii</sup>	119.91 (5)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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C13—H13 $\cdots$ O3 <sup>iii</sup>	0.93	2.53	3.410 (11)	157
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Symmetry code: (iii)  $-x+y+4/3, -x+2/3, z-1/3$ .